Fraunhofer
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Solid-State Battery Roadmap 2035+

Index of Abbreviations

3C	consumer, computing, and communications
811 (NMC811)	lithium nickel manganese cobalt oxides with Ni:Mn:Co-ratio of 8:1:1 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$)
AAM	anode active material
AGV	automated guided vehicle
AM	active material
BEV	battery electric vehicle
CAGR	compound annual growth rate
CAM	cathode active material
CC	current collector
cEV	commercial electric vehicle
DEC	Diethyl carbonate (organic solvent used in liquid electrolytes)
DMC	Dimethyl carbonate (organic solvent used in liquid electrolytes)
EC	Ethylene carbonate (organic solvent used in liquid electrolytes)
EMC	ethyl methyl carbonate (organic solvent used in liquid electrolytes)
ESS	electrical energy storage (stationary storage)
EV	electric vehicle
HE-NMC	high energy lithium nickel manganese cobalt oxides
KPI	key performance indicator
LCO	lithium cobalt oxide
LFP	lithium iron phosphate
LGPS	$Li_{10}GeP_2S_{12}$
LIB	lithium-ion battery
LiOx-concept	SSB cell concept with lithium anode and oxide solid electrolyte
LiPo-concept	SSB cell concept with lithium anode and polymer solid electrolyte
LiPON	lithium phosphorus oxy-nitrides
LISICON	lithium super ionic conductor
LiSu-concept	SSB cell concept with lithium anode and sulfide solid electrolyte
LLO	lithium-rich layered oxides
LLZO	lithium lanthanum zirconium oxide
LMFP	lithium manganese iron phosphate
LPS	lithium phosphorus sulfide, lithium thiophosphate
LTO	lithium titanate
NASICON	sodium super ionic conductor
NCA	lithium nickel cobalt aluminum oxides
NMC	lithium nickel manganese cobalt oxides
NMC811	lithium nickel manganese cobalt oxides with Ni:Mn:Co-ratio of 8:1:1 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$)
NMCA	lithium nickel manganese cobalt aluminum oxides
OEM	original equipment manufacturer
PEO	polyethylene oxide
pEV	passenger electric vehicle
PHEV	plug-in hybrid electric vehicle
PVDF	polyvinylidene fluoride
SC	solid catholyte
SE	solid electrolyte
SEI	solid electrolyte interphase
SiMP	Si-microparticles
SiNP	Si-nanoparticles
SiSu-concept	SSB cell concept with silicon anode and sulfide solid electrolyte
SSB	solid-state battery

Solid-State Battery Roadmap

Contents

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Preface

This roadmap on solid-state batteries (SSB) was developed as part of the accompanying project BEMA II funded by the Federal Ministry of Education and Research (BMBF) under the initiative „Battery 2020". Fraunhofer ISI is supporting the German battery research with a roadmapping and monitoring process, strategic information processing and status seminars for the exchange of information on scientific progress and technology transfer. As part of the accompanying project, updates of the roadmap "High-energy batteries 2030+ and prospects for future battery technologies" (2017) are produced. In addition to the solid-state battery roadmap, a roadmap on next-generation batteries and an update on high-energy LIB will be developed in 2022 and 2023. The roadmaps also complement and support the competence clusters funded under the umbrella concept Battery Research Factory (Dachkonzept Forschungsfabrik Batterie), such as the BMBF competence cluster for solid-state batteries FestBatt.

In the umbrella concept the BMBF brought together all previous funding measures and programs for battery research under one roof – including the funding initiative Battery 2020. An important part of the umbrella concept is the establishment of battery competence clusters to strengthen and further develop R&D competences in future-relevant topics. Currently, competence clusters and innovation platforms are being funded in Germany in the following areas: (intelligent) battery cell production, recycling and green batteries, battery utilization concepts, battery materials, solid-state batteries, analytics and quality assurance. The "BattFutur" young talent promotion initiative also contributes to building up expertise. Another important focus of the umbrella concept funding is the implementation of the R&D results within the framework of the "Research Institution for Battery Cell Production" (FFB) initiative. It includes the establishment of a research infrastructure and research production lines for large-scale validation and transfer of promising R&D concepts to industrial production.

Vorwort

Die vorliegende Roadmap zu Feststoffbatterien (SSB) entstand im Rahmen der BMBF-geförderten Begleitmaßnahme BEMA II zur Förderinitiative Batterie 2020. Das Fraunhofer ISI begleitet hierbei die deutsche Batterieforschung mit einem Roadmapping- und Monitoring-Prozess, strategischer Informationsaufbereitung und Statusseminaren zum Austausch über den wissenschaftlichen Fortschritt und Technologietransfer. Im Rahmen der Begleitmaßnahme sollen u. a. Updates der Roadmap „Energiespeicher-Roadmap (Update 2017) – Hochenergie-Batterien 2030+ und Perspektiven zukünftiger Batterietechnologien" (2017) entstehen. Neben der Feststoffbatterie-Roadmap werden in 2022 und 2023 eine Roadmap zu „alternative Batterietechnologien" sowie ein Update zu „Hochenergie LIB" erarbeitet. Die Roadmaps ergänzen und unterstützen hierbei auch die unter dem Dachkonzept Forschungsfabrik Batterie geförderten Kompetenzcluster wie z. B. den BMBF-Kompetenzcluster für Feststoffbatterien FestBatt.

Im Dachkonzept Forschungsfabrik Batterie führte das Bundesministerium für Bildung und Forschung (BMBF) im Jahr 2020 alle bisherigen Fördermaßnahmen und -programme zur Batterieforschung – auch die Förderinitiative Batterie 2020 – unter einem Dach zusammen. Ein wichtiger Teil des Dachkonzepts ist der Aufbau von Batterie-Kompetenzclustern zur Stärkung und Weiterentwicklung der F&E-Kompetenzen in zukunftsrelevanten Themen. Aktuell werden in Deutschland Kompetenzcluster und Innovationsplattformen in folgenden Bereichen gefördert: (intelligente) Batteriezellproduktion, Recycling und grüne Batterien, Batterienutzungskonzepte, Batteriematerialien, Festkörperbatterien, Analytik und Qualitätssicherung. Zum Kompetenzaufbau trägt auch die Nachwuchsförderinitiative „BattFutur" bei. Ein weiterer wichtiger Schwerpunkt der Dachkonzeptförderung ist die Umsetzung der F&E-Ergebnisse im Rahmen der Initiative „Forschungsfertigung Batteriezelle" (FFB). Sie beinhaltet den Aufbau einer Forschungsinfrastruktur und Forschungsproduktionslinien zur großskaligen Validierung und Überführung von erfolgversprechenden F&E-Konzepten in die industrielle Fertigung.

Executive Summary

Introduction

Although the automotive sector remains the driving force behind the technological development and optimization of lithium-ion batteries (LIB), these high-energy batteries are currently spreading into a wide range of other mobile and stationary applications. However, the potential for further optimization of liquid electrolyte-based LIB is diminishing and the limits of this technology are expected to be reached within the coming decade. Therefore, alternative or next generation technologies need to be developed and their progress monitored. A new generation of so-called solid-state batteries (SSB) is under development and could reach the market in larger volumes in the next years. While current LIB are based on liquid electrolytes, SSB rely on solid electrolytes and show promise of improvements in several key performance indicators (KPI) for batteries. As a result of an extensive literature review and an in-depth expert consultation process, this roadmap summarizes and critically discusses the current and future developments at the material, component, cell and application level, while benchmarking with the anticipated developments of LIB in the next ten years.

Key Results

Materials, Components, Production and Cell Concepts
Various materials are taken into consideration for the components of SSB. Lithium metal and silicon are the most promising **anode** active materials (AAM). Li metal anodes show potential for having the highest energy densities, but the technology for processing them is not yet well-established for large-scale manufacturing. Si-based anodes, on the other hand, are considered as the technology of choice for next-generation LIB. However, the energy densities of Si anode-based SSB typically being achieved are lower than Li anode-based ones, yet research is intensifying. Promising **cathode** active materials (CAM) are Ni-rich layered oxides (NMC, NCA), lithium iron phosphate (LFP) and in the long-term future potentially sulfur or high-potential materials. Currently, SSB cells with the highest energy densities can be achieved by using NMC/NCA layered oxides. LFP materials are interesting mainly because of their lower costs and greater stability.

The key component of SSB is the solid electrolyte (SE). Currently, three groups of SE materials seem most promising, namely oxide electrolytes, sulfide electrolytes and polymer electrolytes. **Oxide electrolytes** generally exhibit high mechanical and chemical stability, but require high-temperature processing (sintering), are brittle and have a relatively poor ionic conductivity. **Sulfide electrolytes** are mechanically softer and more malleable than oxide SE and easier to process (no sintering is necessary). On the other hand, the materials are currently only available on a research scale and the chemical compatibility to Li metal and high-potential CAM is limited. **Polymer electrolytes** are the most established amongst all SE in terms of material availability and production technologies. Limited ionic conductivities at room temperature, poor chemical compatibility with high-potential CAM and a low limiting current density due to the ionic conduction mechanism are challenges on the path to a broader market implementation. Other types of SE are being developed (e.g. halides), but are still in an early state of research.

In this roadmap report, four promising **cell concepts** are discussed in detail:

- Li metal anodes and layered oxide cathodes with (1) oxide and (2) sulfide SE,
- (3) Si anode and layered oxide cathode with sulfide SE, and
- (4) Li anode and LFP cathode with polymer SE.

Experts expect an expansion of the pilot production of the abovementioned polymer-based SSB and the initial pilot production for SSB cells with Si anodes and sulfide SE by around 2025. Pilot production for SSB with Li metal anodes and oxide SE could start from 2025 and the sulfide SE-based SSB from about 2028. Further improvements in the chemical compatibility between the solid electrolytes and the active materials, especially lithium anodes and high-potential cathodes, are required for widespread market implementation.

Key Performance Indicators of SSB
As SSB come closer to being applied, they need to demonstrate performance improvements in comparison to state-of-the-art liquid electrolyte LIB. The most relevant KPI are the energy density, safety, lifetime, costs and fast charging capability. The **energy density** is particularly relevant for mobile

applications. Many types of SSB have the potential to outperform state-of-the-art LIB in terms of energy density. According to the calculations, with all three SE SSB could reach volumetric energy densities of up to 1150 Wh/l and gravimetric energy densities of up to 350 to 500 Wh/kg with Li anodes. The **safety** of SSB is anticipated to be high, even at the cell level, as they do not contain flammable liquids. Lithium metal, on the other hand, is highly reactive and sulfide SE can react with water to form the toxic gas hydrogen sulfide. The **long-term stability and lifetime** of SSB is expected to be comparable to or even exceed that of state-of-the-art LIB, as the absence of liquids could reduce the degradation effects. On the other hand, volume changes during battery discharge or recharge pose additional challenges on the solid-solid interfaces. The **cost** of SSB is of great importance for their implementation, but cannot be realistically estimated at present. Initially, higher costs compared to state-of-the-art LIB have to be expected. The **fast-charging** capability is relevant for certain applications. The limited ionic conductivities of most SE and Li-deposition kinetics currently pose challenges for fast charging. Lastly, SSB face ongoing competition from liquid electrolyte LIB, whose KPI are also continuously being improved.

Applications
The only solid-state batteries currently on the market on a larger scale are polymer SSB used in some buses. The greatest limitation for polymer SSB is the high operating temperature of between 50–80 °C, which limits the possible applications to systems that are in regular use. Further developments reducing the operating temperature might lead to a broader implementation of polymer SSB in different applications, even in the automotive sector.

In general, the automotive market represents the driving force behind SSB developments and is expected to be the main application area for SSB in the medium and long term. Oxide and sulfide-based SSB, however, are not expected to emerge onto the automotive market on a larger scale within the next 5 years. Before that, the initial market for inorganic SSB could be the consumer market (e.g., laptops, smartphones, and power tools), as requirements and testing procedures may be less stringent. For oxide SSB, the automotive market is likely to be its initial application, possibly in parallel with industrial heavy-duty equipment and equipment for harsh environments due to their potential robustness. Due to the higher initial costs, the high-end sectors will be targeted with SSB first.

Once cost reductions are achieved through the economies of scale, SSB could become more attractive for more applications such as trucks and stationary storage. After 2035, SSB could be used for other applications such as passenger aviation.

Market Aspects
The current global production capacity of SSB is estimated to be below 2 GWh, almost exclusively based on polymer SSB. It is anticipated that this capacity will increase significantly, especially with the emergence of oxide and sulfide electrolyte-based SSB onto the market between 2025 and 2030. The total capacity of the SSB market is estimated to be 15–40 GWh in 2030 and 55–120 GWh in 2035, which is still relatively small compared to the total LIB market of 1–6 TWh around 2030 and 2–8 TWh by 2035. SSB market shares of currently less than half a percent could increase to over one percent by 2035, which means that liquid electrolyte LIB will still dominate the market for the foreseeable future and SSB are expected to take some time to become a major technology in the global market. Nonetheless, SSB have the potential to gain more and more of the market share if they deliver the promised KPI improvements and penetrate mass markets such as the automotive sector.

Geographically, SSB R&D, especially in terms of cell concepts, production processes & equipment and pilot production, is dominated mostly by Asia (Japan, South Korea and China) and the USA. The EU has certain competences, mainly in the R&D of materials, but currently it lags significantly behind when it comes to the industrial level and pilot production (with the exception of polymer SSB).

Key Challenges

Technical Challenges and their Implications
A variety of solid-state battery concepts, based on different classes of solid electrolytes, have been developed. Each of these SSB technologies face various technological challenges such as the scale-up of material production, compatibilities between components, as well as production challenges, as described in detail in the roadmap. At the moment, it is not clear, which of these technologies will be able to deliver the promised KPI improvements. This uncertainty necessitates

»**Solid-State Batteries are a big bet on the future – The effort will pay off!**«

Prof. Dr. Jürgen Janek,
Justus Liebig University Giessen & Coordinator of
BMBF cluster of competence FestBatt

parallel development and thus investment in different approaches, which requires large investments from funding agencies, OEM and other investors.

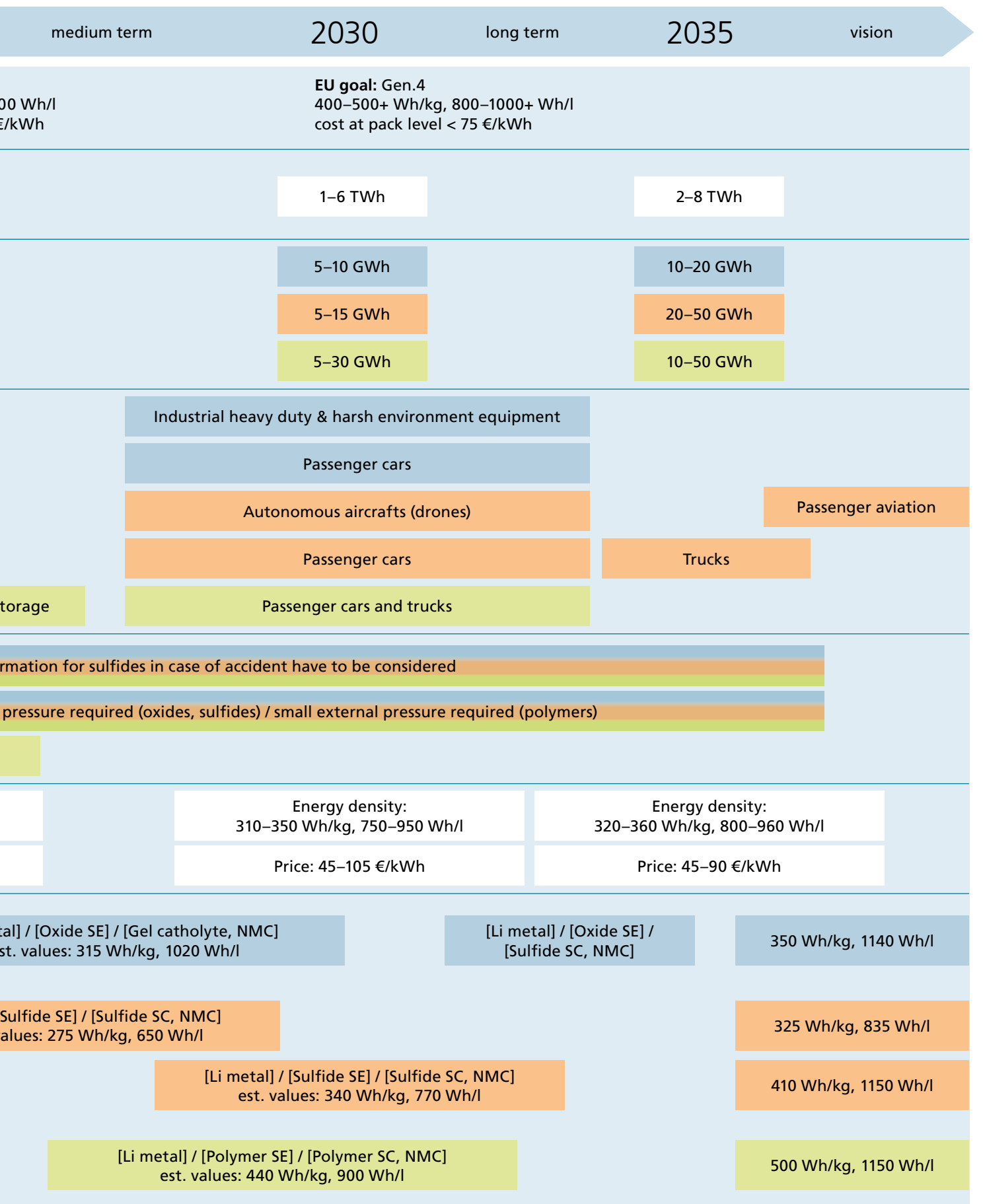**Competition with State-of-the-art LIB**

Since SSB compete with liquid electrolyte LIB, their KPI can be considered as a benchmark. Development efforts to improve liquid electrolyte LIB are ongoing, so the benchmark is continuously improving. Furthermore, as initial SSB costs may be higher compared to state-of-the-art LIB, the gains in other KPI need to justify the higher costs. First applications may therefore be more likely to be realized at the premium end of the market.

Challenges and Chances for the EU

The SSB innovation system is currently dominated by Asian and US players in most technology areas. Although the EU shows a certain competitiveness in SSB research, it clearly lags behind in patenting, product development, production technologies, pilot production and start-up and industry activity. The early stage of SSB development offers a chance for the EU, to be active from the outset of technological development. While the upscaling efforts in LIB production are currently heavily dominated by non-European players, Europe still has an opportunity to play a leading role in the development of SSB technology. However, in order to establish European players, corporate and public funding beyond research is necessary, and more development efforts at higher TRL levels need to be supported in the EU.

Solid-state battery roadmap "Cell to Application" (discussion in Section 5.2)

	2021/22	short term	2025
Political Goals			**EU goal:** Gen.3 350–400 Wh/kg, 750–100... cost at pack level < 100 €...
LIB market	400 GWh		0.5–2 TWh
SSB market	< 2 GWh		0–1 GWh / 0–5 GWh / 2–15 GWh
SSB applications	Busses	Industrial applications, e.g. AGV	Stationary s...
Cell integration		Safety aspects of metallic lithium and H$_2$S fo... High volume changes have to be compensated → high external... needs heating to 50–80°C	
KPI LIB	Energy density: 230–300 Wh/kg, 600–750 Wh/l / Price: 90–175 €/kWh		Energy density: 250–330 Wh/kg, 650–850 Wh/l / Price: 60–130 €/kWh
SSB Cell concepts + SSB KPI	[Li metal] / [Polymer SE] / [Polymer SC, LFP] 240 Wh/kg, 360 Wh/l		[Li met... es... [Si/C] / [... est. v...

EU goal: Gen.4
400–500+ Wh/kg, 800–1000+ Wh/l
cost at pack level < 75 €/kWh

00 Wh/l
€/kWh

1–6 TWh	2–8 TWh

5–10 GWh	10–20 GWh
5–15 GWh	20–50 GWh
5–30 GWh	10–50 GWh

Industrial heavy duty & harsh environment equipment

Passenger cars

Autonomous aircrafts (drones)

Passenger aviation

Passenger cars

Trucks

torage

Passenger cars and trucks

rmation for sulfides in case of accident have to be considered

pressure required (oxides, sulfides) / small external pressure required (polymers)

Energy density: 310–350 Wh/kg, 750–950 Wh/l	Energy density: 320–360 Wh/kg, 800–960 Wh/l
Price: 45–105 €/kWh	Price: 45–90 €/kWh

tal] / [Oxide SE] / [Gel catholyte, NMC]
st. values: 315 Wh/kg, 1020 Wh/l

[Li metal] / [Oxide SE] /
[Sulfide SC, NMC]

350 Wh/kg, 1140 Wh/l

Sulfide SE] / [Sulfide SC, NMC]
alues: 275 Wh/kg, 650 Wh/l

325 Wh/kg, 835 Wh/l

[Li metal] / [Sulfide SE] / [Sulfide SC, NMC]
est. values: 340 Wh/kg, 770 Wh/l

410 Wh/kg, 1150 Wh/l

[Li metal] / [Polymer SE] / [Polymer SC, NMC]
est. values: 440 Wh/kg, 900 Wh/l

500 Wh/kg, 1150 Wh/l

Zusammenfassung und Kernergebnisse

Einleitung

Während der Automobilmarkt immer noch die treibende Kraft hinter der technologischen Entwicklung und Optimierung von Lithium-Ionen-Batterien (LIB) ist, verbreiten sich diese Hochenergiebatterien derzeit auch in einer Vielzahl anderer mobiler und stationärer Anwendungen. Das verbleibende Optimierungspotenzial von Flüssigelektrolyt-LIB verringert sich jedoch durch die fortschreitende Weiterentwicklung immer weiter. Es wird erwartet, dass diese Technologie innerhalb des nächsten Jahrzehnts an ihre technischen Grenzen stößt. Aus diesem Grund bedarf es der Entwicklung von Batterietechnologien der nächsten Generation, deren Fortschritt stetig beobachtet und bewertet werden sollte. Eine neue Generation sogenannter Feststoffbatterien (engl. solid-state battery – SSB) befindet sich in der Entwicklung und könnte in den kommenden Jahren in größerem Volumen auf den Markt kommen. Während gegenwärtige LIB auf flüssigen Elektrolyten basieren, bestehen Feststoffbatterien aus Festelektrolyten und versprechen Verbesserungen bei mehreren wichtigen Leistungsparametern (engl. key performance indicator – KPI). Als Ergebnis einer umfassenden Literaturrecherche und eines fundierten Expertenbefragungsprozesses fasst diese Roadmap die aktuellen und zukünftigen Entwicklungen auf Material-, Komponenten-, Zell- und Anwendungsebene zusammen und erörtert diese kritisch, während sie gleichzeitig einen Vergleich mit den erwarteten Entwicklungen von LIB in den nächsten 10 Jahren anstellt.

Schlüsselergebnisse

Materialien, Komponenten, Produktion und Zellkonzepte
Für die Komponenten von Feststoffbatterien werden sehr verschiedene Materialien in Erwägung gezogen. Vielversprechende **Anoden**aktivmaterialien (AAM) sind Lithium (Li) und Silizium (Si). Li-Metall-Anoden versprechen die höchsten Energiedichten, jedoch sind die Verarbeitungstechnologien noch nicht in der Großserienfertigung etabliert. Anoden auf Si-Basis kündigen sich zwar als die bevorzugte Technologie für die nächste Generation von LIB an, gegenüber Li-Metall-Anoden werden typischerweise allerdings nur geringere Energiedichten in SSB erreicht. Vielverspechende **Kathoden**aktivmaterialien (engl. cathode active materials – CAM) sind Ni-reiche Schichtoxide (NMC, NCA), Lithiumeisenphosphat (LFP) und langfristig möglicherweise auch Schwefel oder Hochvoltmaterialien. Durch die Verwendung von NMC/NCA-Schichtoxiden werden derzeit die höchsten Energiedichten in SSB-Zellen erreicht. LFP-Materialien sind wegen ihrer geringeren Kosten und höheren Stabilität von Interesse.

Die Schlüsselkomponente von Feststoffbatterien ist der Festelektrolyt (engl. solid electrolyte – SE). Derzeit gibt es drei vielversprechende Gruppen von SE-Materialien, nämlich Oxid-Elektrolyte, Sulfid-Elektrolyte und Polymer-Elektrolyte. **Oxid-Elektrolyte** weisen im Allgemeinen eine hohe mechanische und chemische Stabilität auf, erfordern jedoch Hochtemperaturproduktionsschritte bei der Verarbeitung (Sintern), sind spröde und haben eine verhältnismäßig schlechte ionische Leitfähigkeit. **Sulfid-Elektrolyte** (auch Thiophosphat-Elektrolyte genannt) sind mechanisch weicher und formbarer als Oxid-SE und sind somit einfacher zu verarbeiten (zudem ist kein Sintervorgang notwendig). Nachteile des Materialsystems sind die begrenzte Verfügbarkeit, die sich derzeit auf den Forschungsmaßstab beschränkt, sowie die sich derzeit auf den Forschungsmaßstab beschränkt, und die begrenzte chemische Kompatibilität mit Li-Metall und Hochvolt-CAM. **Polymer-Elektrolyte** sind die etabliertesten Materialsysteme unter allen SE, was sich auch in der Materialverfügbarkeit und Produktionstechnologie widerspiegelt. Begrenzte ionische Leitfähigkeiten bei Raumtemperatur, schlechte chemische Kompatibilität mit Hochvolt-CAM und eine niedrige Grenzstromdichte aufgrund des Ionenleitmechanismus sind Herausforderungen auf dem Weg zu einer breiteren Marktimplementierung.

In diesem Roadmap-Bericht werden vier vielversprechende Zellkonzepte im Detail diskutiert:

- Li-Metall-Anoden und Schichtoxid-Kathoden mit (1) Oxid- und (2) Sulfid-SE,
- (3) Si-Anode und Schichtoxid-Kathode mit Sulfid-SE und
- (4) Li-Anode und LFP-Kathode mit Polymer-SE.

Experten erwarten eine Erweiterung der Pilotproduktion der oben genannten polymerbasierten SSB und eine erste Pilotproduktion für SSB-Zellen mit Si-Anoden und Sulfid-SE bis etwa 2025. Die Pilotproduktion für SSB mit Li-Metall-Anoden und Oxid-SE könnte ab 2025 beginnen und für die Sulfid-SE-basierte SSB mit Li-Metall-Anode ab etwa 2028. Für eine breite Marktimplementierung sind weitere Verbesserungen der chemischen Kompatibilität zwischen den Festelektrolyten und den Aktivmaterialien, insbesondere bei den Lithiumanoden und Hochvoltkathoden, erforderlich.

KPI von Feststoffbatterien

Um relevante Marktanteile in batteriebetriebenen Anwendungen erreichen zu können, müssen Feststoffbatterien im Vergleich zu hochmodernen Flüssigelektrolyt-LIB Verbesserungen aufweisen. Die wichtigsten KPI sind Energiedichte, Sicherheit, Lebensdauer, Kosten und Schnellladefähigkeit. Die **Energiedichte** ist besonders wichtig für mobile Anwendungen. Unterschiedliche Materialkombinationen von Feststoffbatterien haben das Potenzial, die hochmodernsten LIB in Bezug auf die Energiedichte zu übertreffen. Nach eigenen Berechnungen könnten Feststoffbatterien mit Li-Anoden mit allen drei SE volumetrische Energiedichten bis zu 1150 Wh/l und je nach SE gravimetrische Energiedichten von 350 bis 500 Wh/kg erreichen. Die **Sicherheit** der Feststoffbatterien wird selbst auf der Zellebene als hoch eingeschätzt, da sie keine brennbaren Flüssigkeiten enthalten. Metallisches Lithium allerdings ist hochreaktiv und Sulfid-SE wiederum können mit Wasser reagieren und das giftige Gas Schwefelwasserstoff bilden. Es wird erwartet, dass die **Langzeitstabilität und Lebensdauer** von Feststoffbatterien mit der von Flüssigelektrolyt-LIB vergleichbar oder sogar etwas besser sein wird, da durch die Abwesenheit von Flüssigkeit die Degradationseffekte verringert werden könnten. Auf der anderen Seite stellen Volumenänderungen während des Entladens oder Aufladens der Batterie zusätzliche Herausforderungen an die Festkörper-Grenzflächen dar. Die **Kosten** der Feststoffbatterien sind äußerst wichtig für die Markteinführung, können jedoch im Moment nicht realistisch eingeschätzt werden. Anfänglich muss mit höheren Kosten im Vergleich zu aktuellen LIB gerechnet werden. Auch die **Schnellladefähigkeit** ist für diverse Anwendungen relevant. Begrenzte ionische Leitfähigkeiten der meisten SE und die Li-Abscheidungskinetik stellen derzeit Herausforderungen für das Schnellladen dar. SSB stehen in einem ständigen Wettbewerb mit Flüssigelektrolyt-LIB, deren KPI ebenfalls kontinuierlich verbessert werden.

Anwendungen

Die einzigen derzeit in größerem Umfang auf dem Markt befindlichen Feststoffbatterien, sind Polymer-SSB, die in einer Kleinserie von Elektrobussen verwendet werden. Die größte Einschränkung von Polymer-Feststoffbatterien ist ihre hohe Betriebstemperatur von 50 bis 80 °C. Diese beschränkt mögliche Anwendungen auf Systeme, welche regelmäßig genutzt werden. Zukünftige Entwicklungen, die Betriebstemperatur zu reduzieren, könnten zu einem breiteren Einsatz von Polymer-Feststoffbatterien in verschiedenen Anwendungen führen, auch im Automobilsektor.

Generell stellt der Automobilmarkt die treibende Kraft hinter den SSB-Entwicklungen dar und wird voraussichtlich mittel- und langfristig der Hauptanwendungsbereich für SSB sein. Es wird jedoch nicht erwartet, dass oxid- und sulfidbasierte Feststoffbatterien in den nächsten fünf Jahren in größerem Umfang auf dem Automobilmarkt auftauchen werden. Davor könnten anorganische SSB zunächst einen Markteintritt im Consumer-Markt erfahren (z. B. Laptops, Smartphones und Elektrowerkzeuge), da die Anforderungen weniger streng sein könnten. Für oxidische SSB wird der Automobilmarkt wahrscheinlich die erste Anwendung sein, möglicherweise parallel zu Anwendungen in der Schwerindustrie sowie aufgrund ihrer potenziell hohen Robustheit, bei Ausrüstung für raue Umgebungen. Im PKW-Bereich werden SSB angesichts der höheren Anfangskosten zunächst in den oberen Marktsegmenten eingesetzt werden. Kostenreduzierungen durch Skalierungseffekte könnten dazu führen, dass Feststoffbatterien für weitere Verwendungen attraktiver werden, wie z. B. LKW und stationäre Speicher. Nach 2035 könnten SSB möglicherweise in anderen Anwendungen wie der Passagierluftfahrt eingesetzt werden.

Marktaspekte

Die derzeitige weltweite Kapazität für die Produktion von Feststoffbatterien wird auf unter 2 GWh geschätzt und basiert fast ausschließlich auf Polymer-Feststoffbatterien. Es wird erwartet, dass diese Kapazität erheblich ansteigen wird, insbesondere mit dem Markteintritt von SSB auf Oxid- und Sulfidelektrolyt-Basis zwischen 2025 und 2030. Die Gesamtkapazität des SSB-Marktes wird im Jahr 2030 auf 15–55 GWh und im Jahr 2035 auf 40–120 GWh geschätzt, was im Vergleich zum gesamten LIB-Markt von 1–6 TWh um 2030 und 2–8 TWh im Jahr 2035 gering ist. Der Marktanteil von SSB, der derzeit weniger als ein halbes Prozent beträgt, könnte bis 2035 auf über ein Prozent ansteigen. Dies bedeutet, dass LIB mit flüssigen Elektrolyten den Markt auf absehbare Zeit dominieren werden und es einige Zeit dauern dürfte, bis die SSB eine wichtige Technologie auf dem Weltmarkt ist. Trotzdem haben Feststoffbatterien das Potenzial, einen immer größeren Marktanteil zu gewinnen, wenn sie die versprochenen KPI-Verbesserungen erbringen und sich auf Massenmärkten, wie z. B. dem Automobilsektor, durchsetzen.

Festkörperbatterien sind eine große Wette auf die Zukunft – Der Einsatz lohnt!«

Prof. Dr. Jürgen Janek,
Justus-Liebig-Universität Gießen & Koordinator des
BMBF-Kompetenzclusters FestBatt

Geografisch gesehen wird die Forschung und Entwicklung von SSB, insbesondere in Bezug auf Zellkonzepte, Produktionsprozesse und -anlagen, sowie Pilotproduktion, hauptsächlich von asiatischen (Japan, Südkorea und China) und den amerikanischen Akteuren dominiert. Die EU verfügt über Kompetenzen, vor allem bei der Forschung und Entwicklung von Materialien, bleibt aber derzeit auf Unternehmensebene und bei der Pilotproduktion deutlich zurück (mit Ausnahme von Polymer-SSB).

Zentrale Herausforderungen

Technische Herausforderungen und ihre Auswirkungen
Es wurde bereits eine Vielzahl von Festkörperbatteriekonzepten entwickelt, die auf unterschiedlichen Klassen von Festelektrolyten basieren. Jede dieser SSB-Technologien ist mit verschiedenen technologischen Herausforderungen konfrontiert, wie z.B. mit der Skalierung der Materialproduktion, der Kompatibilität zwischen den Komponenten sowie den Herausforderungen bei der Produktion, die in der Roadmap ausführlich beschrieben werden. Derzeit ist nicht klar, welche dieser Technologien in der Lage sein wird, die versprochenen KPI-Verbesserungen zu erzielen. Diese Ungewissheit erfordert eine parallele Entwicklung und damit Investitionen in verschiedene Ansätze, was hohe Investitionen von Förderorganisationen, OEM und anderen Akteuren erfordert.

Wettbewerb mit Flüssigelektrolyt-LIB
Da Feststoffbatterien mit Flüssigelektrolyt-LIB konkurrieren, können deren KPI als Benchmark betrachtet werden. Gleichzeitig zur Entwicklung neuer Technologien werden große Bemühungen unternommen, um die Flüssigelektrolyt-LIB zu verbessern, so dass sich der Benchmark kontinuierlich verbessert. Da die anfänglichen Kosten für SSB im Vergleich zu modernen LIB höher sein können, müssen Verbesserungen bei anderen KPI die höheren Kosten rechtfertigen. Eine erste Anwendung könnte daher der PKW-Premiumbereich sein.

Herausforderungen und Chancen für die EU
Das SSB-Innovationssystem wird derzeit in den meisten Technologiebereichen von asiatischen und amerikanischen Akteuren dominiert. Obwohl die EU eine gewisse Wettbewerbsfähigkeit in der SSB-Forschung aufweist, liegt sie bei der Patentierung, der Produktentwicklung, den Produktionstechnologien, der Pilotproduktion sowie den Start-up- und Industrieaktivitäten deutlich zurück. Dennoch bietet das frühe Stadium der Entwicklung von Feststoffbatterien der EU die Chance, früh in der technologischen Entwicklung aktiv zu sein. Während die Skalierungsbemühungen in der LIB-Produktion derzeit stark von nicht-europäischen Akteuren dominiert werden, hat Europa immer noch die Möglichkeit, eine führende Rolle bei der Entwicklung der SSB-Technologie zu spielen. Um allerdings europäische Akteure in der Industrie zu etablieren, sind private und öffentliche Fördermittel jenseits der Forschung nötig und mehr Entwicklungsbemühungen mit höherem TRL müssen gefördert werden.

1. Introduction & Motivation

1.1. Introduction

The global shift toward electric mobility is leading to huge demand for batteries and driving the broad diffusion of batteries in mobile, stationary storage, and other applications. The share of electric vehicles sold annually is currently around the 10 % level and is expected to pass the "tipping point" in the next few years. This marks the entry to a mass market with full market diffusion between 2030 and 2050, which implies an emerging global battery ecosystem with a growing demand for lithium-ion batteries of 0.5–1.5 TWh by 2025, 2–4 TWh around 2030, and most probably more than 10 TWh in the decades beyond 2030.

Lithium-ion batteries based on liquid electrolytes (LIB) are the most advanced, competitive and established battery technology and have enabled the rise of these emerging markets. Currently, there are no technological alternatives suitable for electric vehicles. Any future alternative technology would have to outperform LIB in one or more key performance parameters such as energy density, safety, lifetime, costs or in other aspects, such as sustainability or resource availability.

In the same way that LIB are considered an important alternative to the use of fossil fuels, especially in the transport sector, it will be equally important to have alternative battery technologies to LIB in the future in order to avoid dependency on a single technology. A diversification of alternative and next generation technologies is needed for technical reasons, e.g., to better meet application-specific requirements, as well as for environmental and other non-technical reasons, e.g., to reduce the environmental footprint of batteries (raw materials, energy, water, CO_2, etc.). Prospective technologies have to be monitored and assessed with respect to their development potential, and their advantages or disadvantages in the context of potential applications.

SSB are regarded as very promising candidates, which could be competitive with LIB in the near future in automotive applications, but which might enter the market via other (niche, premium, special) applications in the next years. Do SSB represent a real alternative to the benchmark technology LIB, which is currently undergoing further optimization and improving its performance?

Status quo of liquid electrolyte Li-ion batteries and their limits

Lithium-ion batteries are well established in applications requiring the storage of large amounts of energy in a limited volume or with strict weight restrictions. Motive applications and most prominently electric vehicles have pushed the development of higher energy density batteries. Over the last decade of automotive battery development, the average energy densities of passenger car battery cells have increased from approximately 150 Wh/kg (and 260 Wh/l) to 250 Wh/kg (and almost 600 Wh/l) at present, with transition metal-based oxides as the cathode active material and graphite as the anode active material. This progress has been achieved mostly due to improved material performance. However, a large part of the improvement in total energy density can be attributed to optimizing cell design and reducing the passive components which add to the weight and volume of battery cells. On the downside, storing a lot of energy in a small volume always poses a certain safety risk. Among other cell components, the liquid electrolyte, which is based on organic and flammable solvents, is one issue of concern.

In order to satisfy the demand for even higher energies stemming also from new industries like electric aviation, completely new concepts have to be introduced on the material level.

Research has been done on Li metal and conversion- or alloying-type anode active materials, in particular, for several years due to their high energy properties. Lithium metal, which theoretically has the highest energy density of all Li-battery anode materials, would certainly open the door to a whole new level of energy density and is therefore considered very promising by many researchers. While Li metal is already used in non-rechargeable batteries, it plays only a minor role in rechargeable high-energy cells, due to performance and stability issues, either associated with the electrolyte chemistry or the deposition of lithium during charging. Other approaches like the use of silicon as the anode active material can already be found in commercial cells today, but again have long-term stability problems.

It is clear to say that introducing higher energy densities to lithium-batteries means relinquishing many of the desirable properties of established material systems like a high structural stability and low volume change. As a result, and to maintain the

safety and stability of batteries, the next generation of lithium-batteries will not only have to incorporate one single material innovation, but a number of changes in all parts of the battery cell and respective production processes.

Introduction to the concept of solid-state-batteries

One innovation which addresses several of the safety and stability issues mentioned is the use of solid electrolyte materials. Switching from liquids to solids can avoid leakage in the event of damage. Furthermore, some of the solid electrolyte materials under investigation are non-combustible and mechanically robust, thus minimizing the effects of battery damage. The mechanical and chemical properties of solid electrolytes not only affect safety, but also many microscopic processes in the battery cell, which may lead to greater stability of the electrochemical system, particularly for high energy anodes. Often, solid electrolytes are considered an enabler for Li metal anodes, because their high density and robustness might prevent dendrite growth, a process occurring during lithium deposition, which eventually leads to an internal short-circuit and battery failure.

Research is ongoing on various inorganic and organic solid electrolytes. The main classes are ceramic oxides, sulfides and polymer-salt complexes. Their properties such as ionic conductivity, stability but also processability vary strongly and each class has its own advantages and disadvantages. The cell concepts rendered possible by these electrolytes are as diverse as the materials themselves and consequently a whole range of lithium solid-state batteries are being developed simultaneously in research and industry.

Motivation for this SSB roadmap

Given the market diffusion of LIB, it is important to monitor and assess SSB progress to understand the maturity of this technology, individual materials to cell concepts, the problems to be solved and the frame conditions required to enable successful market entry. SSB are still in the R&D phase with uncertainties concerning the materials and systems of choice, and compatible production technologies capable of scaling up this technology.

This calls for a strong focus on the technology's state-of-the-art and potential developments, while bearing in mind its potential applications and their requirements.

Conventional LIB will be the benchmark and competing technology at the time of potential market entry of SSB technologies.

With a roadmap process, it is possible to systematically monitor and assess SSB in a short (< 2025), medium (< 2030), and longer (> 2030) timeframe and can track both scientific advancements and industrial deployment at the same time. This roadmap can be used as a tool to consolidate scientific research with expert opinions in order to detect where challenges and bottlenecks have to be addressed and to point science, industry and policy in the right direction for supporting SSB technologies.

Focus of this roadmap

This roadmap focuses on Li-based SSB for high-volume automotive applications as potential alternatives to liquid electrolyte-based LIB. However, they could also be successful on non-automotive markets.

The general introduction in Chapter 1 outlines the international market development and R&D activities and explains the relevance and the methodology for this roadmap. Chapter 2 describes the SSB components with respect to the state-of-the-art, advantages, disadvantages and challenges for further development. Besides the electrolyte materials, the respective interfaces between the components are discussed as well. Chapter 3 addresses the production aspects of SSB with a focus on scalability and market entry and discusses processing of the components as well as the availability of raw materials and economic aspects. Chapter 4 discusses and compares promising cell concepts and industrial activities. Chapter 5 provides an illustration of the full SSB roadmap and summarizes the steps from materials to cells and cells to applications. Chapter 6 draws conclusions from the overall findings and presents an outlook. The main results of the roadmap are summarized at the very beginning of this report.

1.2. Market Developments

The global battery market is currently dominated by lead acid batteries and lithium-ion batteries (LIB). The market analysis made here focuses on LIB. Electric mobility applications are the main driver for the growing market share of LIB. Overall, the global demand for LIB was 250 to 280 GWh in 2020. Initial calculations for the year 2021 indicate a capacity of around 400 GWh. The market has seen recent annual growth of between 30 % and over 40 %. The share of solid-state batteries in the global demand for LIB is currently less than 0.5 %, and the technology readiness level of most solid-state batteries is still too low to enable realistic predictions of their future market share.

Market growth developments
By 2030, global demand for LIB could reach more than 3 TWh per year (Figure 1) [1]. Most technical reports and market forecasts predict a global demand of 1 to 4 TWh for the year 2030. Maximum scenarios assume a demand of up to 6 TWh. After 2030, the market will continue to grow. By then, new markets, e.g., individual passenger aviation and many others could reach a relevant market share, which will further increase demand. In the long term, a global battery demand of more than 10 TWh per year is considered to be realistic [1].

The European demand for LIB-cells is estimated at 20–30 % of the global demand. In Europe, electric mobility is an even stronger driver of LIB demand than it is globally. This is due to the high sales figures of car manufacturers from Germany and France, for example.

Application sectors with the highest battery demand
The main driver behind the growing global LIB market is electric mobility in the form of electric vehicles (EV). The market for electric passenger cars already generates the highest demand among LIB applications today (Figure 1). In addition to electric cars, other LIB applications include commercial EV (cEV), stationary storage (ESS) and portable/wearable devices for consumer, computing, and communications (3C).

Electrified passenger cars (pEV) such as battery EV (BEV) or plug-in hybrid EV (PHEV) already account for more than 50 % of LIB demand today. In the future, this share will increase to over 80 %. The global demand for LIB for electric cars increased from 90 GWh in 2019 to 130–160 GWh in 2020.

Commercial vehicles (e.g., e-buses or e-trucks) do not yet play a major role, but could develop into another main market by

Figure 1: Illustration of the demand for LIB between 2020 and 2040 by market segment.
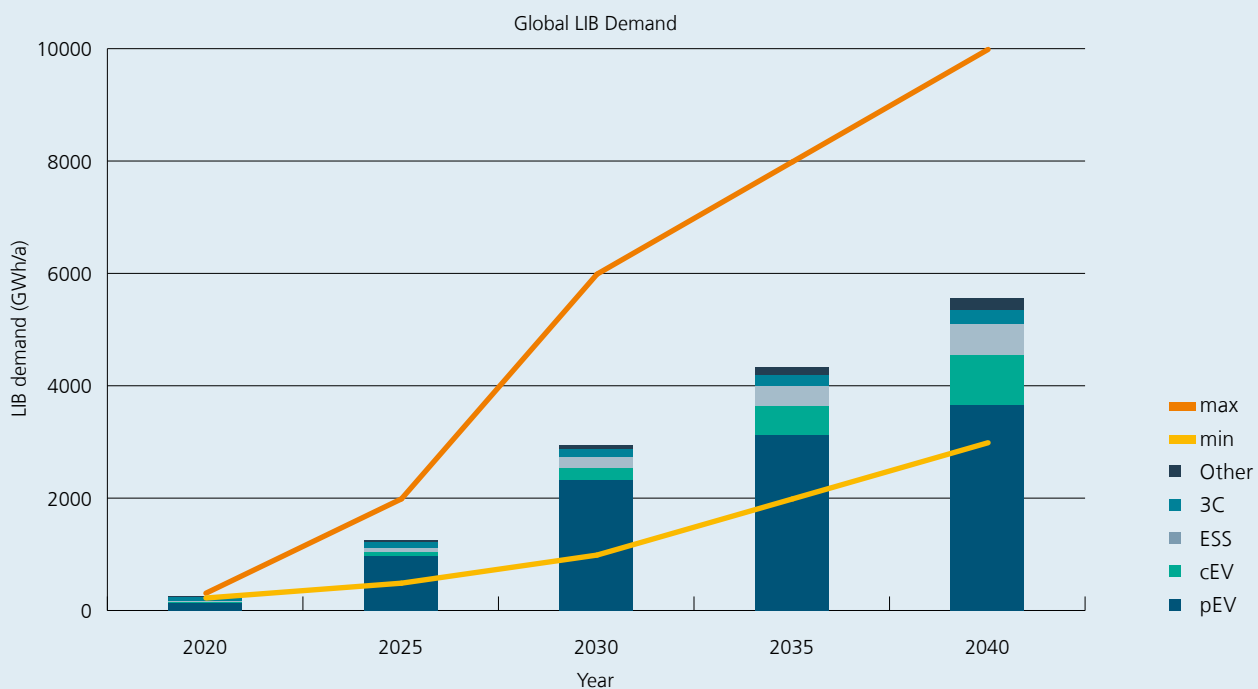
2030 and beyond. There are smaller numbers of heavy-duty commercial vehicles, but they have significantly higher battery capacities. Sales of light commercial vehicles like delivery vans or vehicles for craftsmen are increasing rapidly. The battery capacities of such vehicles are comparable with those of passenger cars [1].

The market for *ESS* is growing strongly, but at a low overall level. According to rather conservative forecasts, the annual demand from stationary applications could amount to about 100 GWh in 2030. More optimistic forecasts project demand of 200 to 300 GWh per year by then [1].

3C applications are already established LIB markets that will continue to grow. Smaller single-digit growth rates are forecast for the established market of laptop, tablets and mobile phones. The segment of power tools and portable household applications is considered a strong growth market for the next few years, with growth rates of 15–20 % annually. Other electronic and consumer applications such as cameras and drones are currently comparatively small, but could develop much more dynamically in the future.

Micromobility applications such as eBikes or scooters also represent a growing market. Growth rates are in the range of 8 to 14 % CAGR to date. Demand could roughly double by 2030.

Other transport sectors, e.g., trains, ships and airplanes, will begin or continue to push electrification efforts in the next few years. In addition to purely electric alternatives, hybridization of propulsion systems may be a frequent option in shipping, for example. In aviation, the need for batteries will probably only increase on a large scale after 2030 [1]. The battery demand for the categories micromobility and other transport sectors is comparatively low and is assigned to the category "Other" in Figure 1.

Global and regional developments of cell and component production

Given the predicted increase in demand for battery cells, global production capacities will have to increase significantly in the future. 1 TWh of production capacity was installed at the end of 2021, according to initial calculations. Most of the factories are located in Asia, especially China, Korea, and Japan. The announced capacities suggest installations of around 3 TWh by 2025 and the share of production in Europe and the United States will increase by then. By 2030, production capacities may exceed 4.5 TWh. In total, a cumulated production capacity of more than 9 TWh has been announced by different companies up to 2030. However, a consolidation of these announcements and stakeholders is expected, and these capacities might only be realized well beyond 2030 [1].

It is likely that Europe will develop production capacity of about 1.5 TWh by 2030, partly built by Asian, but increasingly also by European stakeholders. Due to this trend, Europe's capacities will account for approx. one third of global production by 2030.

Market revenues and battery cost developments

In total, the LIB cells sold in 2020 had a market value of 35 billion euro. Due to the predicted growth of the market, revenue may increase to over 125–225 billion euro by 2030 [1]. Studies assume current average cell costs of approx. 90 EUR/kWh for state-of-the-art LIB [2]. Forecasts predict a price drop to approx. 70–80 % of the original costs in 2030. The material components for the cell (anode, cathode, separator and electrolyte) account for the largest share of cell costs. The market share of these components was over 15 billion euro in 2020 and will increase to over 90 billion euro by 2030. The most expensive cell component is the cathode, as it often contains valuable raw materials such as cobalt and nickel. Overall, the cathode accounts for about half of the material costs. Compared to material costs, manufacturing costs make up a smaller share of the total cell costs. The added monetary value of cell production (without materials etc.) will be approx. 35 billion euro in Europe and 65 billion euro worldwide in 2030. Beyond battery cell fabrication, the assembly of cells to modules and packs also is another important market. The costs for the pack assembly amount to approx. 17 EUR/kWh. Other affected markets are the machinery and equipment manufacturers producing the systems needed for highly automated cell production. The costs for the installation of production lines in all the announced cell factories amount to approx. 130 billion euro worldwide until 2030. In Europe, battery manufacturers will have to invest approx. 40 billion euro by 2030. In Germany, more than 9 billion euro have to be invested in production lines by then.

In summary, the industry will have to meet a steadily increasing demand for battery cells in the coming years. The medium-term growth potential is very high up to 2030 and beyond. In 2030, the demand for batteries will be between 1 and 6 TWh. Growth rates of well over 20 % are realistic in the coming years. The main driver of demand is the growing market for electric vehicles. This market segment will account for over 80 % of global cell demand in the future. The location of production facilities will shift from Asia to Europe to a certain extent, so that a stronger overall value chain around cell production will emerge in Europe as well.

1.3. Publication and Patent Analysis

The numbers of scientific publications and patent applications in specific fields of science and technology are a measure of the R&D efforts and commercial interest in this field. Details concerning the methods and search strategies are described in Section 1.4.

Publication dynamics, active countries and players

Publications have been increasing over the last 20 years (Figure 2), and have been particularly strong over the last ten years. Approximately 200 peer-reviewed publications were published in the field of SSB in 2010. These numbers increased to more than 2200 in 2020 and so far the upwards trend seems to continue.

China, the USA, the EU, Japan and South Korea are particularly active in publishing scientific articles in the field of SSB (Figure 2). Over the last five years, the activities in China have multiplied so that more than half of all SSB-related publications in 2020 were from Chinese organizations. Publications have also increased in the other countries, albeit at a lower rate.

The Chinese Academy of Sciences (806) is the organization with the highest number of publications in the last 5 years (2016–2020), followed by the United States Department of Energy (572), and then the German Helmholtz Association (380). These organizations represent China, the USA and Germany, the three countries with the highest publication activity, and each comprise various sub-institutions. The most actively publishing institutions in China are the University of Chinese Academy of Sciences (358), Tsinghua University (294) and the Huazhong University of Science Technology (133). In the USA, the University of California System (173), the University of Maryland College Park (146), the University System of Maryland (146), the Argonne National Laboratory (131) and the University of Chicago (131) had the highest number of SSB-related publications. In Germany, the Research Center Julich (180), the Karlsruhe Institute of Technology (177), and the University of Munster (145) are most active in SSB-related publications. The only other institution or organization that appears in the top-15 is the French Centre National de la Recherche Scientifique CNRS (153).

Patent dynamics, active countries and stakeholders

The number of transnational SSB-related patent applications has been increasing over the last 20 years (Figure 3), with an even higher rate in the last ten years. Transnational patent applications (i.e., patent applications at either the European Patent Office – EPO, or the World Intellectual Property Organization – WIPO) have been analyzed to allow for a fair country comparison.

In terms of the active countries and regions, the situation differs from publications: Japan has led the field of patenting SSB over the last 10 years, followed by the USA, South Korea, the EU, and China. Recently, the application numbers have fallen, or stopped increasing in Japan, the USA and the EU, whereas they continue to grow in South Korea and China. In contrast to publication activities, which are dominated by research organizations and institutions, companies dominate the patenting landscape. The top-15 companies in SSB-related patent applications display the strong dominance of Asian companies. Companies from Japan (Panasonic 113, Fuji Film 67, Toyota 39, TDK 35, Showa Denko 34, Murata 31, Idemitsu 29, Mitsui 29, NGK Insulators 28) and South Korea (LG 138, Samsung 66) are especially prominent, with only two companies in the top-15 not headquartered in one of these two countries (Bosch 38 – Germany, and Nanotek Instr. 28 – USA).

SSB in comparison to LIB

The R&D on lithium-ion battery technology has been increasing over the last 20 years and with it the number of publications and patent applications (Figure 4). A similar trend can be observed for solid-state batteries, which are a sub-group of lithium-ion batteries. The share of SSB-related publications and patent applications has increased from less than 10 % of total LIB figures to approx. 15 % in recent years, which indicates the rising interest in solid-state battery technologies.

Germany and the EU

There has been steady growth in SSB-related publications in the EU and especially in Germany, which is currently the most active country in the EU in this field. These numbers indicate a significant interest in the technology. On the other hand, the number of patent applications is comparatively low in the EU and Germany, and the numbers here have been stagnating or even decreasing slightly since 2017, while they still show significant increases in other regions of the world. The overall low number of patent applications in the EU can be attributed to the small number of companies here that are active in the field of battery technologies compared to, e.g., Japan and South Korea. The few active companies in the EU are currently mostly small companies or startups and only a few larger players exist.

Figure 2: Number of peer-reviewed publications in the field of solid-state batteries and the most active countries/regions for the years 2000 to 2020.
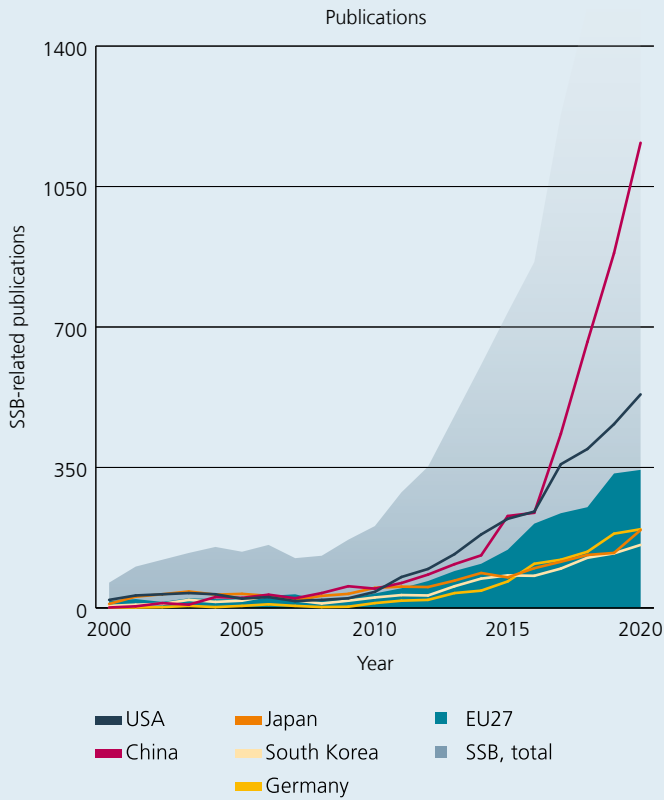

Publications

Figure 3: Number of transnational patent applications in the field of solid-state batteries and the most active countries/regions for the years 2000 to 2019.
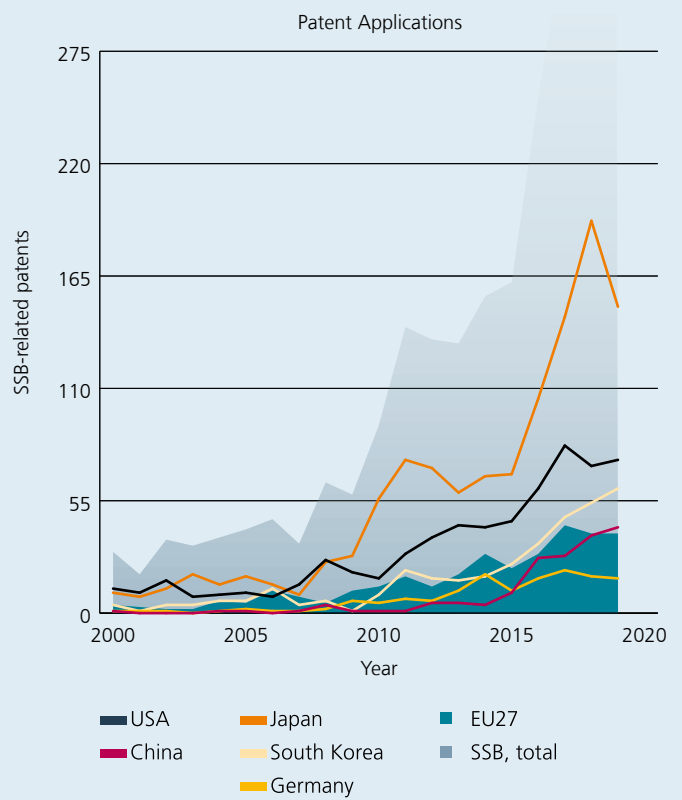

Patent Applications

Figure 4: Number of publications and transnational patent applications in the field of lithium-ion batteries and solid-state batteries between 2000 and 2019 (for patents) and between 2000 and 2020 (for publications). The share of SSB-related publications and patent applications has increased slightly over the last 5 years to approx. 15 % of the total figures for LIB.

SSB vs. LIB
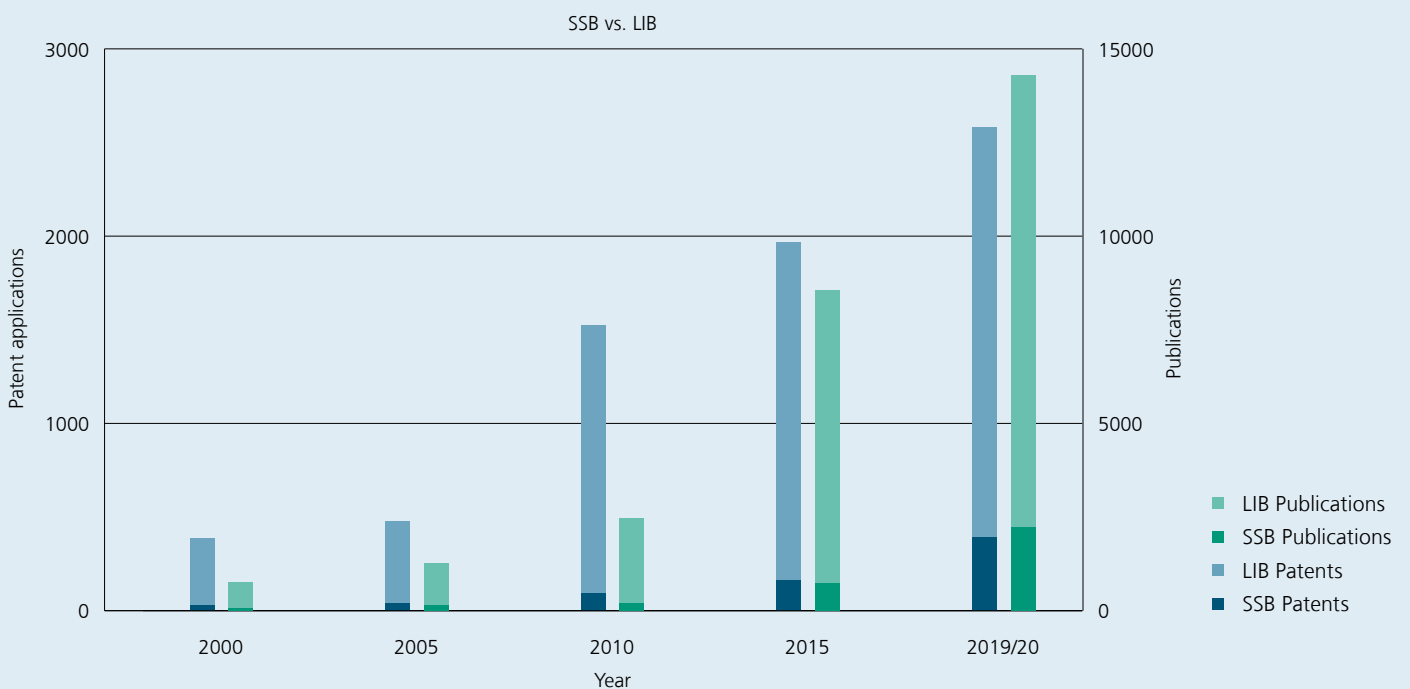
1.4. Methods

A number of interrelated methods were used to draw up the roadmap, which build sequentially on each other (Figure 5).

Desk Research

A **scientific literature review** of the state-of-the-art of SSB technologies marked the start of the activities beginning in June 2021. This was continued throughout the elaboration of the roadmap in order to complement and update important literature identified through interviews, further desk research and as more recent literature appeared during the process. The aim was to identify the most important and promising material classes and cell concepts undergoing research, including their individual advantages and bottlenecks as well as the potential solutions to address these bottlenecks. Furthermore, the first performance parameters were extracted with respect to, e.g., ionic conductivities, chemical and mechanical stability, material compatibility, etc.

The literature review, which was supported by initial expert interviews, led to the first roadmap including time frames and scope from materials to cells and applications. In addition, a questionnaire was developed for an online survey of experts intended to answer or consolidate open questions from the literature.

A **market literature review** complemented the scientific literature review during the process in order to obtain market data on lithium-ion batteries as a benchmark for SSB, and to identify concrete SSB concepts, including any announcements concerning market introduction and key performance parameters. The sources used included market studies, technology reports, articles, information from company homepages, etc.

On a more aggregated level, **publication and patent analyses** were used to depict past R&D dynamics, current trends, and competitors at regional, country, and organizational level. The peer-reviewed publications were extracted from the Web of Science using a keyword-based search. This approach using peer-reviewed publications was assumed to identify "key publications", which allow for a comparison of R&D activities between countries and key organizations. The total number of patent applications were identified via a keyword search in the World Patents Index (WPI) database. To narrow the search to patent applications with higher economic value, it was limited to transnational patent applications, i.e., patent applications either at the European Patent Office (EPO) or the World Intellectual Property Organization (WIPO), as these are always aimed at several foreign patent offices and require a high

investment in the patent application process. Another major advantage of transnational patents is a fair country comparison, as differences in national patenting systems lead to the overassessment of certain countries if only national patent applications are regarded. The publication and patent activities indicate the position of German and EU activities in an international context, with respect to LIB as a benchmark, and in the time until 2019/2020. These analyses are strategically important to assess the competition as well as potential partnerships.

Interviews

Approx. 25 interviews with international experts were conducted during the roadmapping process. The first set of interviews were intended to outline the roadmap concept, the online survey concept, and to answer questions insufficiently addressed in the literature, especially concerning market assessments. Additional expert interviews were conducted based on the survey results in order to prepare the expert workshop (see below) and after the workshop in case of open questions. The expert interviews covered the different material classes and cell concepts to further harmonize and validate the findings. The interviews thus served to shape the roadmap's structure and content. On the one hand, this ensured it is in line with the scientific community. On the other hand, the interviews also served to check the consistency of outcomes from other methods and pinpoint major uncertainties and broad agreement. Furthermore, close and continuous interaction with the FESTBATT-cluster [3] took place during summer and autumn 2021 for support with technical questions.

Online Survey

Based on the desk research and the initial interviews, a questionnaire for an online survey was prepared. This was conducted between 20.09.2021 and 18.10.2021 among German experts in the field of SSB technology. Approx. 50 experts participated in the survey. The survey contained questions with qualitative and semi-quantitative answer options on the properties of oxide, sulfide and polymer solid electrolytes, the market potential of anode and cathode active materials, assessments of SSB cell concepts and production challenges for the different components and material classes of SSB as well as estimations of the global situation and competition in SSB R&D, and market developments. Results of the survey are shown and discussed throughout this roadmap. Based on the results of the online survey, the scope of the roadmap was

Figure 5: Summary of the methodology for compiling this roadmap.
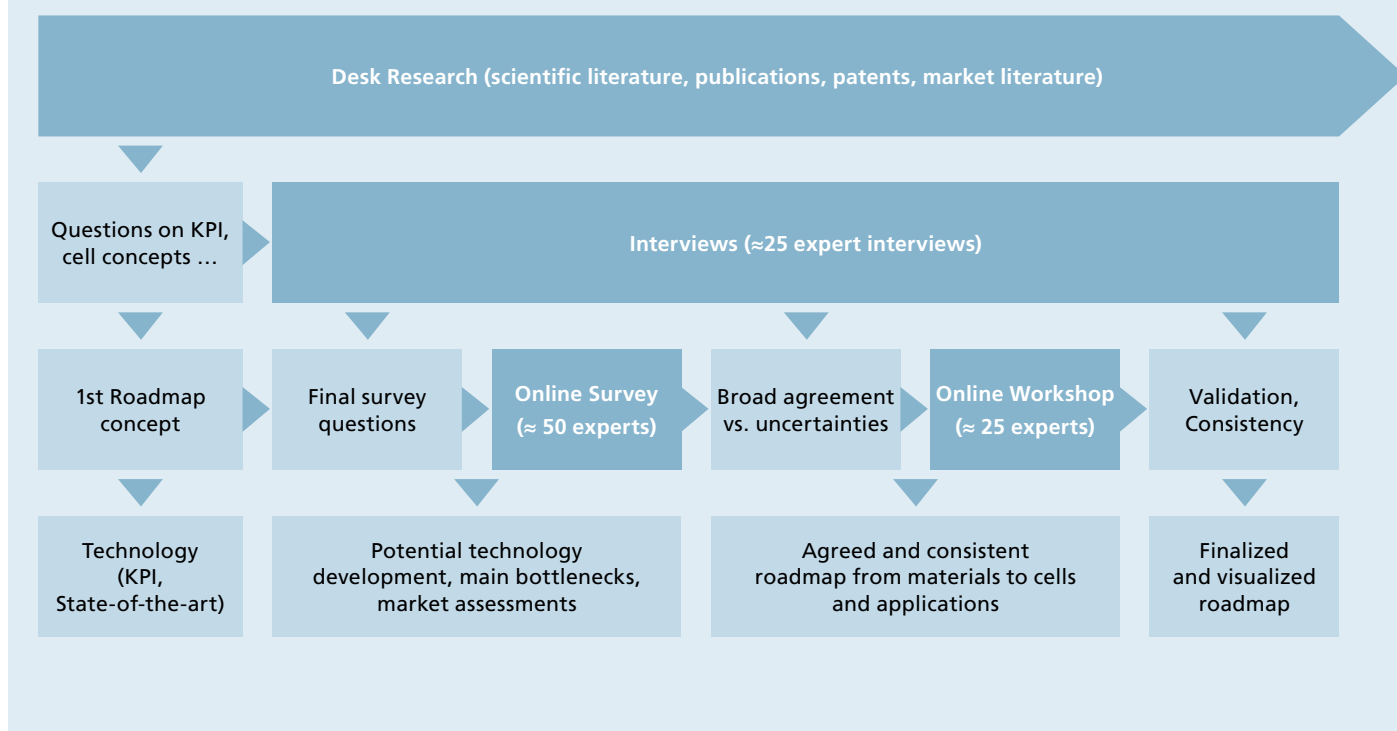
refined and the roadmap concept adapted. Content-wise the results helped to harmonize technology and market assessments, and to quantify and benchmark the assessments.

Expert workshop

The insights gathered through interviews, desk research and the survey were complemented by an expert online workshop, hosted on 26.10.2021. Approx. 25 European experts from science and industry with expertise in solid electrolyte research, SSB cell concept development, battery production and automotive applications attended and participated in this workshop. During the workshop, the state of research of the three main solid electrolyte material classes (oxides, sulfides and polymers) was discussed using a collaborative real-time online whiteboard. The workshop focused on discussing the challenges and related solutions concerning the materials and cell concepts as well as the respective time frames and production milestones. Furthermore, the roadmap as presented in this report was discussed at the level of materials, components, cells and potential applications. KPI as well as the development of markets were debated. This workshop served to validate the roadmap, but also to supplement and correct it by including recent inputs, updates and harmonization.

Quantification and estimation of KPI

To assess the potential technical and economic KPI of solid-electrolyte cell concepts, we performed calculations at the level of materials and cells based on expert assumptions or technical parameters published in literature. We used a cell design tool developed by Fraunhofer ISI for energy density and cost, which can be configured to different material, electrode and cell parameters as well as a calculation tool for energy density published by Betz et al [4].

In summary, more than 100 mainly national and European but also international experts contributed to the roadmap. After the workshop, the roadmap team and authors of this report finalized the roadmap including the latest literature reviews, graphics, and consolidating texts.

The roadmap is to be understood as a technology roadmap with an international perspective and not restricted to the national or European level only. The screened literature and markets were international. However, the experts contributing to the roadmap were mainly from Germany and Europe, and might have a certain bias with respect to their background and perspective.

2.   Components of Solid-State Batteries

2.1.   Solid-State Battery: From Material to Cell

General structure of lithium-ion batteries
Lithium-ion battery cells consist of two electrodes, the anode and the cathode, each composed of a current collector, an anode / cathode active material (AAM/CAM) and inactive materials such as binders and conductive agents. A separator in-between the electrodes and a liquid electrolyte containing lithium-ions provides ionic conductivity and prevents electronic conductivity (Figure 6). During battery charging, external voltage is applied to the electrodes, Li+-ions are deintercalated from the CAM, transported through the electrolyte to the anode and intercalated in the AAM. This process is reversed during discharging. The redox potential between cathode and anode can be utilized as a power source for external appliances.

The CAM typically consists of sub-micrometer primary particles that aggregate to micrometer-sized secondary particles. Polymer binders provide the mechanical stability of these particle-based layers and nano- to micro-sized carbon additives, which cover the CAM surface and result in a conductive network, enable electronic conductivity. The CAM should account for a large fraction of the total weight of the electrode components (ideally more than 90 wt.%) in order to achieve high energy densities.

The AAM typically consists of either spherical or plate-like graphite particles. Depending on the desired power capability, smaller or larger particles are used. Similar to the CAM, binders and carbon additives are added.

The porosity of the electrodes typically varies between 25 to 35 vol.%, depending on the desired power capability. Higher pore volumes yield larger electrode-electrolyte interface areas and thus higher power capabilities. On the other hand, higher porosity leads to lower volumetric energy density. To achieve high energy densities, the general target is to reduce the amount of passive components, e.g., by reducing the thickness of separator layers, increasing the AM (active material) content, or reducing porosity.

The carbon additives in the material mix provide the electronic conductivity, the electrolyte provides the ionic conductivity, and the binder ensures the mechanical stability of the electrodes. All three components act on the surface of the AM particles. As a result, there is a trade-off between the volume shares and the interfaces of these three components in electrodes and these have to be well balanced. During charging and discharging, the AM particles undergo volume changes, which pose challenges to the functionalities such as electronic conductivity. The liquid electrolyte, however, ensures good ionic contact to the AM particles at all times.

Structure of solid-state batteries
The general electrochemical set-up of a LIB, as described above, also applies to lithium-ion solid-state batteries (Figure 6). The difference is the (at least partial) replacement of the liquid electrolyte with a solid electrolyte (SE). Therefore, the ionic contact between electrolyte and AM has to be established by creating intimate contact, e.g., in the case of particle-based AM by mixing and compacting the SE particles with the AM particles. Porosity in the AM layers represents unused volume and should be avoided. Furthermore, in contrast to liquid electrolytes, volume changes in the AM during charging/discharging cycles may affect the ionic contact between the solid electrolytes and the AM, which typically necessitates the application of external pressure to the cells.

In all-solid-state batteries, the liquid electrolyte is completely replaced, while several solid-state battery concepts initially consider the use of liquid electrolytes as catholyte or anolyte to guarantee sufficiently high ionic conductivity, especially at the interface between the electrolyte and the active materials. In our roadmap, we consider these solid/liquid hybrid cell concepts (battery cells that contain solid and liquid electrolytes) as representing an intermediate step to all-solid-state batteries.

Figure 6: Exemplary structure of a state-of-the-art liquid electrolyte lithium-ion battery and a solid-state battery with lithium anode.

Liquid electrolyte LIB

Current collector

Anode active material

Separator

Current collector

Cathode active material

Solid-state battery

Current collector

Li metal anode

Solid electrolyte
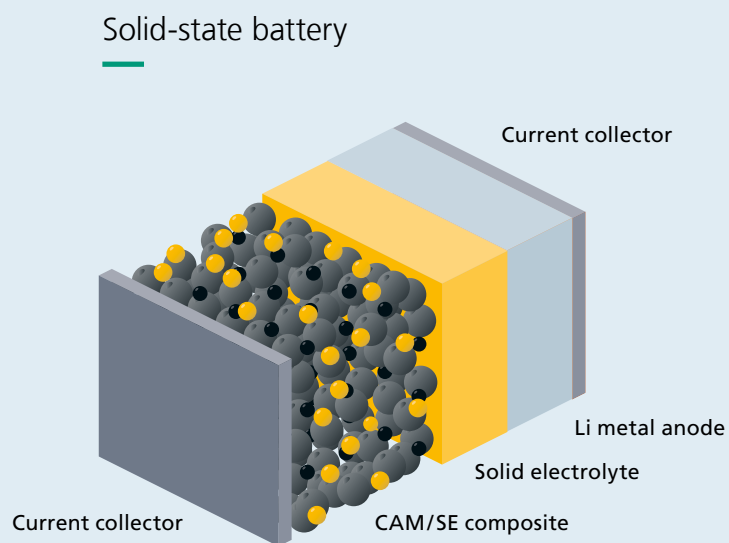
Current collector

CAM/SE composite
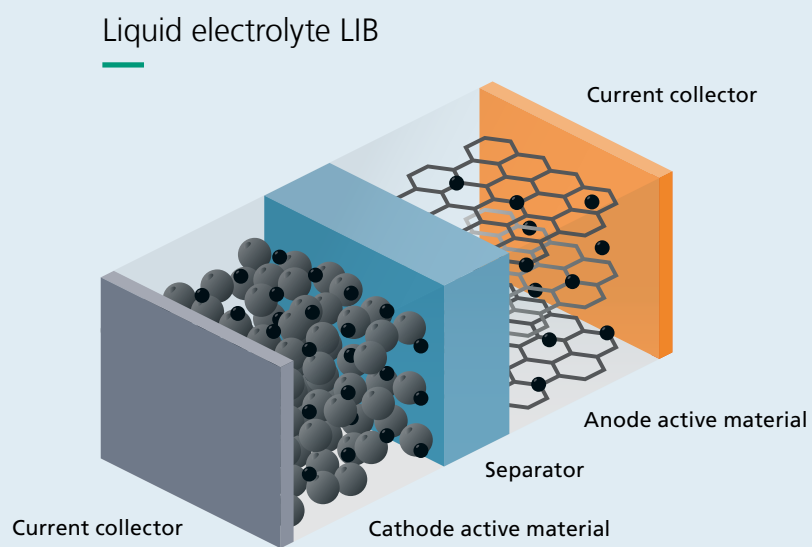
Figure 7: The general structure of solid-state batteries combines a solid electrolyte separator with an anolyte, a catholyte, and anode and cathode active materials. Various options exist for each of these components, opening up a wide range of possible combinations.

Current collector	Anode active material	Anolyte	Separator	Catholyte	Cathode active material	Current collector
	▪ Lithium metal	▪ Solid	▪ Solid	▪ Solid	▪ LFP	
	▪ Silicon	▪ Oxide	▪ Oxide	▪ Oxide	▪ NMC	
	▪ Graphite	▪ Sulfide	▪ Sulfide	▪ Sulfide	▪ NCA	
	▪ LTO	▪ Polymer	▪ Polymer	▪ Polymer	▪ Sulfur	
		▪ (Liquid)		▪ (Liquid)	▪ High-voltage cathode, e.g. LMNO	

Various options are available for each of the main components of SSB cells, namely anode and cathode active materials, anolyte, catholyte and SE separator, which can be combined in manifold ways (Figure 7). This large variety of combinations means numerous possible cell options, many of which are being considered by R&D institutions and/or companies (Section 4.2). Those options currently considered most promising or relevant are discussed in more detail in Sections 4.2–4.6.

Components of SSB

The main components of the SSB cell are the anode and cathode active materials and the solid electrolytes. Various materials are suitable for use in SSB:

Anode active material:

The most promising anode active materials to achieve high energy density are lithium metal and silicon. Lithium metal anodes are considered the most promising as they enable the highest possible energy density on the anode side.

Cathode active material:

The most promising CAM in the near future are transition metal-based oxides (NMC, NCA) and lithium iron phosphate (LFP). These materials are commonly used in state-of-the-art LIB, and supply chains and processing routes are already established.

Solid electrolytes:

Obviously, the most relevant component in a SSB is the solid electrolyte. Three main groups of solid electrolyte materials, namely oxides, sulfides and polymers, have received the most attention in recent years. The *oxide solid electrolyte* group consists of numerous diverse materials, all containing lithium and oxygen as the main components as well as various other elements. They can be sub-divided into groups, of which garnet-type oxides seem promising for application in SSB. The *sulfide solid electrolyte* group consists of numerous diverse materials, all containing lithium and sulfur as the main components as well as other elements, such as P, Si, Ge, or halides. The group of argyrodites seems especially promising for application in SSB. The *polymer solid electrolyte* group is currently dominated by polyethylene oxide (PEO), which is already in commercial use in SSB. The development of novel polymers is ongoing and beyond the polymer itself, additives and Li-salt can strongly influence the performance of the SE. Recently, further types of SE are being explored (e.g. halides), however, their development is in a very early stage and they are therefore excluded from an in-depth discussion in this report.

All these components and materials are discussed in more detail in the following sections as are aspects concerning materials availability and sustainability.

2.2. Anode

Since their commercialization in the 1990s, rechargeable lithium-ion batteries have been based on graphite intercalation type anodes [5]. Graphite has a practical specific capacity of close to 360 mAh/g at a low potential of approximately 0.1 V vs. Li. Graphite is available by mining natural sources or by high-temperature synthesis starting from carbon precursors. Graphite has a density of 2.15 g/cm³, which results in relatively balanced thicknesses of the anode and cathode layers in full cells. The stability of battery cells is significantly affected by the mechanical and chemical properties of the specific graphite materials. The volume change during intercalation of Li is more than 10 %, which can be accommodated by an electrode even with low porosity, but which still requires special binders to maintain the mechanical stability of the anode. The surface of graphite is chemically reactive with typical electrolytes, which leads to the formation of a solid electrolyte interface layer (SEI) during the first charging process [6]. The SEI is chemically passivating, which eventually leads to a stable interface, but consumes lithium at the same time, which is then no longer available for the reversible electrochemical storage reaction. The SEI's stability is also temperature-dependent and might eventually lead to degradation of the battery cell. Graphite has been demonstrated to function in several solid electrolyte cell concepts as well.

Silicon as next generation material
With the increasing demand for high energy cells, silicon has become a prominent additive to graphite materials in the form of silicon oxide (SiO_x) or silicon nanoparticles [7]. It has a theoretical capacity of more than 3500 mAh/g, which corresponds to a volume change of more than 300 %, placing a high burden on the mechanical stability of the electrode composite structure and the SEI. The chemical stability of silicon against typical electrolytes is also rather low, which causes a high loss of lithium in the irreversible SEI build-up reactions.

There are several approaches to overcome the described challenges and to utilize silicon, either as a stand-alone anode active material, or in a composite with graphite. Using a graphitic/carbon matrix to embed the Si-particles is often described as one way to stabilize the electrode, both mechanically and chemically. A graphitic matrix can host Li-ions and hence contribute to the anode capacity as well as provide a relatively rigid yet porous structure in which the Si-particles can undergo a large volume change without putting too much stress on the macroscopic electrode structure. At the same time, if graphitic or other carbon-based particles cover the Si-particle surfaces, the SEI might not form directly on the Si-surface and hence would not have to withstand the high volume expansion during cycling. Si-nanoparticles (SiNP) are

used for this concept [8]. Since the lithiation potential of silicon of approximately 0.3 V is slightly higher than that of graphite, the Si-particles have to undergo full lithiation and hence volume change before the intercalation potential of graphite is reached. For this kind of "deep cycling" of silicon in silicon/graphite composites, nano-sized particles provide the best overall mechanical stability and hence long-term cycling stability, but are costly to manufacture. There are several approaches to utilize silicon with a particle size in the micrometer range (SiMP) [9–11] to enable more cost-efficient anodes. A volume change in the order of 300 %, however, often leads to fracturing of the SiMP and thus to a low cycling stability. So far, SiMP are more suitable for anode concepts that are fully based on the lithiation of silicon alone and only use graphitic or carbon-based materials to provide a mechanically stable and electrically conductive matrix. By limiting the anode potential and hence the charge cut-off voltage at cell level, it is possible to limit the degree of lithium-silicon-alloying, e.g., at an effective capacity of 1000 to 2000 mAh/g ("limited cycling") with a correspondingly smaller volume change [12]. Silicon has been demonstrated as a potential anode material in SSB concepts [13, 14].

High power material LTO
As discussed, volume change during intercalation as well as chemical instabilities are major influencing factors for degradation effects in battery cells. A material with high structural and chemical stability is lithium titanate (LTO, $Li_4Ti_5O_{12}$) [15]. In the insertion reaction, which takes place at a high average potential of 1.55 V vs. Li, three additional Li-ions per formula unit can be accommodated in the structure, leading to a specific capacity of 175 mAh/g, and a volume change of less than 1 %. Operation at high potentials (vs. Li) at the anode side prevents the build-up of a SEI, but also results in a low cell voltage and hence low energy density on cell level. The power capability and long-term stability of the material is excellent and LTO-based cells can achieve a stability of several 1000 cycles and tolerate charge / discharge in minutes. Solid-state battery concepts utilizing LTO anodes have been demonstrated [16]. It is likely that, similar to liquid electrolyte-based batteries, LTO might play a role in high-duty solid-state batteries rather than mass applications.

Lithium anode for highest energies
Many solid-state battery concepts target the utilization of a lithium metal anode (LMA). This is one of the major drivers toward SSB in general. Lithium metal is the anode material with the highest theoretical specific capacity (4860 mAh/g) [17]. Moreover, lithium also has a very high volumetric capacity (2046 mAh/cm³) and the lowest reduction potential with -3.04 V vs. a standard hydrogen electrode (corresponding to 0 V vs. Li), which enables high voltage and high energy cells. There are several possible concepts for Li metal anodes, e.g., supported by inactive materials or direct plating on a current

collector during the charge process. There are even concepts (and first applications) using lithium metal directly as a lightweight current collector. Consequently, the anode would only consist of the lightest alkali metal. Drawbacks of Li metal-based systems concern the high chemical reactivity of lithium, which places high demands on the stability of adjacent materials, and electrochemical lithium deposition that can ideally result in flat plating or also in undesired dendrite growth, particularly with inhomogeneous current densities. These tree- or needle-like lithium metal structures, which can form during cycling, may eventually penetrate the separator and result in internal short circuits. So far, dendrite formation is one of the biggest challenges to the utilization of lithium metal in rechargeable batteries [17].

With regard to the concepts discussed, battery experts see the highest technological potential for solid-state batteries in the utilization of lithium metal as the anode material, followed by silicon (Figure 8). Graphite and LTO are considered to have rather low potential. From a market perspective, experts rated silicon anodes having high potential, followed by graphite and LTO. From today's perspective, the market potential of lithium metal anodes is very uncertain due to major challenges at material, cell concept and manufacturing level.

Figure 8: Expert survey assessment of technological and market potential of several anode active materials for solid-state batteries.
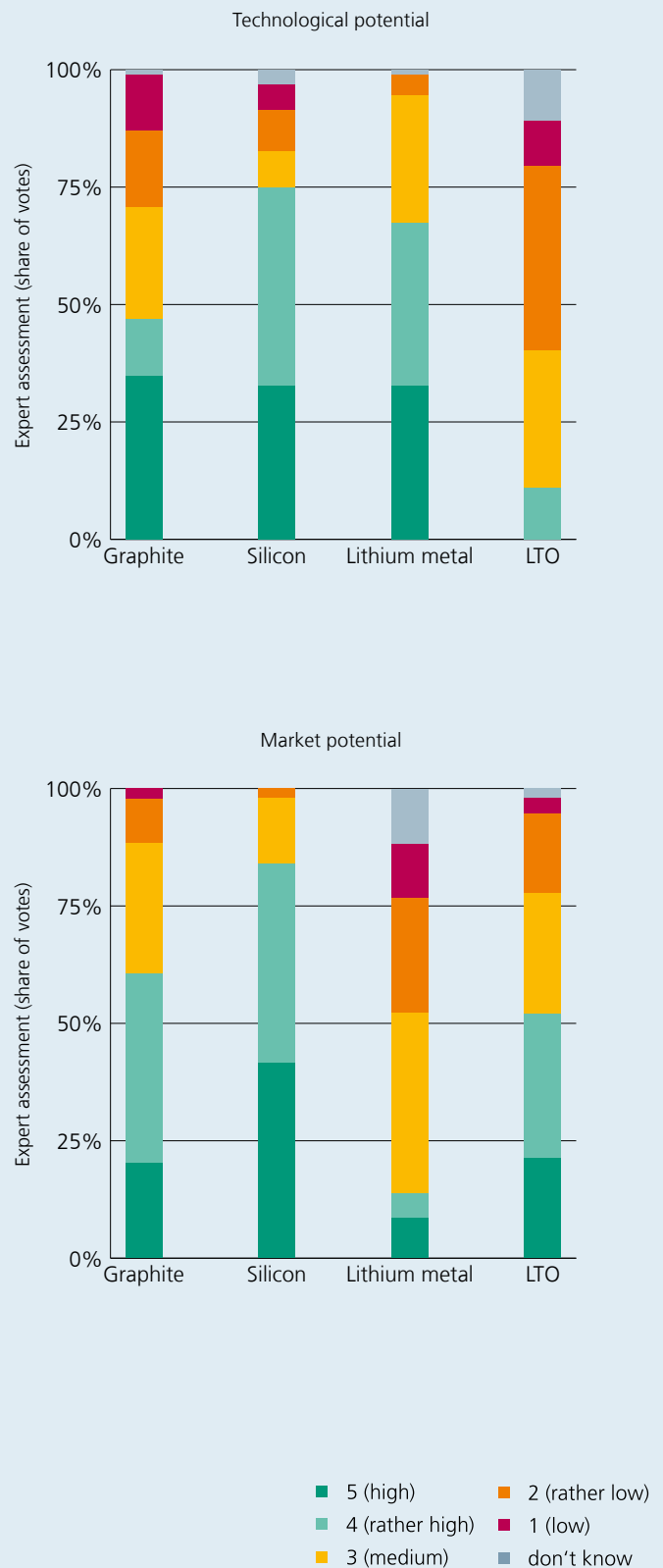
2.3. Cathode

A large variety of cathode active materials are discussed as potential materials in solid-state batteries. The same economic and ecological drivers exist for the further development or substitution of materials for solid-state batteries as for liquid electrolyte-based batteries. Beyond that, chemical and processing compatibilities in solid-state batteries can constitute additional technical requirements for the materials in SSB.

The roadmaps and R&D programs of established cell manufacturers and their customers from the automotive sector envisage the utilization of several established as well as new active materials in the coming years [18–21]. Recent trends aim at using three different classes of materials: (1) highest energy materials represented by Ni-based layered oxides, (2) highest performance or highest stability materials represented by well-understood mixed transition metal lithium nickel manganese cobalt oxides (NMC) and (3) lower cost materials represented by lithium iron phosphate (LFP) or Mn-based materials.

Ni-rich high energy materials
In particular, Ni-rich layered oxides (NMC, NCA) with a potential of approximately 3.8 V vs. Li promise higher energy density and high compatibility with established manufacturing processes. In the passenger car sector, NMC layered oxides (LiMO_2, M = Mn, Co, Ni and dopants) are predominantly used today. The lithium content of the layered oxides corresponds to a theoretical capacity of about 275 mAh/g with complete deintercalation of the lithium. However, in practical applications, the structural stability of the materials limits the maximum reversible deintercalation of lithium (Li$_{1-x}MO_2$, $0 < x < 1$). The established benchmark material NMC622 (LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$) currently achieves about 170 to 180 mAh/g in conventional LIB, and development targets for NMC811 (LiNi$_{0.8}$Mn$_{0.1}$Co$_{0.1}$O$_2$) are above 200 mAh/g. An essential prerequisite for such high capacities is to improve the intrinsic stability of the delithiated crystal structure of the materials and the electrode-electrolyte stability, for both liquid and solid electrolytes. The stability of the delithiated crystal structure can be improved, for example, by changing the Mn:Co:Ni ratio or by doping with other elements, such as aluminum – which is the case in NCA (Li(Ni,Co,Al)O$_2$) cathode materials [22]. Due to the low chemical stability of NMC811, stabilizing coatings are already used in material and LIB production. Several cell producers as well as several automotive OEM have announced plans to develop and commercialize NMC-like materials that go beyond NMC811. It is likely that some cathode materials will be commercialized in the upcoming years that share similar chemical compositions, but differ in doping levels, coatings, gradient of chemical composition (e.g., core-shell) and other properties. Due to their high share of Ni and low share of Co, the distinction between

the highest Ni NMC type and NCA type is no longer applicable. As a result, these materials are often considered as representing a convergence of NMC and NCA to "NMCA" [23–26]. The molecular formula can be specified as LiNi$_{1-x-y-z}$Co$_x$Mn$_y$D$_z$O$_2$ with x < 0.05, (1-x-y-z) > 0.9 and with D being a dopant such as Al or Mg [27]. Further reducing the Co content and increasing the Ni content, e.g., the end member LNO (LiNiO$_2$), could require difficult synthesis procedures, which create concentration gradients across the particle cross-section or core-shell structures [22, 28]. Further increases in energy density will require substitution of the classical layered oxide cathodes NMC/NCA with high capacity cathodes such as layered Li-rich high energy NMC (LLO or HE-NMC) [29].

Higher performance and stability materials
Although they do not have the highest energy densities, several established materials are still of interest for LIB due to their overall performance and stability, especially in applications that can be considered "high duty". The spinel-type oxide LMO (LiMn$_2$O$_4$), which has a high potential of 4.1 V vs. Li, is used today primarily as an additive in NMC- or NCA-based cathodes to improve their performance and stability. The substitution of Mn with Ni in LMNO (Li(Mn,Ni)$_2$O$_4$) leads to a significant increase in cell voltage (4.6 V vs. Li). This material could be used in high voltage cells in the future, but most likely not on automotive mass markets. NMC622 is currently widely used. It offers good thermal and cycling stability combined with reasonably high energy density. Recent material developments [22] aim to further improve the properties of these materials. For example, single crystalline NMC622 particles seem to open up further possibilities to extend the stability window, so that corresponding materials offer increased capacity and electrochemical stability.

Lower cost materials
Another branch of cathode active material development aims at lower cost materials. In recent years, several international automotive OEM have expressed an interest in using LFP-based (LiFePO$_4$) batteries for future low-range and low-cost EV. This development is driven by cost advantages at battery pack level resulting from the low metal and synthesis cost of LFP, but also by their good safety properties that allow direct integration of large volume cells in the battery pack [30, 31]. The practical capacity of LFP is around 160 mAh/g with an average potential of 3.3 V vs. Li. The overall energy density at pack level does not match NMC- or NCA-based batteries, but the concept could be feasible for smaller EV with limited cruising range. LFP is also of interest beyond automotive applications, e.g. for stationary storage. The energy density of the material could be increased by substituting Fe with Mn (LMFP, Li(Mn,Fe)PO$_4$), which has a higher cell voltage than LFP.

Other approaches include the utilization of Mn-based materials, particularly Li-rich layered oxides (LLO) due to their high

theoretical capacity and their potential low cost. While the crystallographic structure of these materials deviates from NMC, they are often termed high-energy NMC (HE-NMC), e.g., NMC370 or NMC820 ($Li_{1+x}Mn_{0.7}Ni_{0.3}O_{2+y}$ or $Li_{1+x}Mn_{0.8}Ni_{0.2}O_{2+y}$). As Mn is significantly cheaper than Ni, these types of LLO could mean lower cell costs.

Alternative materials

Besides these types of intercalation cathode materials, other compounds are being discussed as high-energy or low-cost alternatives. Particularly the use of Li-free conversion materials such as sulfur or iron sulfide (FeS_2) with high specific capacity could be possible in solid-state battery concepts in combination with a lithium metal anode. The lithium necessary for the electrochemical reaction could be introduced in the respective battery cell concepts via the anode by tailoring the thickness of an initial anode layer.

Based on the assessment in the expert survey (Figure 9), conventional layered oxide materials have the highest technological potential for application in solid-state batteries, followed by medium price and medium performance materials such as LFP, or high voltage materials. The potential of other materials such as sulfur is not yet clear, as the respective cell concepts still have many unresolved technological as well as production-related issues.

Interestingly, from a market perspective, layered oxide materials and medium cost materials, such as LFP, were rated equally high by the experts. This assessment might reflect the current automotive industry trend toward a lower cost strategy for some segments of the vehicle market. Resource availability also plays a significant role as a driver of material cost: With the increasing volume of the battery market and the related growing demand for specific metals, the pressure might grow to reduce cobalt and also nickel and copper.

Figure 9: Expert survey assessment of the technological and market potential of several cathode active materials for solid-state batteries.
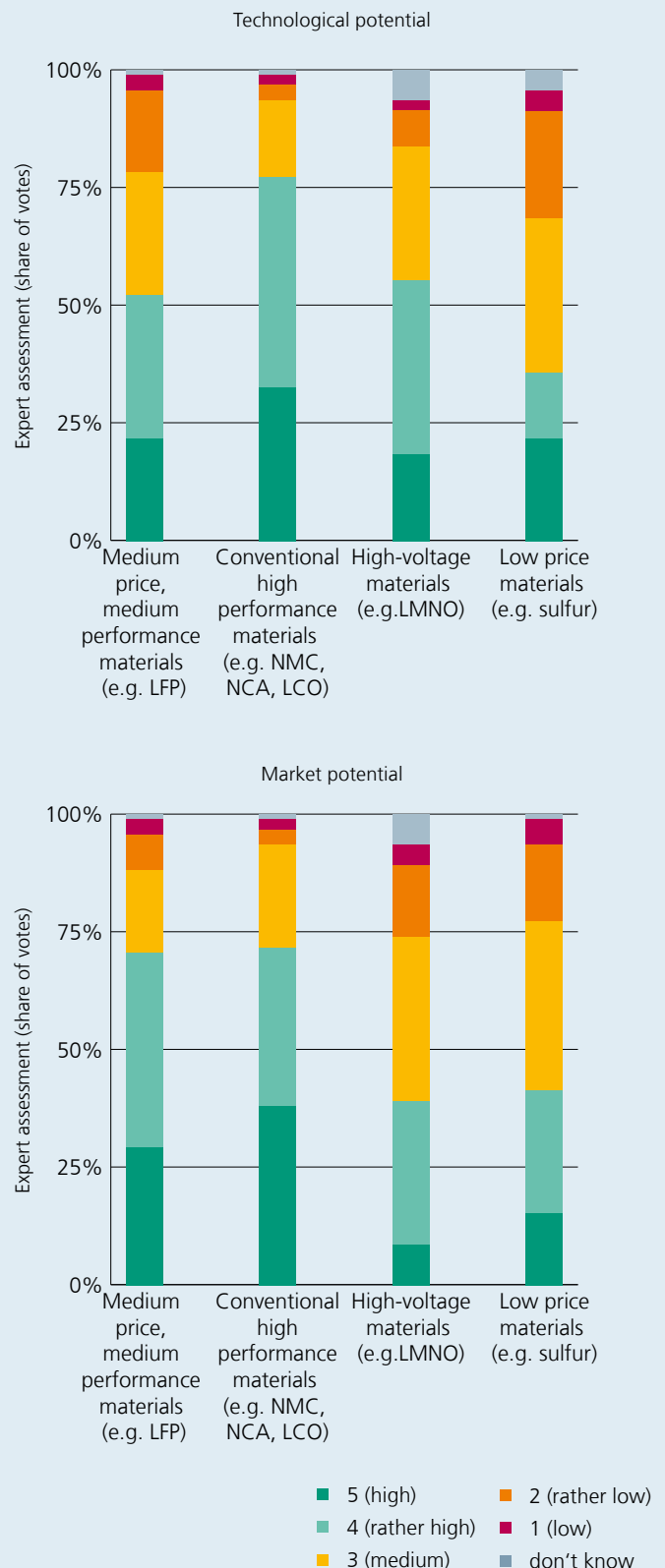
2.4. Solid Electrolytes

2.4.1. Oxide Electrolytes

Oxide solid electrolytes are not a sharply defined class of materials, but instead represent a group of compounds containing lithium and oxygen as well as other components such as, e.g., phosphorous, titanium, aluminum, lanthanum, germanium, zinc or zirconium. Batteries with an oxide separator marked the first attempts to work on a solid-state rechargeable battery. The first research projects began in the 1970s with thin film battery approaches. In 1980, at the same time as lithium-ion batteries (LIB) were developed, research was also done on solid oxide batteries with bulk layers [32].

Advantages

Good mechanical stability is the most important unique selling point of oxides compared to other material systems and simultaneously their biggest advantage. In addition to mechanical stability, oxide electrolytes are usually chemically stable and provide a large electrochemical window. For this reason, oxide electrolytes are compatible with high-voltage cathode materials. Their chemical stability also lower the requirements on the processing environment. They do not need stringent dry room conditions or an inert gas atmosphere. Some oxides are also chemically stable with lithium metal, which, combined with good mechanical properties, makes them a promising SE separator material and enables the use of Li metal anodes.

The wide variety of different materials also offer advantages. Various substituents can be used to create a large variety of compounds, which open up opportunities to find material systems with high ionic conductivity [32, 33].

Another advantage of oxide electrolytes is their insensitivity to temperature [34]. An oxide battery is able to function even in high-temperature environments, because of their mechanical and chemical stability. Some oxide sub-classes are even stable toward thermal runaway [35]. This property leads to exclusive niche markets for these batteries, e.g., in drilling applications, mines, autoclave applications or applications for firefighters.

Challenges and possible solutions

The mechanical properties of oxide electrolytes are not only advantageous: oxides are also stiff and brittle. State-of-the-art LIB processing is a foil-based roll-to-roll process, which means the material has to go through bending and rolling processes. All these steps are problematic if the material involved is stiff and brittle. A composite material, for example, a mixture of oxides and polymers, could reduce brittleness and stiffness [33]. On the downside, this would also reduce the ionic

conductivity. Mixing different components leads to hybrid and composite material systems, which are discussed in Section 4.

The solid-solid interface between the active materials and the oxide material is another challenge. It is hard to establish good ionic conductivity between the materials. Good interfacial contact is required to keep the interfacial resistance low and the overall performance high. Because of the stiffness of the materials, it is difficult to keep the different layers in permanent contact. The volume changes caused by charging and discharging cannot be compensated, because the material lacks flexibility. For this reason, the material compound must be constantly exposed to external pressure.

The compatibility with Li metal anodes mentioned above as an advantage does not apply to all oxide sub-classes. Some oxide electrolytes react chemically with Li metal. Therefore, protective layers must be applied between the Li metal anode and the oxide separator. This coating can be deposited onto the anode or onto the SE separator. Alternatively, an artificial solid electrolyte interphase (SEI) can be formed by additives in the electrolyte during initial cycling, i.e., a kinetic passivation layer. Furthermore, at higher current densities, despite their mechanical stability, oxides are also prone to penetration by lithium dendrites, which can grow along the grain boundaries of the solid electrolyte [36]. One way to avoid these problems with Li metal is to use alternative anode systems, e.g., silicon anode materials, but this comes at the cost of lower energy density.

Sintering is a necessary processing step for oxide materials (with bulk layer structure) to obtain dense layers with lower grain boundary resistances, thus enabling higher ionic conductivities. The range of sintering temperatures varies widely between the different oxide sub-classes (400–1300 °C) [32, 37–39]. High sintering temperatures are a disadvantage because of high energy consumption and related high costs. It has already proven possible to reduce the sintering temperature from originally over 1000 °C to below 800 °C for garnet-type oxides [32, 40, 41]. However, the lower sintering temperature may have a negative effect on ionic conductivity. It becomes even more problematic if the material has to be annealed with the cathode active material (CAM) during cathode production. The CAM is not stable at such high temperatures and decomposition reactions occur. One approach is to use additives to lower the annealing temperature. This method has already successfully reduced the temperature for an annealing process with LCO as the CAM together with oxide SE to 700°C [40]. Another alternative process is to fill CAM after sintering into a porous oxide electrolyte [42]. Furthermore, an alternative processing is to fill CAM after sintering in a porous oxide electrolyte [43]. In addition, it is possible to coat cathodes with a protective layer, which makes them more resistant to thermal effects. Dry processing routes such as aerosol deposition could be used to produce oxide layers

Figure 10: Radar chart of the relevant properties of oxide electrolytes.
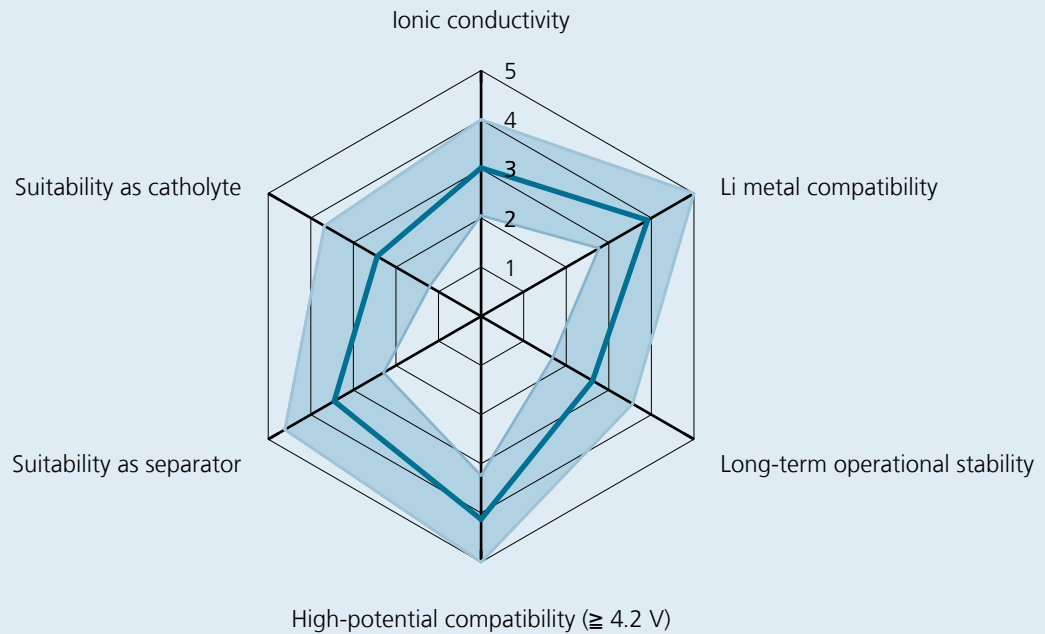
Oxides Electrolytes

- **Ionic conductivity:** The ionic conductivity of oxides is moderate and lies between that of sulfides and polymers.
- **Li metal compatibility:** The specific compatibility with Li metal depends on the oxide material class. However, oxides generally show a higher electrochemical and mechanical stability compared to sulfides and polymers.
- **Long-term operational stability:** Oxides are brittle. Due to volume changes during cycling, interfacial contact is reduced and cracks can form. Their electrochemical stability is high, which limits aging and decomposition reactions.
- **High potential compatibility:** Their wide electrochemical window means oxides can work with high potential cathodes.
- **Suitability as separator:** Their high mechanical and electrochemical stability toward Li metal makes oxides promising for use as a separator.
- **Suitability as catholyte:** The conductivity of oxides is too low when using high energy cells and thick catholytes. Sulfides are probably more suitable.

that require lower temperature annealing steps and no longer need high-temperature sintering. However, these processes are still rather immature and an option only in the long term.

The ionic conductivity of oxides is high enough for application as a SE separator. However, it is too low to allow use as a catholyte within thick cathodes, which are used specifically for high-energy cells. Substituents can be used to increase ionic conductivity, but conductivities significantly above 1 mS/cm at room temperature have not yet been reached. It is possible to use a hybrid approach with a mixture of gel and solid electrolyte as the catholyte. This option also simplifies the cathode processing, as annealing of CAM together with SE can be prevented. Alternatively, composite approaches can be used that

combine oxide separators with a sulfide catholyte with higher ionic conductivity. Furthermore, to increase the performance of the catholyte, a polymer component can be added to the oxide, which improves the wetting properties of the catholyte despite lower conductivity (composite approach).

To achieve higher energy densities in the batteries, inactive materials such as the solid electrolyte or the SE separator should contribute only low mass fractions. Oxides have a high specific density compared to sulfides and polymers, which makes it essential to manufacture thin layers of oxide separators. However, the fabrication of homogeneous and thin oxide films is very complex and has so far been limited to wet chemical processing. However, recent developments in dry

Table 1: Current challenges and possible solutions of oxide electrolytes:

Challenges	Possible solutions	Severity of the challenge
Brittleness	▪ Composite Materials (e.g. PE) ▪ Additives	MEDIUM
Sintering temperature	▪ Alternative processing ▪ ultrafast high-temperature sintering (UHS) ▪ CAM filled in porous SE ▪ Decrease sintering temperature with additives ▪ Increase temperature stability of CAM via coatings	MEDIUM TO HIGH
Performance as catholyte	▪ Increase ionic conductivity with additives ▪ Composite materials (sulfide or polymer share) ▪ Hybrid cell concepts (mixture of gel and solid electrolyte)	MEDIUM
Li metal stability (besides Garnet-type)	▪ Artificial SEI ▪ Protective coating ▪ Alternative anode material (e.g. Si)	MEDIUM
Thin film processing	▪ Dry Processing ▪ Additives	LOW TO MEDIUM

processing have managed to manufacture thin oxide films, so that this processing route might be an option in the long term [44]. Concrete alternative processes could be aerosol deposition or extrusion.

Oxide material sub-classes

Oxide solid electrolytes can be categorized into NASICON (Na-ion conducting glasses, only referring to the crystallographic structure here), garnet, and perovskite type electrolytes (both crystalline ion conductors) as well as lithium phosphorus oxy-nitrides (LiPON). The biggest difference between these sub-classes is their ionic conductivity and the production effort involved in terms of sintering temperature and processing environment.

LiPON sub-class

LiPON glassy phases play a special role among the oxide materials. Since one of the main problems with solid-state batteries is limited ionic conductivity, ensuring a short transport distance for ions was one way to solve this problem. Even before the development of solid-state electrolytes for large format solid-state-batteries, work had been done on thin-film solid-state macro batteries based on LiPON and the first publications appeared in the 1970s [45]. One of the first LiPON glass solid-state electrolytes was developed at Oak Ridge National and consisted of a nitrided $Li_2O-P_2O_5$ glass matrix [46]. These thin layers achieved an ionic conductivity of 2×10^{-3} mS/cm and were produced by a sputtering process. There are various combinations of micro-battery cells on the market using LiPON, most commonly with a $LiCoO_2$ cathode and a Li metal anode.

Through its SEI, this electrolyte sub-class is apparently electrochemically stable and allows a large number of cycles. In addition, no thermal treatments are required for the manufacturing process. Furthermore, the electrolyte is mechanically stable [32]. The electrolyte can be used with all the different electrode materials. LiPON is impenetrable to lithium dendrites, due to low ionic conductivity. However, the ionic conductivity of the LiPON sub-class is very low. To achieve high currents, this sub-class can only be used as a separator material in the form of very thin layers. Its use in a large-format pouch cell is not technically feasible. The only applications on the market are micro batteries, for example, for medical devices.

NASICON-type

NASICON-type oxides ($Li_{1+x}A_xTi_{2-x}(PO_4)_3$ LATP with A = Al, Cr, Ga, Fe, In, La, Sc and Y) were first investigated for batteries with a bulk layer structure in the early 1990s [32, 47, 48]. At that time, ionic conductivities of about 1 mS/cm were achieved. Later, $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) was discovered and an ionic conductivity of 6.65 mS/cm was achieved by adding chromium [49]. All tests were carried out in laboratory cells under laboratory conditions. Originally, the name comes from sodium (Na) conducting oxides. In the context of solid-state batteries, however, Na has since been replaced with lithium. The LATP NASICON-type solid-state electrolyte has some advantages, such as good stability in ambient atmosphere and thus low processing environment requirements. In addition, the sintering temperature is only 600–700 °C. This is the lowest temperature for oxide materials (apart from LIPON thin-film oxides). Process optimization can lower this temperature to below 400 °C [38, 39]. NASICON-type electrolytes have the highest ionic conductivity among the oxides. This could be sufficient for use as the catholyte in high power cells with thin active material layers. The solid electrolytes are also stable in the presence of high potential (5 V) cathodes.

On the other hand, a disadvantage of LATP is its chemical instability toward the lithium metal anode [32, 50–52]. LAGP barrier layers can be applied to block direct contact and enable stable redox reactions [52]. However, even LAGP exhibits only limited stability toward Li metal in the long term and is expensive, because of the germanium it contains. Compared to garnet-type and perovskite-type oxides, NASICON-type oxides have the lowest thermal resistance. Thermal runaways can occur with LAGP and LATP at onset temperatures of approx. 300 °C, as demonstrated in a test setup [35].

Garnet-type

The garnet-type is one of the best known and most promising material sub-class within the oxides. Garnet solid electrolytes were first developed with $Li_6ALa_2Ta_2O_{12}$ (A=Sr, Ba) composition, and achieved ionic conductivity of 4×10^{-2} mS/cm in 2005 [53]. Subsequently, following optimization of the composition to $Li_7La_3Zr_2O_{12}$ (LLZO), ionic conductivities of around 1 mS/cm were achieved [54]. Advantages of garnet-type electrolytes a wide electrochemical stability window. Additionally, the material can be compatible with cathodes up to 6 V vs. lithium [55]. Their chemical stability in the presence of Li metal anodes is worth highlighting [53]. No other oxide material sub-class for bulk layer structure batteries is stable in the presence of Li metal without further treatment, e.g., coatings or an artificial SEI. The thermal stability of the garnet-type oxide is the highest among the oxide sub-classes [34]. In fact, the garnet-type oxide is even stable toward thermal runaway [35]. With additives, ionic conductivities of approx. 1 mS/cm can be achieved, which makes them suitable for use as a separator.

A disadvantage of garnet-type materials is the need for lanthanum (La), which is limited in terms of the available resource quantities and locations. Producing the garnet-type requires high sintering temperatures of over 1000 °C, which incurs costs and limits the compatibility with certain cathode active materials as the catholyte in an annealing process together with CAM. Compared to other oxides, it requires the highest

temperatures. It is possible to reduce the temperature, but lower temperatures usually have disadvantages for the ionic conductivity. The conductivity of maximum 1 mS/cm at room temperature is still too low for application as a catholyte.

Perovskite type

Perovskite-type oxides account for only a small share of the current research on oxide electrolytes. They were discovered in the 1980s, just before the NASICON-type or garnet-type sub-classes. LLTO ($Li_{3x}La_{2/3-x}TiO_3$) is the most prominent representative of this class and shows ionic conductivity of approx. 1 mS/cm [56]. The materials are already used, among others, in fuel cells and chemical reactors [56].

The perovskite-type has no clear advantages over the garnet-type or NASICON-type sub-classes. However, because it was researched after the LISICON-type and before the other two sub-classes, it was briefly considered promising, due to its relatively high conductivity compared to LISICON. The thermal stability is higher than NASICON-type oxides, but lower than garnet-type oxides. A slight thermal runaway at an onset temperature of approx. 250 °C is theoretically possible and has been demonstrated in a test setup [35]. LLTO electrolytes are not stable in the presence of Li metal and decompose in a reduction process.

Conclusions

Oxide electrolytes are promising due to their high mechanical stability. The garnet-type is the only electrolyte material sub-class across all the electrolyte classes that is stable in the presence of Li metal without requiring an additional protective layer. On the downside, oxide electrolytes are stiff and brittle, and require high-temperature sintering, which makes the overall processing costly and difficult, especially for the cathode composite. Furthermore, the ionic conductivities of oxide electrolytes are relatively low (e.g., compared to sulfide electrolytes), which makes the oxides suitable mainly as SE separators or possibly as protective layers for other materials.

Table 2: Overview of oxide electrolyte sub-classes:

Electrolyte sub-class	Ionic conductivity of most promising examples	Suitable as	Market potential
LiPON-type	▪ $\approx 2 \times 10^{-3}$ mS/cm ($Li_{3.3}PO_{3.9}N_{0.17}$)	Separator	LOW
NASICON-type	▪ 3 mS/cm (Li1.3Al0.3Ti1.7(PO4)3)	Separator,	MEDIUM
	▪ 6.65 mS/cm (Li1.5Al0.4Cr0.1Ge1.5(PO4)3)	Catholyte	
Garnet-type	▪ 0.51 mS/cm ($Li_7La_3Zr_2O_{12}$)	Separator	HIGH
	▪ 1.8 mS/cm (Li6.65Ga0.15La3Zr1.90Sc0.10O12)		
Perovskite-type	▪ 1 mS/cm ($La_{0.51}Li_{0.34}TiO_{2.94}$) [48]	Separator	LOW

2.4.2. Sulfide Electrolytes

The group of sulfide solid electrolytes (sulfide SE) represents a variety of compounds all containing lithium and sulfur as the main components, which can be complemented by phosphorous, silicon, germanium or halides, among others. Sulfides are processed in glass, crystalline or glass-ceramic states, which results in manifold properties in this solid electrolyte group.

Advantages
Scientific and industrial interest in sulfide electrolytes has been growing over the last decade, because of the discovery of sulfide-based materials that exhibit ionic conductivities for Li-ions that are similar to or even higher than the liquid electrolytes used in state-of-the-art lithium-ion batteries (LIB) [57–59]. This advantage is enhanced by the fact that sulfides have a Li-ion transference number of virtually 1, which means that 100 % of the ionic conductivity in the electrolyte is based on the transport of lithium-ions [55]. In contrast, the lithium ion transference number of liquid electrolytes is lower than 0.5, as a large part of the conductivity stems from anions in the electrolyte.

The superior conductivity of sulfides compared to oxides is rooted in the greater softness (according to the HSAB concept [60]) and polarizability of sulfur atoms compared to oxygen atoms. As a result, the Li-ions have a weaker interaction with the sulfur atoms and exhibit higher mobility.

Moreover, the softness and plasticity of sulfide-based electrolyte materials offer advantages for processing, enable good interfaces to the anode/cathode active materials, and thus ultimately facilitate cell design. Most sulfide electrolytes can be manufactured by cold pressing or high-pressure calendaring. This avoids expensive high-temperature sintering steps. High-pressure treatment enables very dense layers with good contact of neighboring crystallites (low grain boundary resistance) and good electrode-electrolyte contact. This helps to prevent lithium dendrite formation, since dendrites mostly nucleate and propagate at and along grain boundaries, voids or other defects (see challenges). Furthermore, their plasticity enables better volume change compensation of the active materials during cycling compared to, e.g., brittle oxide materials.
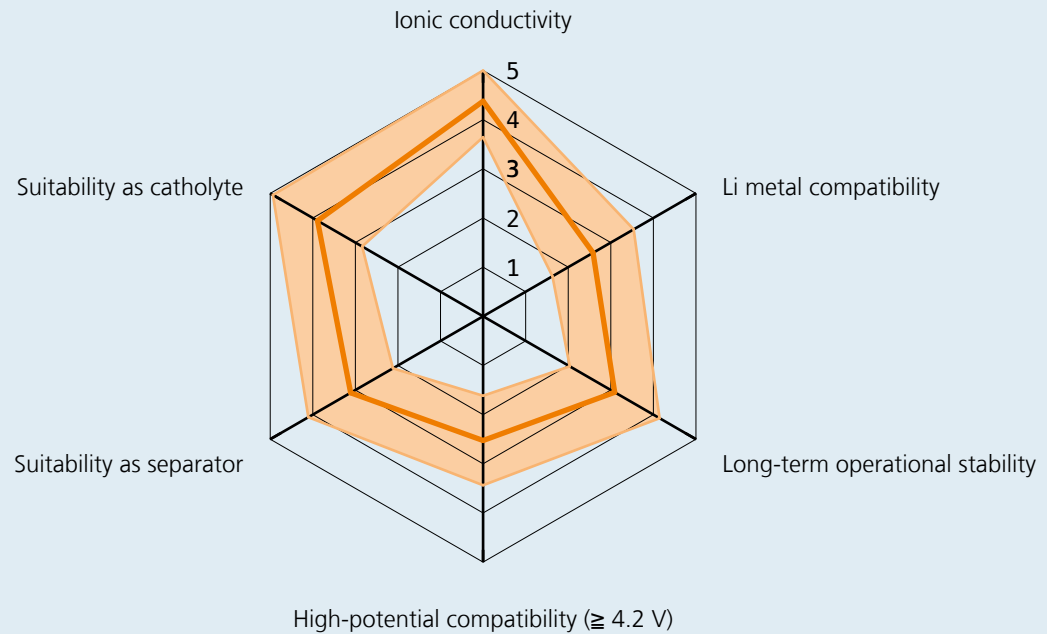
Challenges and possible solutions
An often-stated disadvantage of sulfide electrolytes is their instability in air. Sulfides are hygroscopic and form the toxic gas hydrogen sulfide (H_2S) when in contact with oxygen and especially moisture [61]. Therefore, sulfides have to be handled in a dry atmosphere during manufacturing. According to experts, an inert-atmosphere (e.g., argon) is only necessary in the initial production steps, when the electrolyte is handled in the form of a fine powder. Once the electrolyte forms a compact layer, dry rooms are sufficient. No gas is formed in the sealed battery cell, so there are no problems with battery operation. However, in the event of an accident including battery damage, H_2S formation, as well as SO_2 formation from oxidized electrolytes may be potential safety risks, which have not yet been conclusively evaluated [61, 62]. One possible solution is to add substances to the solid electrolyte that can absorb H_2S and H_2O, such as zeolites [63]. Generally, experts do not rate the moisture instability of sulfides as critical and believe that this will soon be resolved. Sulfides exhibit only a small electrochemical stability window of about 1.7 V vs. Li/Li+ to 2.1–2.3 V vs. Li/Li+, according to first principle calculations [64]. They display higher stabilities in real applications, due to kinetic barriers. Furthermore, there are significant differences between the various sulfide material sub-classes. Nonetheless, sulfides react at low potentials with lithium metal and at higher potentials with the cathode active material (CAM). The cathode electrolyte interphase (CEI), formed by the reaction of the solid electrolyte and the CAM, mainly consists of sulfates and phosphates [65, 66]. Both are Li-ion and electronically isolating, which results in high interface resistances. At the anode, the solid electrolyte interphase (SEI) is formed of decomposition products, such as Li_2S, Li_3P or LiCl. They all have significantly lower ionic conductivities than the solid electrolyte, which results in interface resistances and causes battery performance to deteriorate [67]. Moreover, the formation of lithium dendrites is another major problem at the interface of lithium metal and sulfide solid electrolytes. Several factors influence dendrite formation (see Section 2.2) and must be considered when developing solid electrolytes for use in lithium metal batteries.

The limited interface stabilities at the anode and cathode are the biggest obstacle hindering the application of sulfide SE in SSB. Electrode coatings (e.g., $Li_7La_3Zr_2O_{12}$ at the anode or $LiNbO_3$ at the cathode), which function as an artificial SEI/CEI to avoid direct contact between the SE and the active materials are the most common approach taken to overcome this for both the anode and cathode. Other approaches include doping the SE surface with, e.g., oxygen (exchange of S with O-atoms) to enhance the surface stability, and tailoring the particle sizes of the active material (AM) and SE to minimize interfacial resistances. For the anode, 3D composite lithium metal approaches have recently received increasing attention. The lithium metal is implemented in a 3D host structure, such as a 3D copper current collector or nickel foam, which limits volumetric expansion and counteracts dendrite formation [68, 69]. In addition, the production of defect-free solid electrolytes with minimal electronic conductivities is targeted for stable interfaces and strong dendrite suppression. For the cathode, specially tailored CAM can be used for SSB, like zero-strain CAM. These exhibit very low volume changes during cycling and therefore minimize interface reactions.

Experts are of the opinion that a functioning interface with lithium metal is crucial for the commercialization of sulfide

Figure 11: Radar chart of the relevant properties of sulfide electrolytes.

Ionic conductivity

Li metal compatibility

Long-term operational stability

High-potential compatibility ($\geqq$ 4.2 V)

Suitability as separator

Suitability as catholyte

Sulfides

- **Ionic conductivity:** Sulfides show the highest conductivity of the three electrolyte groups.
- **Li metal compatibility:** Sulfides have a narrow electrochemical stability window and react in contact with lithium metal.
- **Long-term operational stability:** Sulfides are ductile and generally show good interface contacts, but limited electrochemical stability.
- **High potential compatibility:** Sulfides are prone to oxidation at high potentials, making cathode coatings necessary.
- **Suitability as a separator:** Sulfides exhibit low grain boundary resistances, which counteract dendrite formation, but have a lower electrochemical stability than oxides.
- **Suitability as a catholyte:** Especially their high ionic conductivity makes sulfides a promising catholyte material.

electrolytes. There is still not enough knowledge about the specific mechanisms occurring during cycling, and there are still many challenges with Li metal itself, such as dendrite formation. Compatibility with the cathode is very important, too, but this is rated as less problematic than the Li metal interface.

To enable widespread adoption of sulfide SSB, cheap, mass production of the solid electrolyte material is required. While this appears unrealistic for high-cost sulfides containing germanium, such as $Li_{10}GeP_2S_{12}$, it is more realistic for sulfides of the LPS sub-class or the argyrodite sub-class, which only contain readily abundant elements. Nonetheless, there are still many uncertainties concerning the precursor supply chains that have not yet been developed (especially for Li_2S) as well as the

manufacturing processes. In the longer term, however, experts do not evaluate these challenges of scaling up manufacturing and supply chains as representing a major bottleneck.

Sulfide material sub-classes

Sulfides can be divided into glasses, glass-ceramics and crystalline materials. The most prominent sulfide glasses and glass-ceramics are part of the LPS sub-class; promising crystalline representatives are the LGPS sub-class, the argyrodites and Thio-LISCONs.

LPS sub-class

The LPS sub-class has been investigated for several years and entails glasses, as well as glass-ceramics, which derive from the

Table 3: Current challenges and possible solutions for sulfide electrolytes:

Challenges	Possible solutions	Severity of the challenge
Moisture and air stability	▪ Dry rooms ▪ Material coatings ▪ Doping of SE surface (e.g. with oxygen)	LOW
Lithium metal interface	▪ Artificial SEI / coating ▪ Doping of SE surface (e.g. with oxygen) ▪ Tailoring particle size of the solid electrolyte ▪ 3D composite Li metal anodes ▪ Defect-free SE production ▪ Minimize electronic conductivity of SE	MEDIUM TO HIGH
Cathode interface	▪ Cathode coatings ▪ Doping of SE surface (e.g. with oxygen) ▪ Tailored cathode for SSB (e.g. zero-strain cathodes) ▪ Tailoring particle size of the solid electrolyte and active material	MEDIUM
Manufacturing of SE	▪ Scale-up necessary	LOW TO MEDIUM
Precursor / material availability (e.g. Li2S)	▪ Supply chains will develop with the scale-up of production; early contact to material suppliers necessary	LOW TO MEDIUM

binary xLi$_2$S (100 − x)P$_2$S$_5$ system (x = mole percentage) [58, 70]. The most studied glass type is 75Li$_2$S·25P$_2$S$_5$ (75:25 LPS). With 0.28 mS/cm, it achieves the highest ionic conductivity at room temperature for the glasses. Furthermore, the 75:25 LPS shows higher stability at elevated temperatures than other glasses [71].

LPS glass-ceramics are formed by annealing LPS glasses at specific temperatures at which the glass partially crystallizes. Generally, the crystallization of glasses decreases the lithium-ionic conductivity, because of the lower ionic conductivities of crystalline phases [72]. However, for the binary LPS-system, superionic metastable crystalline phases are formed during annealing (for $x \geq 70$). The most promising glass-ceramic is formed by crystallization of the 70:30 LPS glass. The precipitated Li$_7$P$_3$S$_{11}$ superionic crystalline phase shows a very high ionic conductivity of up to 17 mS/cm [58].

Glass-ceramics and especially glasses show higher stabilities toward the electrode active materials than crystalline sulfides. Glasses possess no grain boundaries, which helps to prevent dendrite formation, and their plasticity may compensate volume changes [71]. They are not fully stable in the presence of lithium metal, but form an electronically isolating SEI (as in lithium-ion batteries), which prevents further decomposition and makes the interface stable enough that the battery can be cycled [67]. Nevertheless, a coating is beneficial at the anode and obligatory at the cathode side, because of the interface resistances generated. The members of the LPS sub-class show auspicious properties for commercial applications, but especially glasses have too low ionic conductivities compared to other sulfide sub-classes to be competitive as a catholyte or anolyte material. However, their superior stability, lightweight and

potential low cost make them a promising candidate as a SE separator material. Glass-ceramics, especially the highly conductive glass-ceramic Li$_7$P$_3$S$_{11}$, exhibit very promising characteristics for application in future SSB, but solutions for low-resistance electrode-SE interfaces still have to be developed.

Thio-LISICONs

Thio-LISICONs, such as β-Li$_3$PS$_4$, were introduced in 2000 [73] and are derivatives of the LISICONs, in which oxygen is replaced by sulfur.

They crystallize in the γ-Li$_3$PO$_4$ structure and the softer sulfur enables higher conductivities in comparison to their oxide counterparts. The sub-class includes many different materials with the general formula Li$_x$M$_{1-y}$M′$_y$S$_4$ (M = Si or Ge; M′= P, Al, Zn, Ga, or Sb) and ionic conductivities in the range of 0.0001 mS/cm to 1 mS/cm [67]. Substitutions of other elements lead to even more analogs with varying properties. The group with the formula Li$_{4-x}$Ge$_{1-x}$P$_x$S$_4$ (0 < x < 1) shows the highest conductivities and ultimately led to the discovery of the LGPS sub-class. LGPS has a different structure than the other Thio-LISICONs and is therefore grouped separately [74]. Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ exhibits the highest conductivity with 2.2 mS/cm among the group of Thio-LISICONs [75]. Thio-LISICONs were the first crystalline sulfide electrolyte investigated in the context of SSB, but they show lower Li-ion conductivities in comparison to other crystalline sulfides, and have lower stability than LPS glasses. The usage of Thio-LISICONs in commercial batteries seems unlikely. Since the sub-class is very diverse, further R&D-efforts could lead to improvements in ionic conductivity and stability, which might enable their application.

LGPS sub-class

The discovery of the lithium superionic conductor $Li_{10}GeP_2S_{12}$ (LGPS) in 2011 [57] triggered interest in and accelerated the research efforts on sulfide SE.

LGPS shows an ionic conductivity of 12 mS/cm, which is comparable to that of liquid electrolytes (≈20 mS/cm) [76]. The high conductivity is due to the crystal structure of the LGPS, where chains of edge-connected LiS_6 octahedra and $(Ge_{0.5}P_{0.5})$ S_4 tetrahedra enable rapid 1D Li-ion diffusion along the c-axis. The 1D diffusion is complemented by a slower 2D diffusion in the ab-plane, which makes LGPS a 3D conductor [77]. The 1D conduction pathway is characteristic for the LGPS sub-class [59] and the reason for the reported conductivity. A big drawback of LGPS is that it contains high-cost germanium, which rules it out for mass production. Intensive research is therefore being carried out on isovalent substitutions of germanium by silicon and tin. The most prominent example is $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ with a lithium-ion conductivity of 25 mS/cm, which is the highest reported value of all solid electrolytes, even surpassing liquid electrolytes. However, the structure shows even lower electrochemical stability than LGPS.

Besides the high costs, the electrochemical stability of the LGPS sub-class is problematic. In contrast to the LPS sub-class, they form electrically conductive decomposition products, which result in an unstable, continuously growing SEI with high interface resistance that ultimately leads to the complete decomposition of the electrolyte [78]. As a result, no direct contact between a LGPS-SE and a lithium anode is possible for commercial applications and therefore use as a SE separator material seems unlikely. In contrast, the high conductivity makes the members of the LGPS sub-class a promising catholyte, if a low-cost, germanium-free material with sufficient electrochemical stability can be developed.

Argyrodites

The name originates from the silver (argentum) argyrodite Ag_8GeS_6, which was discovered first [74]. The lithium analog

Li_6PS_5X (X=Cl, Br, I) was discovered in 2008 [79] and has been intensively researched and improved since then. In particular, the chlorine argyrodite Li_6PS_5Cl and its substitutions have beneficial characteristics. It exhibits a lithium-ion conductivity of approx. 2 mS/cm at room temperature [80], but this value can be increased by substitutions (e.g., $Li_{5.5}PS_{4.5}Cl_{1.5}$ reaches ≈12 mS/cm) [81].

Argyrodites form electrically isolating SEIs in contact with Li metal and are therefore not completely stable, similar to the LPS sub-class, but are compatible with Li metal anodes. Nonetheless, interface resistances must be kept minimal, so coatings and other possible interface solutions need to be applied at the anode and the cathode side. Unlike the LGPS sub-class, however, argyrodites do not contain costly metals like germanium and can potentially be produced cost-efficiently based on the precursors Li_2S, P_2S_5, and LiCl. Wet chemical processing methods as well as solvent-free dry methods have been developed.

Argyrodites have been tested in various SSB concepts [32, 74]. They are currently considered one of the most promising solid-state electrolyte material sub-classes for commercial applications. The biggest challenges are interface resistances and decomposition at the SE-electrode interface, but to a smaller extent than for the LGPS sub-class.

Conclusions

Sulfides can be considered one of the most promising solid electrolyte material classes for (all) solid-state batteries in automotive applications today, as they have the potential to enable high-power battery cells. They exhibit high Li-ion conductivities comparable to liquid electrolytes and are therefore promising as a catholyte material unlike oxides. The biggest downside of sulfides is their low electrochemical stability, which results in high interface resistances at the anode and cathode side. The stability toward lithium metal and the prohibition of dendrites are still major challenges and will determine how and when sulfide electrolytes are used in commercial batteries.

Table 4: Overview of sulfide electrolyte sub-classes:

Electrolyte sub-class	Ionic conductivity of most promising examples	Suitable as	Market potential
LPS sub-class	▪ 0.28 mS/cm (75:25 LPS-glass) ▪ 17 mS/cm ($Li_7P_3S_{11}$ glass-ceramic)	Separator (LPS glasses) Catholyte, anolyte, separator (LPS glass-ceramics)	MEDIUM
Thio-LISICONs	▪ 2.2 mS/cm ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$)	No commercial use foreseeable today	LOW
LGPS sub-class	▪ 12 mS/cm ($Li_{10}GeP_2S_{12}$) ▪ 25 mS/cm ($Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$)	Catholyte	MEDIUM
Argyrodites	▪ 2 mS/cm (Li_6PS_5Cl) ▪ 12 mS/cm ($Li_{5.5}PS_{4.5}Cl_{1.5}$)	Catholyte, anolyte, separator	HIGH

2.4.3. Polymer Electrolytes

Polymer electrolytes can be seen as an intermediate technology between liquid electrolytes (as used in state-of-the-art lithium-ion batteries) and solid electrolytes. This section only discusses polymer solid electrolytes (SE), while gel electrolytes, which are more closely related to liquid electrolytes when considering the underlying ion-conduction mechanism [82], are mentioned in Section 2.5. Of all the solid electrolytes discussed, polymer SE can be considered the most similar to liquid electrolytes, since they are semicrystalline (or even fully amorphous [83]) at room temperature, and are used in batteries well above their glass transition temperature or even their melting temperature. In contrast to inorganic solid electrolytes, polymer SE are already implemented in some applications, such as Bolloré's Bluebus [84], even though they still have some disadvantages that prevent the exploitation of their full potential.

The properties of solid polymer electrolytes are defined by the interplay of three components: the polymer matrix, the lithium salt, and (optional) additives. Every polymer SE consists of a polymer matrix, in which lithium salt is dissolved. The transport of the dissolved Li-cations takes place through the motion of the polymer segments [85]. Since this transport is only possible in the amorphous or liquid phase, the glass transition temperature is a critical parameter of polymer electrolytes, as it marks the temperature region above which the polymer chains exhibit higher mobility [86]. At higher temperatures, the mobility of the polymer chains is increased, resulting in greater ionic conductivity, while mechanical stability decreases. Optimizing the trade-off between mechanical stability and ionic conductivity is crucial for polymer SE.

The most commonly used polymer matrix by far is poly(ethylene oxide) (PEO) [82]. Its performance is often improved by additives, which are used, for example, to promote the formation of localized amorphous regions in the inherently semicrystalline PEO in order to improve lithium-ion transport. However, it is still not completely understood what leads to the increase in ionic conductivity. Furthermore, additives can be used to improve dendrite resistance, because the unmodified PEO electrolytes are too weak to prevent the growth of lithium metal dendrites at operating temperatures (i.e., at which reasonable ionic conductivity is achieved).

Advantages
In general, the main advantages of polymer electrolytes compared to inorganic solid electrolytes are cost, processing aspects, and the flexibility of the material. Compared to liquid electrolytes, they have classical 'solid-state' benefits, such as the mechanical stability and a potentially extended calendric lifetime, although these come with some caveats, as discussed below.

The production and processing of polymers are already well established, because this material class is versatile and ubiquitous. The resulting know-how and the fact that often no critical raw materials are needed (with regard to availability, price, toxicity and mining conditions) are the basis for establishing a cost-effective, large-scale production of polymer matrices. Some of these advantages have to be put into perspective when considering the production of lithium salts – besides the price of lithium, proof of an environmentally-friendly extraction technique has yet to be provided, especially against the backdrop of strongly growing demand [87]. However, compared to inorganic solid electrolytes, the demand for lithium here is relatively low, as this is only part of the lithium salt and not the polymer matrix, which is an advantage compared to the other SE discussed. A dry room is required due to the hygroscopic nature of lithium salts and PEO, but this is standard for producing conventional liquid electrolyte LIB [88].

In all-solid-state cell concepts, one issue is how to ensure good contacts at the interfaces between electrode active materials and the electrolyte, analogous to the wetting in conventional battery cells. Due to their flexibility, polymer SE have an advantage here over stiffer or more brittle ceramics. This flexibility offers another benefit when considering the operation of a solid-state battery with a lithium metal anode: Cycling a lithium metal battery leads to considerable volume changes of the components, especially the anode. Polymers can compensate some of this volume change, which lowers the demands on cell casing and module and pack design. Furthermore, polymer SE could be used for rolled-up cell formats, which is not easily possible for other solid electrolytes.

Challenges and possible solutions
The limited ionic conductivity of polymer SE poses a major bottleneck to their commercialization. Even though reasonable ionic conductivity at room temperature (in the order of magnitude of 1 mS/cm) has been reported in various scientific papers [86], the route toward commercialization has yet to be found. The ionic conductivity of polymer SE is strongly temperature-dependent – higher temperatures enhance the mobility of the polymer chains and ionic conductivities above 1 mS/cm are achievable. Therefore, installing temperature management in the battery pack is a useful and already implemented workaround. However, this is associated with a drawback in terms of energy density at pack level, and the need for constant heating and therefore energy consumption to keep the battery cell in an operational state. Lowering the operating temperature of the polymer SSB would reduce the need for temperature management and directly improve the energy density at pack level.

Resistance to dendrite formation is necessary for a polymer SE to be able to outperform liquid electrolytes. However, the mechanical stability of polymer electrolytes is often reduced

Figure 12: Radar chart of the relevant properties of polymer electrolytes.
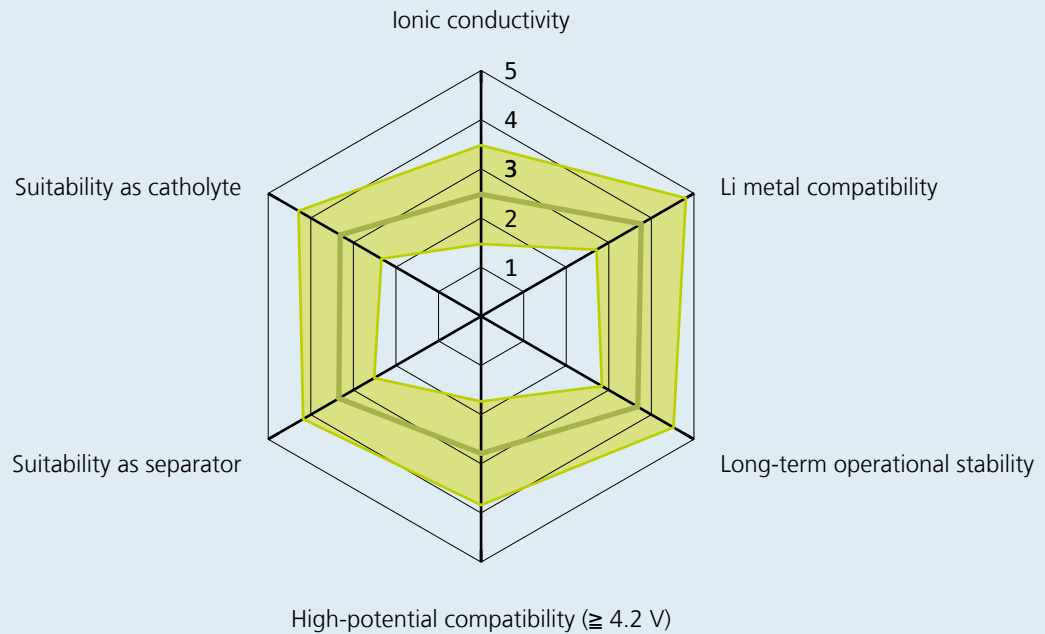
Polymers

- **Ionic conductivity:** In general, the ionic conductivity is insufficient at room temperature. An operating temperature >60 °C is often chosen to allow for reasonable ionic conductivities.
- **Li metal compatibility:** PEO shows high stability toward lithium metal.
- **Long-term operational stability:** The flexibility of polymer electrolytes promotes a long cycling lifetime, if a low-potential cathode and low charging rates are used.
- **High potential compatibility:** Most polymer SE have a limited electrochemical stability window (below 4 V against Li$^+$/Li)
- **Suitability as a separator:** Many polymer SE are known to be mechanically stable enough to resist dendrite formation.
- **Suitability as a catholyte:** If the cell can be operated at a higher temperature, the ionic conductivity is sufficient for use as a catholyte.

when attempts are made to improve their ionic conductivity, e.g., by additives. Long-term stability toward dendrites is desirable to guarantee a long cycle life or to enable increased charging rates. One approach to overcome this challenge is to combine a mechanically stable SE separator with a good ion-conducting electrolyte, but the optimal combination of the respective properties and layer thicknesses of the electrolytes has not yet been determined. Another way to suppress dendrite formation could be direct treatment of the anode in the form of a coating layer [89].

The electrochemical stability window of polymer SE is usually not wide enough to allow the use of high-potential cathodes. Although there are some examples in the literature [90], no

candidate has shown convincing properties beyond lab-scale experiments. Possible solutions include coating the cathode or combination with another electrolyte used as an electrochemically stable catholyte. However, commercialization is not necessarily possible only with high-potential cathodes, considering their cost and the use of critical materials.

One main advantage of inorganic solid electrolytes over liquid electrolytes is the optimization of the cation transference number, which indicates the proportion of cations taking part in the charge transfer through the electrolyte. In conventional battery cells, this transference number is usually around 0.35 [91], i.e., 35 % of the charge transfer is due to the movement of cations, while anions are responsible for 65 %. This

Table 5: Current challenges of polymer electrolytes and possible solutions:

Challenges	Possible solutions	Severity of the challenge
Limited ionic conductivity at room temperature	▪ External heating ▪ New materials and material combinations (polymer, salt, additive) ▪ Composite (organic-inorganic) electrolytes	MEDIUM
Resistance to dendrite formation	▪ Combination of electrolytes (mechanically stable polymer + polymer with good ionic conductivity) ▪ Coatings / artificial SEI ▪ Thin lithium (e.g. "anode-less" concept) ▪ Single-ion conductor	HIGH
Limiting current density (transference number)	▪ Single-ion conductor ▪ Composite (organic-inorganic) electrolytes	HIGH
Compatibility with high-potential cathodes	▪ New materials and material combinations ▪ Coatings ▪ Composite (organic-inorganic) electrolytes	LOW TO MEDIUM

diffusion of ions leads to a concentration gradient, which causes an increase of internal resistance and lithium depletion at the anode. To prevent the emergence of this electric potential counteracting the desired charge transfer, a cation transference number of close to 1 is aimed at, which is the case for inorganic SE in general. However, it is extremely difficult to measure the actual value of the transference number, which prevents a reliable comparison of different materials with respect to this parameter. For polymer SE, the transference number is usually well below 0.5 and has been measured as between 0.17 and 0.6 for PEO/LiTFSI at operating temperature [88, 92]. A strong focus in the research and development of new polymer matrices is on optimizing the transference number, as discussed below.

Different Solid Polymer Electrolytes

Numerous approaches can be taken to alter the properties of the polymer SE: changing the chemistry of the polymer matrix, the lithium salt or the additive(s) and their respective stoichiometry. We provide an overview with a few examples. For a more complete picture of the materials investigated for polymer SE, we refer the curious reader to a number of reviews in this field (e.g., [82, 86, 88, 93]).

Polymer matrix

A wide variety of different polymer matrices are being investigated for use in polymer SE, with PEO the most prominent example. However, polymer matrices not based on polyethers, such as polycarbonates, are also attracting significant scientific attention, as reviewed in [86] and shown in Table 6.

Crucial properties for the polymer matrix include the ability to dissolve Li-salts, which requires the presence of polar functional groups and is indicated by a high dielectric constant, and the mobility of the polymer chain segments, which depends on

the polymer's molecular weight and is indicated by a low glass transition temperature [82, 94, 95]. Distinguishing the polymers by their respective chemical structure is of limited use, since properties can vary strongly within these sub-classes and overlap between them [86].

Lithium Salt

The most commonly used salt in PEO-based electrolytes is $LiN(CF_3SO_2)_2$ lithium salt (LiTFSI), since it lowers the crystallinity of PEO and, therefore, improves the ionic conductivity of the polymer-salt complex [96] compared to other organic lithium salts containing sulfonate anions, such as $LiCF_3SO_3$, or inorganic lithium salts, such as the $LiClO_4$ [86]. Important properties for lithium salts are low lattice energy, to enable the ion pair dissociation, chemical and thermal stability, and cost, of course. The search for novel lithium salts may not only improve the performance of polymer SE, but conventional liquid electrolyte concepts as well. Some novel lithium salts are reported to achieve > 1 mS/cm in combination with PEO conductivities at room temperature [97], [98].

Additives

Additives are often used to improve the mechanical properties of the electrolyte or to hinder the crystallization of the polymer-salt complex (i.e., by plasticizers) at low temperatures, in order to increase ionic conductivity [82]. Nanofillers, for example, can enhance the salt dissociation and reduce the mobility of the anions [99], and significantly improve the interface stability toward the lithium anode [93]. Nanofillers are separated into active fillers, such as γ-$LiAlO_2$ [100], which participate in the conduction of lithium-ions, and passive fillers, such as Al_2O_3 and SiO_2 [101] or carbon particles [102], as shown in Table 6. The grain size of the nanoparticles (1D-nanofillers) has a considerable impact on the properties of the resulting polymer-salt-nanofiller electrolyte [103]. When ceramic

nanoparticles are used (e.g. LLZTO), the electrolyte system is often referred to as a composite electrolyte, and combines the properties of a polymer SE with an oxide electrolyte. Depending on the proportion of the ceramic particles in the polymer system, the resulting system is called 'ceramic-in-polymer' or 'polymer-in-ceramic' [104]. Examples of other investigated nanofillers include graphene oxide (2D), which is reported to significantly increase ionic conductivity and tensile strength [105], metal-organic frameworks (3D) [106] and halloysite nanotubes (3D) [107], which were investigated in polymer SE for lithium-sulfur batteries. To combine nanofillers with the polymer, both can be blended [82], while hot-pressing the nanofillers with the polymer matrix and the salt is another (solvent-free) approach [103].

Using ionic liquids (i.e., salts that are molten below 100 °C) as additives is another intriguing approach to improve the properties of different polymer-salt complexes, with Pyr_xTFSI being a prominent example [108]. While this can enhance the polymer SE's ionic conductivity, and mechanical and thermal stability, the cost of the ionic liquids poses a challenge for their large-scale use. Ionic liquids can improve the stability of the SEI on the electrodes by mitigating the gas evolution, which decreases the interface area. Even though the interfacial resistance of ionic liquids to the lithium anode needs to be optimized, they are still considered a promising way to significantly increase the performance of polymer SE in the medium term.

Due to the aforementioned trade-off between the ionic conductivity and mechanical stability of the polymer matrix, a widespread approach is to decouple these two properties in so-called composite polymer electrolytes that combine two different polymers, one optimized for ionic conductivity, and one providing the mechanical rigidity required. Block copolymers are usually made by combining PEO with a second (or more) polymer block(s), with a prominent example being the triblock copolymer polystyrene-PEO (PS-PEO-PS) [109]. However, the decoupling of ionic conductivity and mechanical stability is not perfectly resolved in block copolymers, as indicated by the observation of reduced conductivity, which is partially attributed to the occurrence of 'dead zones', which emerge in the case of PS-PEO-PS at the PS/PEO interface [110].

Finally, it should be pointed out that not all polymer SE exhibit the conventional binary ionic conduction mechanism; some polymer SE are so-called single-ion conductors, in which ionic conduction is based solely on cations and not on anions. Approaches to reduce the mobility of anions have attracted considerable scientific attention [111, 112]. By pinning anions to the backbone of the polymer matrix, as demonstrated in the composite polymer electrolytes PEO-PFSILi [111], for example, cationic transference numbers of more than 0.9 were achieved. Furthermore, suppressing anion movement can reduce dendrite formation, which can improve the lifetime and safety of the battery.

Conclusions

Solid polymer electrolytes are undergoing extensive research due to their potential use in a lithium metal battery and their advantages in terms of low cost, flexibility and good processability. Many different combinations of polymer matrices, lithium salts and a large number of additives have been investigated over the past decades and show promising potential for future development. The main challenges facing polymer SE are the comparatively low ionic conductivity at room temperature, compatibility with (high-potential) cathodes and the lithium anode (dendrite resistance). However, some of these challenges have already been overcome or are not considered too serious, as indicated by the fact that polymer SE are the only all-solid-state electrolytes that are already being used in commercial applications.

Table 6: Overview of different components in solid polymer electrolytes:

Component	Sub-class	Examples
Polymer Matrix	Polyether-based	Poly(ethylene oxide) (PEO)
	Polyether-based	Polyethylene carbonate (PEO-EC); Poly(propylene carbonate) (PPC); Polycaprolactone (PCL); Poly(trimethylene carbonate) (PTMC)
	Nitrile-based	Succinonitrile (SN); Poly(acrylonitrile) (PAN)
	Other	Polysiloxane; Poly[bis(methoxy-ethoxy-ethoxy)phosphazene] (MEEP)
Lithium Salt	Inorganic	$LiBF_4$, $LiPF_6$, $LiClO_4$, $LiAsF_6$
	Organic	$LiN(CF_3SO_2)_2$, CH_3SO_3Li, $LiN(SO_2C_2F_5)_2$, $LiC_2F_5SO_3$
Additives	Passive fillers	Al_2O_3, SiO_2, TiO_2, ZrO_2
	Active fillers	γ-$LiAlO_2$, Li_3N, $LiAlO_2$
	Ionic liquids	Pyr_xTFSI

2.5. Other Materials and Components

Much of the scientific research dedicated to the development of solid-state batteries focuses on exploring new electrolyte materials, especially oxide, sulfide and polymer electrolytes and their compatibility with different cathode and anode active materials, as discussed above. However, these material classes do not cover all the existing electrolyte materials or other components under investigation. Although we cannot provide an exhaustive review of all the electrolyte materials that might play a role in the future of SSB, selected approaches are outlined in the following. Subsequently, we present the most common materials used as current collectors in SSB. Further aspects of SSB cells and packs (e.g., cell cases, housings) are beyond the scope of this report.

Halide and Borate Solid Electrolytes

Borates

Originally, boron-containing electrolytes (commonly referred to as borates, e.g. lithium borohydride – $LiBH_4$) were developed for use as rocket fuel or for hydrogen storage applications [74]. The material exhibits high ionic conductivity in a high-temperature phase structure for Li-ions and this is even higher for Na-ions. Thermal treatment and further development of the composition have achieved 70 mS/cm for sodium and 6.7 mS/cm for lithium. Recent process innovations achieve good ionic conductivities not only at high temperatures but also at room temperature (e.g., by mechanical alloying, elemental substitutions, bimetallization and anion mixing) [74]. The borates have acceptable stability toward reduction and oxidation. Additionally, they have suitable mechanical properties (soft) as well as low density, which enables high energy densities at cell level. On the downside, borates are instable in the presence of air. Low temperatures seem to be problematic, because of the need to maintain the high-temperature phase structure (50–110 °C, depending on the chemical composition) required for high ionic conductivities. So far, the commercialization of borates has been prevented by the synthetic pathway, which is challenging, low-yielding, and expensive [113]. This encouraged the search for alternative low-cost processing routes, as reviewed recently [114, 115]. Even though an ionic conductivity high enough for use in batteries was already achieved in 2007 [116], so far, only one borate-based cell concept has been demonstrated in the laboratory [117]. Therefore, no statement can be made about the future viability of this electrolyte class. Due to the good ionic conductivity for Na-ions, borates may be especially interesting for sodium-based batteries in the future.

Halides

Halides are chemical compounds containing halogen atoms (F, Cl, Br, I, At) and can be classified into three groups: halides with group 3 elements (Sc, Y and La), halide structures with group 13 elements (Al, Ga and In), and halides with divalent metals (e.g., first transition metals). Especially the first two groups have ionic conductivities that are high enough for use as SE in SSB (> 0.1 mS/cm) [118]. Halide raw materials can be produced by compacting powders at room temperature. They combine mechanical stability with flexibility and can achieve better interfacial stabilities with the electrodes than sulfide-based electrolytes [118, 119]. Furthermore, they exhibit high stability toward oxidation, which is necessary for use in high voltage cell concepts [120]. On the downside, they are sensitive to moisture in the environment during processing, have rather low ionic conductivity, and react with Li metal [119]. To achieve higher ionic conductivities, rare-earth elements (such as Y, Er, Sc or In) have to be included (e.g., Li_xScCl_{3+x} with up to 3 mS/cm). Novel low-cost components such as $Li_{2.25}Zr_{0.75}Fe_{0.25}Cl_6$ have already achieved ionic conductivities of 0.98 mS/cm [118]. Over the last few years, many laboratory cell concepts have been reviewed, which often contain a sulfur protection layer toward the anode [121–125]. Due to their stability in contact with coated CAM and instability in the presence of Li metal, halides are most suitable as the catholyte in SSB [120]. Research has only recently begun on using borates and halides in SSB and they have only been used in laboratory cells, so far, which is why the path to commercialization is considered to be even longer than that for oxides, sulfides and polymers.

Gel electrolytes

Gel electrolytes consist of a polymer matrix (e.g., polyethylene oxides, polymethyl methacrylate (PMMA), polyacrylonitrile (PAN) or polyvinylidene fluoride (PVDF)), which is infiltrated with a liquid electrolyte consisting of a conducting salt and a solvent. Various material combinations and processes have been investigated to keep the polymer content as low as possible [126]. These approaches have achieved ionic conductivities of more than 3 mS/cm at room temperature [127].

Gel electrolytes represent the transition between liquid electrolytes and solid polymer electrolytes, and were developed to combine the advantages of both types of electrolytes. Their ionic conductivity is supposed to be comparable to liquid

electrolytes and surpasses that of SE, especially at low temperatures and the material is compatible with high voltage cathodes (compared to polymer solid electrolytes). Furthermore, gel electrolytes decompose slower than liquid electrolytes. However, gel electrolytes also have their disadvantages, such as leakage and flammability [127].

Current Collectors

Copper and aluminum foils are established materials for LIB current collectors. Both have good thermal and electronic conductivity and can be produced with a foil thickness of a few micrometers. Due to relatively high raw material costs, the Cu-foil used for the anode is significantly more expensive than the Al-foil used for the cathode. Aluminum, however, lacks electrochemical stability in LIB and hence cannot be used at the anode side. Depending on the choice of active materials, Al-foils and Cu-foils can also be used as current collectors in SSB. Additional requirements might emerge on the cathode side due to the substitution of liquid with solid electrolytes, but aluminum seems to show good compatibility with most of the SE materials currently under investigation. For SSB concepts that have an intercalation or conversion/alloying type anode with an active material, Cu-foils can be used as the current collector similar to liquid electrolyte-based LIB. For concepts featuring a Li metal anode, the use of a Cu-foil coated with a Li-layer is also possible. Anode-free concepts, where the Li is directly plated onto the substrate during the charging process of the cell might require different current collectors, since the Li-deposition process is significantly influenced by the surface and chemical properties of the substrate. For Li metal anode concepts, several current collector materials are under investigation, ranging from surface-modified Cu-foils to nickel or stainless-steel substrates.

2.6. Compatibility between Components

When discussing cell concepts, it is not sufficient to discuss the individual components in an isolated way; these must be examined in terms of the challenges when combining electrolytes with certain cathode or anode active materials.

Each possible combination of cathode, anode and electrolyte calls for a detailed discussion of the challenges and possible solutions. It is not possible for us to provide this for all the possible combinations, but the short overview given below outlines the most important challenges that arise when combining different electrolyte classes with the different active materials. A differentiation into sub-classes, as presented in Section 2.4, was omitted here, as the challenges are generally similar. However, it should be kept in mind that they can vary for different sub-classes or specific materials. Since the challenges for combinations with transition metal oxides (NMC, NCA, LMO, LCO) are also rather similar, they are not discussed separately. Coating the active materials is a common approach to tackle some of the challenges discussed. Coated active materials are therefore distinguished in the following from uncoated active materials, i.e., active materials with no coating to intentionally improve the stability toward interfacing materials. The discussion focuses on the electrochemical compatibility, processability and lifetime of the respective active material-electrolyte combinations.

(Electro)chemical compatibility
The interfaces between the different components are critical when designing solid-state battery cells. The electrochemical stability window of an electrolyte indicates at what electric potential the electrolyte is reduced (anode) or oxidized (cathode). Sulfides have a rather narrow electrochemical stability window, which limits the electrode active materials with which they can be readily combined. For solid polymer electrolytes, the combination with high-potential cathodes poses a challenge, while their electrochemical stability window does not hinder combination with the anodes discussed.

Besides electrochemical compatibility, the chemical stability of the electrolyte material is a challenge that needs to be addressed. Coatings of the cathode active material can prevent decomposition reactions of sulfides at the respective interfaces. Oxide electrolytes have exceptional electrochemical and chemical stability.

Processability
The cost-effective processing of the components into a cell presents further challenges. Oxide electrolytes have to be sintered with the cathode, which can be harmful to the active materials due to the high temperatures involved. Because of their instability toward polar solvents such as water, sulfides have to be processed using nonpolar solvents. However, conventional binders like polyvinylidene fluoride (PVDF) and carboxymethyl cellulose (CMC) show poor solubility in nonpolar solvents and cannot be used [128]. Therefore, other binders have to be used such as styrene – butadiene rubber and silicon rubber. In general, binders are necessary in sulfide SE/active material composites to enable sufficient mechanical stability. However, the addition of binders also reduces the ionic conductivity of the electrolyte and, therefore, their use needs to be minimized.

Lifetime
Finally, other disadvantages might only be revealed when the battery cell is being used. Under cycling, the volume of the electrodes can change significantly, which exerts considerable stress on the interfaces. Liquid electrolytes and solid polymer electrolytes can usually compensate for these volume changes quite well, which is generally not the case for oxide and sulfide electrolytes. A common approach to guarantee good interface contacts during cycling is to apply external pressure on the cell. Moreover, the lifetime can be limited by the aspects mentioned under chemical and electrochemical compatibility. When using a lithium metal anode, the resistance to dendrite formation is crucial to prevent a short circuit.

As discussed above, the main challenges facing oxides are their processability, while the main challenges for sulfides concern their electrochemical compatibility. Polymers seem to be rather versatile, with still unresolved challenges when paired with high-potential cathodes. Many strategies are already being developed to tackle the challenges discussed including different coatings of the components or optimized processing techniques.

Table 7: Compatibility of active materials with solid electrolyte classes. The severity of the challenge is indicated by the color coding (green: no particular compatibility challenge, yellow: medium compatibility challenge, red: significant compatibility challenge):

Cathode			Oxides	Sulfides	Polymers
LFP	uncoated	(Electro) chem. compatibility	No particular challenge	Slow decomposition reactions	No particular challenge
		Processability	Sintering with SE needed, brittle	Polymer binder needed	No particular challenge
		Lifetime	No particular challenge	Slow decomposition reactions	No particular challenge
	coated	(Electro) chem. compatibility	No particular challenge	No particular challenge	No particular challenge
		Processability	Sintering with SE needed, brittle	Polymer binder needed	No particular challenge
		Lifetime	No particular challenge	No particular challenge	No particular challenge
NMC, NCA, LMO, LCO	uncoated	(Electro) chem. compatibility	No particular challenge	Decomposition reaction	Limited el. chem. stability window
		Processability	Sintering with SE needed, brittle	Polymer binder needed	
		Lifetime	Volume change	Volume change and decomposition reactions	Limited el. chem. stability window
	coated	(Electro) chem. compatibility	No particular challenge	No particular challenge	Limited el. chem. stability window. Potential shielded by coating
		Processability	Sintering with SE needed, brittle	Polymer binder needed	No particular challenge
		Lifetime	Volume change	Volume change	Limited el. chem. stability window. Potential shielded by coating
Sulfur		(Electro) chem. compatibility	Theoretically stable. Not yet shown.	Decomposition reaction	No particular challenge
		Processability	Sintering with SE needed, brittle	No particular challenge	No particular challenge
		Lifetime	Volume change	Decomposition reaction	No particular challenge

Cathode

Electrolyte	Parameters	Oxides	Sulfides	Polymers

Anode

Anode	Parameters	Oxides	Sulfides	Polymers
Si	(Electro) chem. compatibility	No particular challenge	Narrow el. chem. Stability window	No particular challenge
	Processability	Composite anode (3D): sintering with SE needed, brittle Layered anode (2D): sintering with SE needed, brittle	Polymer binder needed	No particular challenge
	Lifetime	Volume change	Volume change	
Li metal	(Electro) chem. compatibility	LLZO stable Other oxides instable with Li	Highly reactive, low potential	No particular challenge
	Processability	No particular challenge	No particular challenge	No particular challenge
	Lifetime	Volume change	Volume change	Dendrite formation
LTO	(Electro) chem. compatibility	No particular challenge	No particular challenge	No particular challenge
	Processability	Sintering with SE needed, brittle	Polymer binder needed	No particular challenge
	Lifetime	No particular challenge	No particular challenge	No particular challenge
Graphite	(Electro) chem. Compatibility	No particular challenge	Narrow el. chem. Stability window	No particular challenge
	Processability	Sintering with SE needed, brittle	Polymer binder needed	No particular challenge
	Lifetime	Volume change	Volume change	No particular challenge

Anode · **Oxides** · **Sulfides** · **Polymers**

3. Solid-State Battery Production

3.1. Processing of SSB

3.1.1. Cathode and Cathode-Composite Processing

State-of-the-art liquid electrolyte LIB production technologies are well-established [129] and batteries in the hundreds of GWh storage capacity range are already being produced (Section 1.2). For the manufacturing of solid-state batteries, however, certain production steps vary significantly. In the following pages we focus on the production aspects that are specifically required for SSB. In this section we discuss the different approaches for SSB cathode production.

The cathode active materials (CAM) used in solid-state batteries (SSB) may be chemically the same as in current lithium-ion batteries (LIB), layered oxides such as lithium nickel manganese cobalt oxides (NMC) and lithium nickel cobalt aluminum oxides (NCA) are most common. Lithium iron phosphate (LFP) is also used, especially for polymer SSB. There are two main options for processing the cathode active materials, which will be discussed in the sections that follow: wet processing and dry processing.

Wet processing

The first option for the production of the cathode are slurry-based, wet chemical approaches, which are already established and applied in the gigafactories for state-of-the-art LIB production and enable a high throughput. Usually, N-methyl pyrrolidone (NMP) is used as a solvent and mixed with the binder polyvinylidene fluoride (PVDF), a conductive additive and the CAM. For SSB, the solid electrolyte (SE) is added to the slurry as well, which has implications on the solvent and binder used. Sulfides react with polar solvents, such as NMP and therefore require the use of nonpolar organic solvents, such as e.g. xylene [128, 130, 141]. As PVDF is not soluble in nonpolar solvents, rubbers such as styrene – butadiene rubber (SBR) and silicon rubber (SR) have been adopted. The slurry is then casted onto the current collector (aluminum foil) and the solvent is evaporated. Since NMP is toxic and strictly regulated, a demanding and expensive solvent recovery process is necessary, which would most likely be the case for other organic solvents (e.g. xylene) as well. After the drying process, the electrode is densified to ensure good contact between the SE and the CAM. An electrode porosity close to zero is aimed for, but a certain degree of elasticity, for example by adding a binder, is beneficial to prevent crack formation. If a ductile sulfide SE is used as catholyte, a calendering step similar to state-of-the-art LIB is applied. Contrastingly, for the brittle oxide electrolyte materials, a calendering step alone is not sufficient, and a sintering step is necessary to ensure low porosity and low grain boundary resistance in the cathode. Only low-temperature sintering (≈ 700 °C) is possible for the cathode sintering, since high sintering temperatures (≥ 1000 °C) lead to side reactions and partial decomposition of the CAM [41, 131, 142]. Therefore, a compromise between good particle contact between SE and CAM with low interfacial resistance, and minimized side-reactions and processing costs is necessary. To avoid the sintering step, alternative approaches are being investigated, for example melt infiltration of the solid electrolyte into the porous cathode structure [143]. The film drying of wet-processed cathodes is energy intensive and costly. Wet processing currently shows the highest market maturity for sulfide and oxide SE. For polymers an extrusion process using no solvent is already established and used commercially [144].

Table 8: Production approaches for cathodes, their advantages and challenges:

Production method	Advantages	Challenges & Disadvantages
1. Wet processing	▪ Established process (for state-of-the-art LIB) ▪ High throughput ▪ Sulfide electrolytes: calendering/cold-pressing possible	▪ **Solvent recovery** ▪ **Film drying** ▪ Oxide electrolytes: Sintering (expensive, CAM decomposition) ▪ Sulfide electrolytes: Limited options of solvents and binders ▪ Polymer electrolytes: Extrusion process is cheap and established
2. Solvent-free (or reduced) concepts (e.g. extrusion, dry calendering, etc.)	▪ **Solvent-free / reduced** ▪ Cost and energy saving possible by elimination of solvent and drying process ▪ Polymer electrolytes: Established process	▪ **Film uniformity** ▪ Dry processing methods for sulfide and oxide electrolytes: Scale-up ▪ Most research on the topic is done for liquid electrolyte LIB: implementation of SE in the production process must be examined more closely

Dry processes

In the extrusion process, the components of the cathode (CAM, SE, binder and conductive agent) are compounded in the extruder, here a homogeneous mixture is formed which is applied onto the current collector [144][132]. Afterwards, calendering steps are required. Extrusion is already utilized for cathodes with polymer SE. For sulfide and oxide SE, further development is necessary and technical barriers exist, for example owing to their greater hardness. Moreover, other low-solvent or dry processes are being examined with the motivation to reduce or omit the expensive drying and solvent recovery processes. Processes such as dry calendering or dry spraying show the potential to be scaled-up for roll to roll

processing and have currently reached the pilot-production scale [138]. Furthermore, screen printing is another low-solvent method, which only requires small amounts of water (or other solvents) for electrode production. However, it is not compatible with current roll to roll manufacturing, but instead allows customized electrode sizes and thick electrodes. SSB production can benefit from the research and development work being done for liquid electrolyte LIB manufacturing. However, as most approaches are being investigated for liquid electrolytes [138, 145–147], there is a lack of knowledge on how to integrate the SE into the process, and this knowledge needs to be increased.

3.1.2. Anode Processing

Li metal anodes

One of the main drivers towards implementing solid-state batteries (SSB) is the possibility of being able to use lithium metal as the anode active material, which enables the fabrication of batteries with highest energy density [17]. For state-of-the-art LIB graphite or silicon-graphite composites are used as the anode active material, therefore new production methods have to be established to integrate the lithium metal anode into the battery cell. The especially challenging aspects of the anode production are the high reactivity of lithium metal and its adhesive properties. There are different processing options for the Li metal anode, which can be categorized into four groups: extrusion, melt-processing, vapor-based processing and "anode-less" approaches (Figure 13).

Extrusion
The most established process is the production of thin lithium foils using a dry-extrusion process [130–132]. After passing the extruder, the formed lithium foil runs through several high-pressure calendering steps, to lower the foils thickness. To avoid the adhesive lithium sticking to the rollers, the rollers need to be coated, e.g. with polymers such as polyacetal [132]. Up to now, it is still very challenging to produce thin lithium

foils < 30 µm with a low defect rate [130, 133]. Only a few manufacturers can produce foils < 50 µm and prices increase with the decreasing thickness of the foil. After calendering, the foil is laminated onto the current collector or the solid electrolyte separator.

Meltprocessing
A second option is the preparation of the Li anode by melt processing, where lithium is liquefied at about 180 °C and then deposited onto a non-porous electrolyte or current collector, or infiltrated into a porous anode scaffold or a porous electrolyte [130, 134]. The method is especially applicable for porous structures and enables the production of very thin foils. However, compared to the extrusion process it has not been well established, it requires a vacuum or inert gas atmosphere and also high safety precautions due to the reactivity of liquefied lithium.
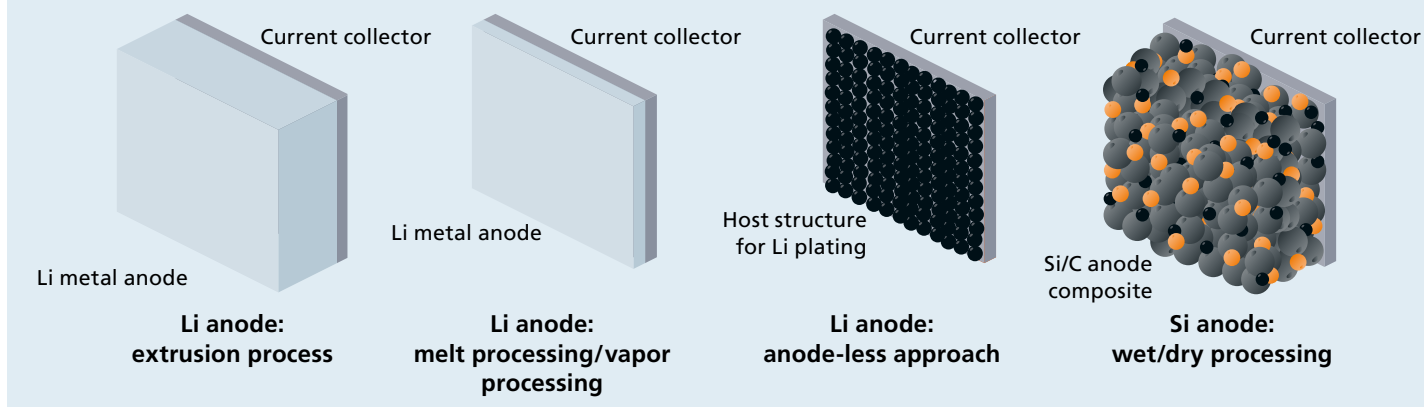
Vapor-based processing
Another approach is vapor-based processing, such as sputtering. The main advantage is that very thin, high-quality films of lithium can be manufactured [130]. Vacuum evaporation techniques are already applied for thin film solid-state batteries [135], but it is doubtful that the technique is feasible for mass producing high-energy bulk SSB, since the throughput is limited and the method is expensive, partly due to the need of a vacuum environment and low deposition rates.

Table 9: Production approaches for anodes, their advantages and challenges:

Production method	Advantages	Challenges & Disadvantages
Li metal		
1. Dry processing (extrusion process)	▪ Established process	▪ **Processing of thin foils** ▪ Li is adhesive (sticks to rolls) ▪ Dry/inert atmosphere needed ▪ Defect rate
2. Melt processing (liquid-phase processing)	▪ Thin layers ▪ Applicable for porous structures	▪ **Immature process** ▪ Liquefied lithium handling: special safety precautions necessary ▪ Vacuum / inert atmosphere
3. Vapor-based processing (e.g. sputtering, evaporation)	▪ High quality and thin films	▪ **Expensive** ▪ Limited throughput and thickness ▪ Vacuum
4. Plating (in-situ anode formation)	▪ No direct handling of metallic Li ▪ Thin layers ▪ No excess Li	▪ **Homogeneity problems** ▪ Not used for large format batteries yet ▪ Pre-treatment (formation) necessary ▪ No excess Li (decreasing capacity as a result of SEI formation)
Graphite/Silicon		
1. Wet processing	▪ Established process (same as state-of-the-art LIB) ▪ High Throughput	▪ **Film drying** ▪ Water-based process critical for some SE
2. Solvent-free (or low) concepts (e.g. extrusion, electrostatic spraying, etc.)	▪ Big cost and energy savings possible: elimination of solvent and drying process	▪ **Film uniformity** ▪ Scale-up ability

Figure 13: Processing approaches for lithium metal and silicon/graphite anodes.

Current collector — Li metal anode — **Li anode: extrusion process**

Current collector — Li metal anode — **Li anode: melt processing/vapor processing**

Current collector — Host structure for Li plating — **Li anode: anode-less approach**

Current collector — Si/C anode composite — **Si anode: wet/dry processing**

Anode-less approaches

For all three of the previous approaches pure lithium metal has to be handled in the production process. At the very least a dry atmosphere is required or even an inert one (e.g. argon) owing to the high reactivity of lithium with water, oxygen and even nitrogen. Specific safety measures are also required in the production, these can vary between the different approaches [130]. To avoid the challenging handling of lithium, scientific and industrial communities view "anode-less" cell concepts as promising [133, 136, 137]. The idea is that during the formation of the battery (in the first controlled charge and discharge cycles), the lithium-ions stored in the cathode are plated onto the anode current collector during the first charging cycle, thereby forming the lithium metal anode *in-situ*. Lithium plating avoids the direct handling of lithium metal, it enables very thin layers to be applied and can–in principal–lead to the highest possible energy densities, since no excess lithium is introduced into the cell. Potentially, by using lithium plating the anode production step can be completely omitted and the anode will be formed during the formation process. Nevertheless, there are still many challenges regarding lithium plating. In particular, the homogeneous deposition of lithium onto the current collector is susceptible to errors. Therefore, current approaches mostly use tailored current collectors or host structures which ease homogeneous deposition [136]. However, this approach minimizes the production benefit of "anode-less" approaches, because the host structure must be integrated into the production process instead of a lithium foil. Moreover, lithium loss due to irreversible reactions such as the formation of the solid electrolyte interphase (SEI) may occur, which reduces the amount of lithium that can be cycled. In order for the cathode capacity to be used in full an alternative source of excess lithium would have to be introduced into the cell. Furthermore, the production of "anode-less" cells has not been scaled up yet and is not established for large format battery cells.

Graphite/Silicon anodes

Graphite and silicon/graphite composite anodes can be manufactured in a wet slurry-based process similar to that used for state-of-the-art LIB. For current LIB, the slurry is mostly water-based [129] and combines graphite (+silicon), a styrene-butadiene rubber (SBR) as a binder, a conductive agent and other additives. For high silicon content or silicon only anodes, there may be a need for greater amounts of specialized binders which can withstand the high mechanical stress caused by Si-particle volume change during de-/lithiation.

In SSB the solid electrolyte (SE) has to be added as an additional component. For sulfide electrolytes an aqueous solvent is not possible, due to their reactivity with water (formation of toxic H_2S). Therefore, an inert atmosphere may be necessary for sulfides during some production steps, especially if SE powders with a high surface areas are involved. The slurry is coated onto a copper current collector after mixing. Coating speeds have already reached 80 m/min, and speeds of 150 m/min hope to be achieved in the future. A disadvantage of the slurry-based method is the drying step which follows and requires a high equipment footprint. Electrode drying and solvent recovery of the anode (for water no solvent recovery is necessary) and the cathode make up approx. 47 % of the total energy consumption of LIB production [138]. Driven by the possibility of huge savings in the costs by omitting the drying processes, new approaches using less or no solvents at all are being intensively investigated. These include extrusion processes, dry printing or calendering and electrostatic spraying [139, 140]. The challenges to this are the production of uniform layers and the possible scale up to reach current electrode production speeds.

3.1.3. Solid Electrolyte Separator Processing

The solid electrolyte (SE) separator production is a completely new production step. Polymer SE are the only class of SE produced on a larger scale today. For inorganic SE, only small production lines and laboratory production are being carried out at present. Generally, three different processing routes are currently being discussed in science and industry, these are presented below.

Wet processing

In the first step of wet processing SE, binder, optional additives and solvents are mixed into a slurry [130]. A water-based process is not possible due to the reactivity of sulfide and oxide SE with water and therefore organic solvents are used. In the case of sulfides in particular, which are also reactive to polar organic solvents such as NMP, the choice of solvent and corresponding binder is limited [128]. For polymer and polymer-oxide composites acetonitrile is often used as a solvent since it can dissolve poly(ethylene oxide) (PEO), has a low boiling point and is stable against most of the inorganic particles, such as LLZO [148] which are commonly added. Similarly to the cathode, xylene is often used as a solvent for the production of sulfide SE together with binders such as styrene-butadiene rubber (SBR) and silicon rubber (SR) [141]. On the one hand, the amount of binder in the SE separator should be as low as possible, as it lowers the ionic conductivity, on the other hand, insufficient amounts of binder can lead to poor interconnectivity of the SE particles, which also limits the ionic conductivity and the stability of the SE separator [128, 141].

To integrate the SE separator into the cell, it can either be applied directly onto the cathode or manufactured separately as a free-standing SE and stacked with the electrodes afterwards [139, 141]. For the latter, the slurry is simply poured into an inert mold or cast onto an inert substrate followed by solvent evaporation [141]. Coating the slurry onto the electrode can be done by several different production methods. Most promising are slurry casting, tape casting and screen printing techniques [130, 140]. After the coating step, the solvent is evaporated. Free-standing SE separators need a certain thickness (>30 µm) to ensure mechanical integrity and are therefore inferior compared to techniques in which the SE is coated onto the electrode, where in principal very thin layers of 5-10 µm can be achieved [141]. To build high energy cells, the solid separators have to be thin and have a similar thickness to polymer separators currently used in state-of-the-art LIB (10-20 µm). For oxide SE with high density and low ionic conductivity, even thinner thicknesses are aimed for. In view of this fact, electrode coating processes will prevail over free-standing separators. Even though the production of thin inorganic separators within the range of 20-30 µm has already been achieved [149–151], there are still challenges to overcome in order to produce uniform and defect-free layers on a mass-scale.

The last step is the layer compaction, where the SE separator layer which has been formed is densified either by pressure application (calendaring or pressing) or temperature treatment (e.g. sintering) to ensure good contact to the electrode, low porosity and high ionic conductivity. Calendering is possible for polymer electrolytes, due to their high flexibility, but also the ductility of most sulfides enables their densification by calendering, which is an advantage compared to oxide electrolytes with regard to production. Most oxide materials are not malleable, hence cannot be sufficiently compacted by pressing. Therefore, an additional high-temperature sintering process is needed, this enables very dense layers with less grain boundaries and high ionic conductivities. However, sintering is very energy intensive and therefore expensive. In the case of a two-step production process of a free-standing SE separator and the cathode, two sintering steps can be applied. This is beneficial, since the cathode active material would not survive high sintering temperatures [131]. In the first sintering step, to densify the solid electrolyte, the highest temperatures are applied. The second sintering step is carried out at reduced temperatures to combine the SE separator with the cathode composite electrode. Since the sintering steps are time-intensive, they slow down production considerably and limit its throughput. Moreover, due to the considerable vapor pressure of lithium at high temperatures, certain amounts of lithium are lost during the sintering process and therefore it is necessary to add excess lithium, for example in the form of Li_2CO_3 [139, 152]. Since oxide separators show very promising properties, there are many ongoing endeavors to ease the sintering process. For example sintering agents, such as Al_2O_3 and Li_3BO_3 have been added to reduce the sintering temperatures [41, 153]. Another approach is ultrafast high-temperature sintering. Joule heating in an inert atmosphere can reduce the sintering time to less than one minute [42].

Where upscaling is concerned, the wet processing route is particularly promising for inorganic solid electrolytes. Polymers can also be processed with a wet process, but since the dry extrusion process is already established and more cost-effective, it seems unlikely that a wet production process will be adapted for polymer SE. The reactivity of some oxide and sulfide SE with water represents another challenge. Consequently, both varieties of inorganic SE have to be processed in a dry environment, for sulfides in particular, a very dry atmosphere with a low dew point should be used. Generally, the wet production process has the great advantage that it can usually be carried over from current LIB production, which facilitates the scale-up and ensures a high throughput if no sintering process has to be applied. The disadvantages are similar to those of the cathode composite production; the extensive and costly processes of solvent recovery and film drying. In addition, the scale-up to mass production remains to be tested for SE and the production of large, thin and uniform SE separator layers is challenging, especially for brittle oxide materials, but also for sulfide electrolytes.

Table 10: Production approaches for solid electrolytes, their advantages and challenges:

Production method	Advantages	Challenges & Disadvantages
Wet processing	▪ Similar process and equipment as for AAM/CAM processing ▪ High throughput ▪ Sulfide electrolytes: subsequent calendering/cold-pressing possible	▪ **Film drying** ▪ **Solvent recovery** ▪ Production of thin layers with low porosity is challenging ▪ **Oxide electrolytes: Sintering (expensive, energy intensive, low throughput, excess lithium needed)** ▪ Sulfide electrolytes: Limited options of solvents and binders ▪ Polymer electrolytes: Extrusion process is cheap and established
Solvent-free (or reduced) concepts (e.g. extrusion, dry calendering)	▪ **Solvent free or reduced** ▪ Extrusion is an established process, especially for polymers ▪ Cost and energy savings are possible owing to the elimination of the solvent and drying process	▪ **Inorganic electrolytes: Production of thin, uniform layers is challenging** ▪ **Oxide electrolytes: Sintering (expensive, energy intensive, low throughput, excess lithium needed)**
Aerosol deposition	▪ **Solvent free** ▪ High quality, thin and dense layers ▪ **Oxide electrolytes: Sintering can possibly be omitted**	▪ **Low throughput (low deposition rate)** ▪ Today: Expensive and immature process ▪ Vacuum needed

Solvent-free concepts

In an attempt to reduce or even eliminate the high costs of solvent recovery and film drying, processes without or with small amounts of solvents are being intensively investigated. For polymer solid electrolytes, the dry extrusion process has already been established. The polymer and a lithium salt are homogenously mixed in an extruder. Then the compound is laminated onto the cathode composite electrode [144]. Subsequent calendering densifies the SE separator and enables a good contact with the electrode. In principle extrusion is possible for inorganic solid electrolytes as well, however, further development is needed. There are also technical barriers owing for example to the increased hardness and lower malleability. Furthermore, it is challenging to produce thin, uniform films without any solvent, and sintering will still be necessary for oxide electrolytes [130].

Moreover, dry processing concepts, which are being investigated for the cathode, can also be applied in solid-state separator production. Dry calendering, dry spraying and screen printing are promising approaches, but still require some research and development efforts, especially for scaling.

Powder-based processing

For oxide electrolytes in particular, alternative production methods are being explored, in order to eliminate high temperature sintering or to lower the temperature considerably. One approach is the powder-based process of aerosol deposition. In this technique, a carrier gas transports the solid electrolyte powder (together forming an aerosol) to the substrate. The carrier gas (e.g. nitrogen or argon) carries the solid electrolyte from an aerosol chamber into an evacuated deposition chamber, where it is deposited onto the cathode [154–157]. The pressure difference between aerosol and deposition chamber enables strong adhesion and compact layer formation. To achieve denser layers an annealing step at 600 °C is followed, high temperature sintering steps can be completely omitted, and unwanted side reactions are prevented [140, 158]. Aerosol deposition enables dense and thin films (1–100 µm)[140] and is also solvent free. However, the technology is still very new, it needs a vacuum to operate, and is expensive and therefore will not be able to be used for larger production in the near future. Further, state-of-the-art aerosol deposition technology shows only deposition rates of about 10 mm³/min, but would have to exceed 1000 mm³/min to be competitive with other manufacturing approaches [133]. A first option to introduce the technique could be for the deposition of very thin coatings, for example for the cathode. However, for bulk solid electrolyte production, the aerosol deposition cannot at the moment compete with extrusion or wet processing techniques, but because of its many advantages, especially for oxide electrolytes, many companies still have it on their manufacturing roadmaps.

3.1.4. SSB Manufacturing Process

The three steps for the manufacturing process of solid-state batteries are the electrode and electrolyte separator production, the cell assembly and the cell finishing [132].

Electrode and Electrolyte Separator Production

The production of the electrodes and the SE separator represent key aspects of the manufacturing process and the different processing options for cathodes, anodes and solid electrolytes are discussed in detail in Sections 3.1.1 to 3.1.3. Different options exist with regard to the process chain, i.e. the order of the processing steps. One option is to start with the deposition of the cathode composite onto a carrier tape or directly onto the current collector, followed by the solid electrolyte deposition on top of the cathode. The anode is manufactured separately (as free-standing foil, or on the current collector) and then stacked with the cathode/separator film and the current collector [140]. Another option is to start with the deposition of the solid electrolyte onto a carrier tape and to deposit the cathode composite on top. In this case, the anode would also be processed separately and finally stacked with the cathode/separator film [140]. Different process chains are possible, however, at this stage of technological development, it is not clear which process chain will establish itself for which SSB technology. Furthermore, deposition processes can vary significantly depending on the materials used, as well as the steps that may be required, such as solvent evaporation, annealing, sintering, and calendaring. Depending on the production processes for the electrodes and the SE separator, a **lamination step** may be required to ensure good contact between the individual components. In this lamination step, the cathode, the solid electrolyte separator, the anode and the current collector are brought together and pressed onto each other via rollers [132].

Cell Assembly

After the electrodes or elemental electrode stacks have been produced, they need to be assembled into stacks. The cell assembly for SSB follows similar steps to those of state-of-the-art LIB, but has certain differences. **Cutting** the elementary stacks is the first step of cell assembly and can be done for example by laser cutting.

The next process step is **stacking**, in which the cut elementary stacks are stacked on top of each other to form a cell stack. Depending on the cell format, either individual sheets or continuous tapes are stacked on top of each other. The cell stack is then pressed together (and potentially heated), to allow for good interface contacts between the individual layers in the stack [130,131]. A crucial difference will be the format of the batteries.

Most state-of-the-art LIB are produced as cylindrical (in terms of numbers) cells, the SE separator and the electrodes are pliable and the winding of the sheets is uncomplicated. In contrast, pouch cells with stacked electrodes are the most convenient cell format for SSB, since the winding of inorganic separator materials, especially oxide materials, is difficult or even impossible. However, cylindrical cells are possible for polymer SSB, and even the possibility of cylindrical sulfide SSB cells is being researched.

Initially, SSB electrodes will be stacked in a parallel configuration, as in state-of-the-art LIB, but bipolar-stacked electrodes are often noted as a possibility to increase the energy density of SSB modules and the cell voltage [128, 130, 159, 160]. A bipolar current collector (CC) functions as CC for two opposing electrodes of adjacent electrochemical units; hence, several units can be connected in series. Similar concepts with liquid electrolyte would require sealing between the individual electrochemical units and would therefore be very challenging in terms of cell design. Bipolar stacking is still far from being used in practice and new CC materials may be needed [128]. In addition, the electrochemical units would need to be produced with near perfect reproducibility, which is not the case yet for SSB.

The final steps of the cell assembly process are **contacting and packaging**. The current collectors are welded to the contact tabs. In the parallel cell configuration, the current collectors of each elementary stack need to be connected; in the bipolar configuration only the outermost current collectors need to be contacted. Finally, the cell stack is packed into a rectangular cell housing, to form pouch-type cells (thermally sealed / glued) or prismatic hard-case cells (welded).

Unlike for liquid electrolyte LIB, the electrolyte filling and degassing steps can be omitted for ASSB or at least for SSB concepts without any liquid electrolyte.

Cell Finishing

After the cell assembly, the final steps of cell production, formation, aging and testing are necessary. During the **formation** step, the cell is passed through the first charging and discharging cycles. Afterwards, during the **aging** step the cells are stored for days or even weeks in a controlled environment and tested to detect defective cells. For state-of-the-art LIB, formation and aging can take up to three weeks and one-third of the manufacturing costs [138]. It is expected that the time for SSB formation and aging will be shortened compared to liquid electrolyte LIB, as SSB are expected to reach a stable operation more quickly [132, 160]. The formation might potentially be even omitted completely for SSB with Li anode [130, 132, 160]. However, especially at the beginning of market entry it is unlikely that cells will enter the market without a thorough aging and quality check, therefore omitting the

formation and shortening the aging process can be considered a long-term goal. **Testing and grading** is the final step of cell production. The battery cells are electrically characterized and sorted according to their properties (grading). This step will be similar for SSB as it is for state-of-the-art LIB.

Comparison of Manufacturing Process to State-Of-The-Art LIB

According to an expert assessment based on a survey (see Section 1.4), between 20 % and 60 % of the state-of-the-art LIB production can be directly transferred to the SSB manufacturing process. The exact percentage will largely depend on the SSB technology and the material combinations in use. Table 8 compares the different production steps of the state-of-the-art LIB manufacturing process with the production process for oxide, sulfide and polymer SSB. For oxide and sulfide SSB,

no mass production has yet been achieved. Therefore, the table shows the manufacturing steps with the highest degree of maturity (based on expert assessments). The manufacturing steps which will be applied once these SSB concepts are launched on the market may vary from the processes outlined. Moreover, only the main production steps are shown for clarity, but additional steps may become necessary, such as the preparation of electrode coatings. Polymer SSB are already produced on a GWh-scale and therefore the commercialized process is described in [144]. The table not only gives an overview of the manufacturing steps for SSB, but also shows which process steps are transferable from the manufacturing process of current LIB. The color code illustrates the transferability of production. Green indicates that the process is the same or can be largely adopted from current LIB production, yellow signifies that the process has overlaps but also some distinct differences and a process marked orange is fundamentally different from state-of-the-art LIB production.

Table 11: Exemplary manufacturing processes for oxide SSB, sulfide SSB and polymer SSB in comparison to the state-of-the-art LIB manufacturing process (green shading: same/similar process as in current LIB production; yellow shading: process shows similarities, but also distinctive differences; orange shading: fundamen-tally different process):

Production Steps	Lithium-Ion	Oxide SSB	Sulfide SSB	Polymer SSB	Long-term goal
Anode	**Wet processing** Slurry mixing and coating, drying, calendering	**Extrusion process (Li-foil)** Extrusion, calendering, lamination	**Extrusion process (Li-foil)** Extrusion, calendering, lamination	**Extrusion process (Li-foil)** Extrusion, calendering, lamination	In-situ Li anode formation
			Wet processing (Si-based anode) Slurry mixing and coating, drying, calendering		
Cathode composite	**Wet processing** Slurry mixing and coating, drying, calendering	**Wet processing** Slurry mixing and coating, drying, low-temperature sintering	**Wet processing** Slurry mixing and coating, drying, calendering	**Extrusion process** Extrusion, calendering	Dry processes or green solvent-based processes
Separator	**Extrusion process** Dry extrusion process (PP) Wet extrusion process (PE)	**Wet processing** Slurry mixing and coating, high-temperature sintering, lamination, low-temperature sintering	**Wet processing** Slurry mixing and coating, drying, calendering	**Extrusion process** Extrusion, calendering	Dry processes or green solvent-based processes
Cell-Assembly	**Cell-Assembly** Stacking, tab welding & packaging, electrolyte filling, formation, degassing and sealing, aging	**Cell-Assembly** Stack pressing, no electrolyte filling and degassing, formation and aging shorter than for LIB	**Cell-Assembly** Stack pressing, no electrolyte filling and degassing, formation and aging shorter than for LIB	**Cell-Assembly** Stack pressing, no electrolyte filling and degassing, formation and aging shorter than for LIB	Completely omit formation and aging

3.2. Material Availability and Sustainability Aspects

As with conventional LIB, there are challenges for SSB production with regard to the raw material extraction, material production and cell production. These challenges need to be overcome in order to improve the sustainability of these technologies and their applications, e.g. in electric mobility. Ecological and social issues with the mining of cobalt ores in the DR Congo, or with the production of lithium from lake water sources in South America are some of the frequently discussed examples of the problematic production conditions [161]. However, these are only two of many examples that have to be discussed in more detail, such as the specific energy-mix in material and cell producing countries. From a resource perspective, lithium-ion solid-state batteries make use of similar components as their liquid electrolyte-based counterparts: Transition metal-based cathode materials, carbon additives, copper, aluminum or nickel current collector foils and hard-case or pouch-type cell housings. Some major differences in resource demand may however arise from the choice of solid electrolyte and anode materials. Several of the SE materials under investigation contain metals, which are currently not present in LIB-cells, such as lanthanum, germanium, zirconium or tin.

Availability of Metals

Zirconium is relatively common in the earth's crust. It is used for example as a component in alloys and the global production is in the order of one megaton per year.

Lanthanum is one of the more abundant rare earth metals and can be obtained as a by-product during the production of other metals. It is used in metallurgy, e.g. as component in cerium alloys. Its overall industrial use is in the region of 50 kilotons per year [162]. An increased use in SSB would significantly increase demand.

Germanium is a relatively scarce element found in a number of minerals. It is typically extracted as a by-product during the production of zinc and other metals. It is used in a number of industrial applications ranging from fiber optics to catalysts and semi-conductors. Due to its scarcity and high cost, around 900 EUR/kg, mass application in batteries is not feasible.

Lithium is obtained by mining minerals and extraction from groundwater and saltwater. LIB already accounts for the majority of the industrial lithium demand today. Demand for Li is expected to multiply in the next few decades. For cathode materials, the demand for lithium will be comparable for SSB and liquid electrolyte LIB technologies. Major changes can, however, be expected from the transition to solid electrolyte materials. Standard liquid electrolyte solutions, e.g. 1M $LiPF_6$ salt in EC/DMC/DEC, contain a share of approximately

0.6 wt.% lithium or approximately 3 g/kWh at the cell level. Little change in the demand for Li can be expected with a transition to polymer SE, e.g. Li salts in a PEO matrix corresponding to few g/kWh at the cell level. The concentration of lithium in inorganic electrolytes is significantly higher. Oxide electrolytes such as LLTO have a Li content of 1.4 wt.%, LAGP and LATP of 2.5 wt.% and LLZO of 5.8 wt.%. Sulfide electrolytes, e.g., of the argyrodite or LPS sub-class, typically contain lithium in the order of 10 to 15 wt.%. The specific Li demand at the cell level will depend on the material choice, the thickness of SE-layer and the share of anolyte or catholyte materials in the electrodes. As an average of the different SE materials, an additional demand for lithium in the region of 10 to 20 g/kWh could result from the transition from liquid to inorganic electrolytes. Compared to the demand of approximately 100 g/kWh for NMC811 cathode materials, the potential contribution of the SE to the lithium demand is still small, but might indeed put additional pressure on the supply of lithium for batteries [163].

The same applies for cell concepts utilizing lithium metal anodes. An additional demand compared to graphite or silicon-based anodes depends on the thickness of the initial Li layer. For a hypothetical electrode configuration with a cathode loading of 6 mAh/cm², an initial Li layer of 5 μm results in a Li demand of approximately 15 g/kWh at the cell level.

Footprint of Refinement, Synthesis and Cell Production

Apart from the use of certain metals and the associated mining and production conditions, the refining, synthesis and finally the cell production processes are also of great importance for the ecological footprint of LIB. Approximately 50 % of the state-of-the-art LIB carbon footprint results from the cell production process, in particular the various drying steps and the conditioning of the dry room atmosphere. As discussed in Section 3.1, some manufacturing steps for state-of-the-art LIB might be transferrable to SSB, which would lead to a similar carbon footprint. Improvements are needed in the production processes in order to make them more energy-efficient, for example with the use of dry coating for SSB [164], which could lead to energy savings. In addition, some processing steps, such as the electrolyte filling and degassing, might not be necessary for SSB, which could also lead to further reductions. However, if SSB production requires high-temperature steps, as might be the case for oxide SE, the carbon footprint of SSB could also increase.

Recycling Aspects

Two main processes have been so far established for the recycling of state-of-the-art LIB. The pyrometallurgical process

which is a high-temperature procedure and the hydrometallurgical process which uses chemical reactions in order to separate the materials. A mechanical separation step precedes the hydrometallurgical process. The recovery of transition metals is already an established process. Further components such as the lithium and the electrolyte are also technically recoverable. However, these processes have not yet been established on a larger scale.

Similar to the recycling of conventional LIB, these established processes can be adapted and applied to solid-state batteries to enable the recovery of their main cell components. The metallic components of solid electrolytes and cathodes are accessible by pyro- or hydrometallurgical recycling processes. The higher proportion of lithium per kWh, especially of inorganic solid-state cells, could lead to an increase in the incentive to recover the Li metal during the process as well. Oxides, sulfides and polymers each require different recycling processes, most of which utilize recycling steps which are already established. In the case of oxide-based electrolytes, pyrometallurgical treatment is probably the most appealing. For sulfides, complex hydrometallurgical processes are most likely to be the most effective and appropriate recycling methods. Additional non-metallic components like sulfur can complicate the process compared to state-of-the-art LIB recycling. In the case of polymer solid electrolytes, the polymers are likely to be thermally utilized for economic reasons. The salts and fillers can be recycled. Theoretically, all components of a material can be recycled in complex wet chemical processes, however, this is not economically viable [165].

For liquid electrolyte LIB, there is so far no enforced and economic process to reuse the liquid electrolyte. The economic recovery of electrolyte may be different for solid-state batteries. In the case of solid-state batteries, it is possible to recover the electrolyte materials in a direct solution process followed by a direct recovery process, to reprocess them and finally reuse them for the production of new battery cells [166]. Due to the electrochemical stability of solid electrolytes, the chemical structure of the material remains unchanged during cycling of the battery, which enables its recovery and reuse without its breakdown into precursors. Energy-intensive pyrometallurgical or hydrometallurgical processes can theoretically be avoided in this way [167]. An alternative would be to dismantle the individual cell components and then directly reuse the solid electrolyte. However, dismantling into individual components is challenging due to the solid connections with partial 3D interfaces between the layers, and is not an established process. Due to the early stage of the development of the SSB, there is still no fundamental knowledge about the extent to which the solid separators being used can be reactivated and processed for a new battery cell. Annealing the material can potentially restore the original ionic conductivity [168].

The solid materials used in part consist of several components unlike liquid electrolyte LIB. Their separation is challenging, which could lead to a more complex recycling chain [169]. Since the composites of catholyte (especially oxides) and cathode active material are structurally similar, their separation, for example, via dissolution is challenging as well [167]. In the mechanical crushing of vehicle batteries, the flammability of organic liquid electrolytes poses a safety risk that is not present with solid electrolytes [167]. A drawback, however, is that SSB partly include reactive Li metal.

The aspects mentioned would all require recycling processes which have been individually optimized for SSB. However, from an industry perspective, it is unlikely that separate recycling processes will be set up for conventional LIB and solid-state batteries, as this would require further pre-sorting of batteries and mean that any possible economic efficiencies would be further delayed. With significant returns of used SSB not expected before 2040, recycling processes may need to be adapted to ensure appropriate compatibility.

Aspects such as 2nd life approaches have not yet been discussed due to the early stage of SSB. One possible factor which needs to be taken into account is material fatigue such as cracks or fractures which increase the contact resistance. Due to the given electrochemical stability, especially for oxides and sulfides, deterioration of the electrolyte material is unlikely to significantly affect the battery's lifetime. If contact detachment is the reason for the end of its first life, then use in a 2nd life application is questionable as this may lead not only to performance losses but also to battery failure.

3.3. Economic Aspects

Market situation

The current utilization of SSB is limited to low-volume electric vehicles and some smaller portable devices, e.g. in cards, sensors or medical applications. However, the thin film battery technology used for the latter group of applications is not comparable to the large-scale battery cells investigated in this report, as it differs both in terms of material and cell design as well as manufacturing.

Small SSB cells featuring a capacity of 100 mAh to 1 Ah are currently in the prototyping phase. They may be utilized in wearable devices or more generally in portable electronics but are not suitable for mobility applications[170]. While an increase of energy density is a clear driver for the adoption of SSB in many markets, the commercial success of SSB will significantly depend on their material, processing and production costs.

Material costs

The future costs of SSB is mainly determined by the cost of active and passive materials and the cost of manufacturing the cells. With the aim of utilizing the same cathode active materials in SSB as in liquid electrolyte-based battery cells, the cost of CAM is likely to be comparable for both technologies. Specific treatments of the CAM particles to ensure chemical compatibility with the SE materials may require additional steps such as particle coating, which could increase costs. $LiNbO_3$, which is used as a coating for the CAM particles, has a relatively high metal value of around 25 EUR/kg. However, due to the low thickness of the coating layer, no significant increase in cell cost is expected from the perspective material costs.

The function of the solid electrolyte in ASSB is carried out by liquid electrolytes and coated polymer separators in conventional LIB. Depending on safety and performance requirements, the cost of these separators is in the region of 0.5 to 1.5 EUR/m^2 [170–173]. Standard electrolytes based on the organic solvents EC/DMC/DEC and fluorinated Li salt cost between 5 to 10 EUR/kg [173, 174]. The costs are mainly determined by the high purity requirements for the components, in particular for the Li salt.

While these figures represent the prices of industrially available materials, there is no large-scale production for SE materials yet and thus there is no industrial benchmark for these materials. Since similar salts are used in a similar concentration in polymer SE concepts and liquid electrolytes, similar prices can also be assumed for both technologies if produced on an industrial scale. Transferring considerations on the cost of liquid electrolytes to inorganic SE materials is not possible due to the huge differences in composition and production processes.

One approach to assessing future inorganic SE costs is to consider the metal value in SE materials. Figure 14 shows the metal value of several inorganic SE materials based on the average market prices in 2021. Due to the high cost of germanium, the compounds LAGP and LGPS stand out from the rest of the materials. A metal value of 100 EUR/kg or more for these materials would most likely not be acceptable for a commercialization of SSB. In contrast, the titanium, lanthanum and zirconium-based oxide compounds LATP, LLZO and LLTO have a low metal value of less than 5 EUR/kg. Due to the high content of the relatively expensive lithium, the sulfides have a metal value of 6 to 13 EUR/kg.

The metal cost of SE materials is only a rough approximation of the final material costs. Battery grade precursors with the required purities are significantly more expensive than their metal value. For typical cathode active materials the precursor cost can be 20 % to 50 % more than their metal value, reflecting the energy and equipment requirements of refining and a process yield of less than 100 %. In addition to these precursor materials, the process of active material manufacturing also makes a significant contribution to cost. For NMC materials with a medium to low Co content, for example, the manufacturing costs amount to 7 to 10 EUR/kg [175], which represents a significant share of the overall material costs of 20 to 40 EUR/kg [176].

It is anticipated that manufacturing costs and overheads for the synthesis and refinement of battery-grade precursors for SE will approach a level which is comparable to that of other functional inorganic materials or even the above-mentioned cathode active materials. For sulfide SE in particular, a supply chain of materials needs to be built from the ground up. The synthesis requires lithium sulfide (Li_2S) as a precursor, which is currently not available on an industrial scale. It is therefore not possible to make an estimation of price for the material. In a scaled-up market, the metal value overhead costs of producing Li_2S could become comparable to the production of other battery materials. However, during the ramp-up phase the cost of sulfide SE could be significantly higher than its metal value.

In order to compare these prices with the benchmark set by liquid electrolytes and polymer separators, a separating solid electrolyte layer of 20 μm can be assumed. This thickness translates to a loading of 40 to 100 g/m², assuming a density of 2 to 5 g/cm³ for the SE materials discussed. Based on these figures, the metal value per area unit of SE (approx. 0.3 to 0.5 EUR/m², processing not included) is comparable to the cost of coated polymer separators. To determine the required amount of solid electrolyte to replace the liquid electrolyte, the porosity of electrodes and separators and with that the volume filling in battery cells needs to be taken into account. In state-of-the-art high-energy LIB, 2 to 3 g/Ah or 500 to 800 g/kWh of liquid electrolyte are required. Assuming similar shares of volume for

Figure 14: Metal cost of several inorganic solid electrolyte materials based on the average metal cost values in 2021.

Metal cost of SE materials
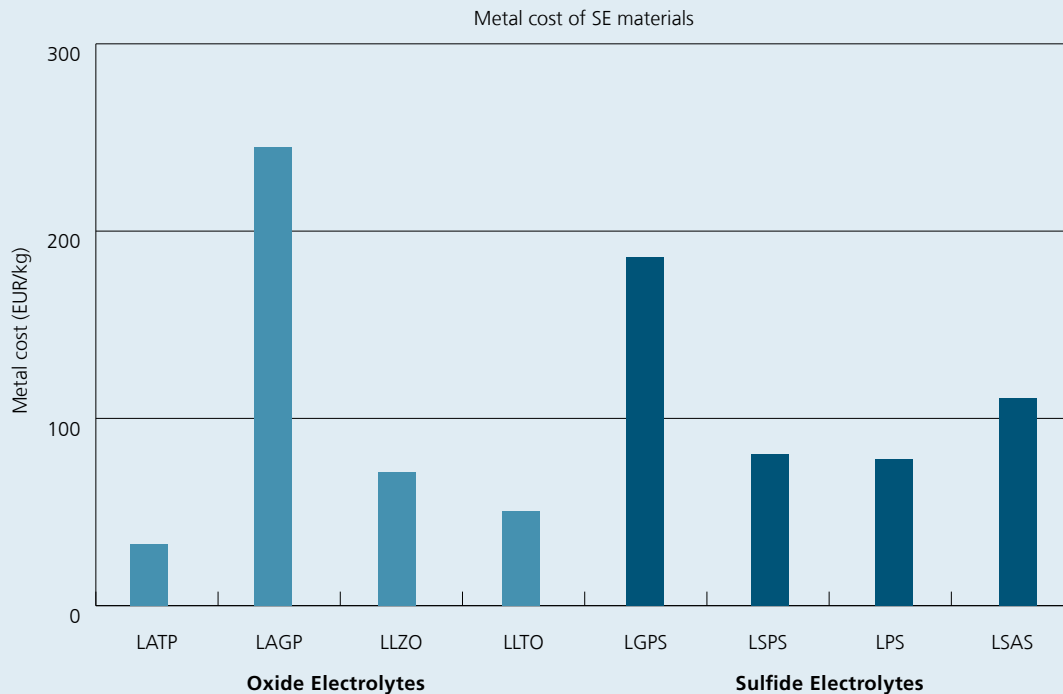
the active materials and electrolytes in LIB and SSB electrodes, 500 to 1500 g/kWh of SE material could be required for SSB. This means that the metal value of SE materials in SSB (3 to 6 EUR/kWh) is already similar or even higher than the final cost of the liquid electrolyte in LIB (3 to 8 EUR/kWh). Cost parity between liquid and solid electrolytes can therefore only be achieved with highly efficient production processes that bring the final material costs of SE close to their metal value.

Looking at lithium metal anodes from the same metal values perspective, the cost of anode materials such as graphite or silicon could be reduced. However, the transferability of the lithium metal value to the cost of lithium anodes is very difficult because the cost, particularly of thin Li foils or layers, will vary greatly from their metal value. The processing of thin layers can be challenging due to the reactivity of lithium and the lack of industrially available processes. Anode-free SSB concepts are a promising way to reduce costs from the materials perspective, but again, a quantitative analysis is not possible at this early stage of technological maturity.

Cell manufacturing costs
As is the case with conventional LIB, material processing and cell manufacturing are large cost components in the final cell costs. When switching from liquid to solid electrolytes, some manufacturing steps can be omitted (see Section 3), which can

reduce cell costs: Particularly the reduction in the formation and ageing time could have a significant impact. On the other hand, there will most likely be manufacturing steps for SSB that go beyond that which can be covered by state-of-the-art manufacturing equipment for LIB. Especially during the ramp-up phase of SSB commercialization, this means higher investments in production infrastructure per GWh capacity since no standardized turnkey solutions exist. But also in an up-scaled production, any additional processing steps can result in higher scrap rates as well as higher energy and material costs. High-temperature sintering steps, e.g. for oxide SE materials, should be considered particularly critically.

Cell production capacities are currently being built up all around the world, requiring investments in the magnitude of billions of Euros. With depreciation periods of 10 years or more, these factories will have to produce LIB cells for many years in order to be considered economically successful. The goal for the economic competitiveness of SSB is therefore not only to achieve cost parity with liquid electrolyte LIB, but to undercut the cost of LIB in order to justify investments in new or additional infrastructure. High compatibility of SSB with state-of-the-art LIB production would certainly help to gain larger market shares in the future. Otherwise, SSB will only be able to establish themselves on the market if they exhibit very significant technological improvements.

4. Promising Solid-State Battery Cell Concepts

4.1. Application KPI of Solid-State Batteries

The R&D on solid-state batteries is driven by potential improvements of several key properties, such as energy density, safety, fast charging ability, price and lifetime, compared to conventional liquid electrolyte batteries. Depending on which of these key performance indicators are to be optimized, different approaches to cell concepts are suitable. However, for most applications several or all of these KPI have to be improved simultaneously. Nevertheless, the following discussion will illustrate the relationship between application KPI and various cell concepts.

Safety

Public discourse regarding the safety of EV has been shaped by how easily they ignite and can be extinguished. Safety is one of the most important aspects, when the transition from liquid electrolyte LIB to SSB is promoted by replacing a flammable liquid electrolyte with a non-flammable solid electrolyte. The absence of liquids, which otherwise would cause leakage reduces the risk of contamination and environmental hazards. Furthermore, a more stable separator lowers the risk of short circuits.

However, SSB are not free of additional risks and potential safety concerns, the most prominent being the use of a lithium metal anode. Lithium metal is highly flammable and tends to form dendrites under cycling. These dendrites can cause short circuits in the battery cell and lead to a thermal runaway. Therefore, the use of a mechanically stable separator is required. Possible ways of reducing the amount of excess lithium are investigated in order to limit the risks that come with lithium metal [177], like the adaption of an in-situ anode. In general, the potential harm that can occur if the battery malfunctions, increases with its energy density.

Regarding the safety of the battery cell, oxides are the most advantageous solid electrolytes since they are less reactive and mechanically stable as mentioned above. Sulfide electrolytes bring an additional safety challenge, since they can react with water to form H_2S, a toxic and inflammable gas.

As discussed above, various safety aspects have to be considered, when comparing different cell concepts. Developments over the next few years will show whether and how SSB can help to reduce the safety risks of EV batteries. Can the overall safety of SSB be improved, even if Li metal anodes are used?

Energy density

One of the most important properties of a battery is its energy density [178]. It can be given in respect to the mass of the battery (cell/module/pack) or to the volume of the battery, i.e. the gravimetric and volumetric energy density, respectively. A main challenge for electric cars is increasing the amount of battery energy stored in electric cars to expand their driving range.

Adopting lithium metal anodes is the main approach to increase energy density when transitioning from conventional LIB to solid-state batteries. Therefore, electrolytes that are chemically compatible with lithium metal and are reasonably resistant against dendrite formation are required. The energy density of the cathodes can be optimized, for example by moving from LFP to nickel-rich NMC.

To increase the energy density, the share of active material has to be maximized, e.g., by manufacturing thinner inactive material components or their replacements or increasing layer thicknesses of anodes or cathodes. Additionally, improvements can be done to minimize the requirements needed on the module or pack level, for example by bringing down the operating temperature for solid polymer electrolytes which allow for a smaller and lighter temperature management system.

The presented approaches are possibilities to improve, gravimetric and volumetric, energy densities. If only one of those parameters is to be improved, further properties can be considered for example the components' specific densities.

As SSB are being developed and commercialized, the energy density of liquid electrolyte LIB is also improving. How well SSB can compete with this moving target depends heavily on the following questions: How well can the high theoretical energy densities of SSB be transferred to cells? Will fast charging and safety requirements be an obstacle to approaching 1000 Wh/l?

Fast charging ability

Refuelling a conventional car takes less time than recharging a battery, which impedes the transition from internal combustion engines to electric vehicles. Reducing the charging time is, therefore, a main goal for new battery concepts.

A high ionic conductivity is required for enabling fast charging. Another challenge for high charge transfer in SSB are the electronic and ionic pathways, which involve a multitude of particle interfaces and, compared to liquid electrolyte systems, a rather limited part of surface area of active material particles that actually contributes to the ionic conduction. The flexibility of polymer electrolytes promotes the manufacturing of good interfaces; however, their low ionic conductivity and the low cationic transference number of most polymer electrolytes hinder fast charging. Inorganic solid electrolytes are less flexible, but at least sulfides achieve a decent ionic conductivity, potentially enabling high charging rates. Oxide electrolytes are limited in their ionic conductivity which makes fast charging with thick active layers for high energy cell concepts challenging.

Due to rapid volume changes fast charging not only stresses the solid electrolyte, but also the entire cell structure. Therefore it must be designed accordingly.Furthermore, fast charging with lithium metal anodes can promote the formation of dendrites, which negatively impacts the safety and the lifetime of the cell.

It remains to be seen: will the interface challenges of SSB be overcome by possible solutions in the cell design, such as material choices and the application of external pressure? How will requirements for fast charging change, when the improved battery energy density extends the car driving range further.

Long-term stability / Lifetime

Batteries that have a long lifetime are beneficial for the total cost of ownership of the respective application. They are also important for applications where replacing the battery is a particularly complex operation.

Conventional liquid electrolyte batteries face the problem of degradation via SEI layer growth, lithium plating, cathode decomposition and particle fracture at the electrodes [179].

Even though these mechanisms can affect the cycling lifetime of a SSB in a similar manner, a prolonged lifetime is a possible advantage over conventional LIB: the absence of liquids could reduce the degradation effects occurring when the battery is at rest, i.e., the calendric lifetime of the battery. However, the interface stability of the solid components poses an additional challenge. Due to limited flexibility of solid materials, the contacts between the materials can deteriorate when changing the volume during cycling.

Compared to inorganic SE, the flexibility of polymer SE can be an important asset to mitigate the stress on the interfaces which is a result of the electrodes' volume changes under cycling, the flexibility of polymer SE can be an important asset compared to inorganic SE. Sulfide SE often require a coating of the electrodes to prevent slow decomposition reactions.

In the next decade, the use of SSB in prototypes will show whether their lifetime can be extended, even if Li metal is used. Can the lifetime of SSB even be improved to the point where higher prices can be justified by undercutting conventional LIB in terms of total cost of ownership?

Price

The price of a battery electric vehicle consists to about one third of the battery cost, which gives rise to a strong economic interest in cost-effective batteries. The price of the battery can therefore be considered the most important parameter of the ones discussed herein.

The cathode accounts for the largest share of the battery price, due to the expensive materials commonly used. The most promising low-price alternative to the high-cost raw materials in the cathode, such as cobalt and nickel, is the use of LFP cathodes.

Most of the SE are not yet produced in large quantities and, therefore, still have to show their impact on the battery cost. The comparatively low amount of lithium needed for polymer SE represents a potential price advantage over the inorganic SE. Moreover, the manufacturing process of polymer SE is often described as rather easy and potentially very cost-effective. A dry room is needed for all categories of electrolytes. However, some sulfide SE require an argon atmosphere, when processed. Due to the high cost of argon, it is very unlikely that these materials can be competitive in large scale applications. The sintering needed when processing oxide SE requires high energies, which comes with additional costs.

The commercialization of the SSB depends heavily on its price, which is influenced by many complex aspects. How will the manufacturing costs of SE and SSB impact battery costs? Will higher energy densities and performance justify higher costs?

4.2. Overview of SSB Cell Concepts

In the last 10 to 15 years, companies as well as research institutes have been developing solid-state batteries. The following is an overview of cell concepts currently researched and developed by various institutions. Due to the large number of possible combinations of different active and electrolyte materials, the sub-classes of individual electrolytes were not considered for the overview. In an online expert survey, a pre-selection of material combinations was evaluated with regard to the most promising cell concepts. The cell concepts as well as the ranking from the survey are shown in Table 9. The orientation of the arrow indicates, whether a cell concept was considered as promising (vertical arrow) or whether the realization of the concept is rather doubtful in the near future (horizontal arrow). The evaluated concepts will be shortly discussed in the following. The most promising cell concepts will be analyzed in detail in Section 4.3 to 4.6.

It should be noted that the list of companies assigned to the individual cell concepts is only exemplary and not complete.

Oxides

A large number of cathode materials is suitable for the use in cells with oxide electrolyte (Section 2.6). Since the focus for applications is usually on high energy densities, the dominance of high-nickel NMC in oxide-based cell concepts is clearly recognizable. LFP would be suitable for the usage as a low-cost active material. Furthermore, high voltage cathodes (>4.3 V vs. Li/Li$^+$) are the subject of current research projects. Due to the possible use of Li metal anodes without a further protective layer to the SE separator, most oxide-based concepts include a Li metal anode, while only very few research projects work with silicon anodes.

Most of the variation between the oxide cell concepts takes place in the different composition of electrolytes. Since the conductivity of oxides is too low for an efficient use as catholytes, hybrid concepts are usually used. Gel and liquid electrolytes in combination with a solid component can be used as catholytes.

The expert survey underlines this assessment: Cell systems with a solid catholyte were classified as less promising and ranked at the bottom, regardless of the active materials (e.g. Li|Oxide|Oxide/LCO or Li|Oxide|Oxide/LFP). Cell systems with a gel electrolyte are further ahead in the ranking. The concept with Li metal anode (Li|Oxide|Gel/NMC) is ranked as one of the most promising SSB concepts, while the cell concept with a SiO$_x$ anode (SiO$_x$/Oxide|Oxide|Oxide/Gel/NMC) is still considered as interesting.

According to the assessment, probably an oxide concept with a Li metal anode and an NMC cathode in combination with a gel-containing catholyte will come to the market first (LiOx-concept). It is discussed in the next Section (4.3) as one of the most promising cell concepts. The gel electrolyte might be substituted by an inorganic solid electrolyte with a good ionic conductivity in the future.

Sulfides

As shown in Section 2.4.2, sulfides exhibit the highest ionic conductivity amongst the solid electrolytes. This high ionic conductivity makes them suitable for use as both SE separator and catholyte/anolyte. The list of cell concepts indicates the variety of different anodes and cathodes, which are combined with sulfides for research and development purposes.

NMC cathodes tend to be used in in high energy applications such as automotive. They must be coated for electrochemical stability, as shown in Section 2.6, and are then compatible with sulfides. Cell concepts for high C-rates are mostly equipped with LCO as cathode material (LTO/Sulfide|Sulfide|Sulfide/LCO). Sulfur as CAM (Li|Sulfide|Sulfide/S) has only been investigated in a few research projects and is unlikely to play a role for the first generations of SSB.

Both Li metal (Li|Sulfide|Sulfide/NMC) and silicon (Si/Sulfide|-Sulfide|Sulfide/NMC) are used as anode materials. As mentioned above, Li metal provides higher energy densities, but sulfides are not electrochemically compatible with lithium and protective layers are needed. This challenge may delay the market entry of such cell systems. For porous electrodes like silicon/carbon, the anode active material has to be mixed with the anolyte for a good ionic contact.

The survey clearly shows the high potential of solid-state batteries with sulfide electrolytes. Two cell concepts with sulfide electrolytes are top-ranked. Both concepts are explained in more detail in Sections 4.4 (LiSu-concept with Li metal anode) and 4.5 (SiSu-concept with Si anode) as the most promising concepts. Other approaches such as high-performance cells or alternative cathode materials were assessed by the experts as rather far from the market.

Table 12: Solid-state battery cell concepts that are considered in R&D and industry:

Anode		Separator	Cathode		Company/ R&D	Expert ranking (most promising cell concepts)
AAM	Anolyte		Catholyte	CAM		
Li metal	—	Oxide	Gel or Gel+Oxide	NMC	ProLogium, Quantum Scape ProLogium	↑
SiO / Gr.	Oxide	Oxide	90 % Oxide 10 % Gel	NMC	ProLogium	↗
Li metal	—	Oxide	Oxide	LCO	R&D	→
Li metal	—	Oxide	Oxide	LFP	R&D	→
Li metal	—	Sulfide	Sulfide	NMC	Solid Power, Samsung-R&D	↑
Silicon	Sulfide	Sulfide	Sulfide	NMC	Solid Power, R&D	↑
LTO	Sulfide	Sulfide	Sulfide	LCO	Toyota-R&D	↗
Li metal	—	Sulfide	Sulfide	S	R&D	→
Li metal	—	Polymer	Polymer	LFP	Blue Solutions – Bollore, Hydro Quebec	↑
Li metal	—	Polymer	Polymer	NMC	Ganfeng Lithium Group, WeLion New Energy Techno-logy, Hydro Quebec	↗
Li metal	—	Polymer	Ionic Liquid	LCO/NCA	Solid Energy	↗
Li metal	—	Polymer	Polymer	S	R&D	→

Polymers

Polymer-based SSB are the only cell types with solid electrolytes already on the market. For example, Blue Solutions offers cells with Li metal anodes and LFP cathodes (Li|Polymer|Polymer/LFP) for buses and stationary storage [180].

Due to the electrochemical compatibility of polymers with Li metal and the performance that can be achieved, Li metal anodes are the predominant active material choice for anodes. In addition, there are some approaches with silicon anodes (Si/Polymer|Polymer|Polymer/LFP), for which the market potential cannot be clearly predicted.

As the electrochemical compatibility on the cathode side is limited, LFP active material is primarily used today. In order to achieve higher energy densities, however, in the long run it is foreseeable that higher potential CAM, such as NMC (Li|Polymer|Polymer/NMC), will be used. Furthermore, experiments are being conducted with sulfur cathode materials (Li|Polymer|Polymer/S) as well as LCO (Li|Polymer|liquid electrolyte/LCO), which is being used in other approaches for higher C-rates.

The cell concept that is already on the market is the one experts found the most promising: The Li anode and LFP cathode cell can achieve a moderate to high energy density at a potentially competitive cost (LiPo-concept). This most promising concept is discussed in detail in Section 4.6. In the long term, a development towards higher energy densities by adopting higher potential cathodes, such as NMC or NCA, is expected. Alternatives with sulfur or LCO are rather unlikely, according to the experts.

4.3. Oxide Electrolyte SSB (LiOx-concept)

Concept

At present, cell concepts incorporate an oxide catholyte do not show sufficiently high ionic conductivity for practical use. A concept which seems to be more feasible and has reached the prototyping stadium is a hybrid concept with oxide separator and gel-containing catholyte. Due to the high mechanical stability against dendrites and the simultaneous electrochemical compatibility of individual oxide electrolyte materials, the use of Li metal in all oxide cell concepts is highly probable. As a cathode active material (CAM), various materials (LFP, NMC, LCO, NCA, etc.) can be used. The advantages of high nickel NMC or NCA cathodes in terms of energy density could lead to these chemistries being commercialized in the near future. In this section, we consider all ceramic electrolyte materials that are not sulfide electrolyte materials as part of the oxide electrolyte class.

Structure

Anode

In this concept, Li metal anodes can be used as a thin layer or with an *in-situ* preparation (Section 3.1.2). Regardless of the initial state, the anode of both types consists of a compact Li layer and thus provides an either flat or structured Li metal anode on a current collector (e.g. Cu-, Ni- or stainless steel foil or mesh). The in-situ approach requires a host structure for a homogeneous lithium deposition.

Cathode

Due to the chemical stability of oxides, all CAM discussed in this report can be used with oxide electrolytes. According to experts, the use of LFP as a cathode material in this concept will enable energy densities comparable to state-of-the-art liquid electrolyte LIB with NMC cathodes. When using NMC with a high nickel content, the energy densities increase accordingly. LCO is considered as too expensive for automotive applications. The use of sulfur as an active material has so far only been demonstrated on a laboratory scale; its commercialization is not expected until the next decade [183].

In the medium term it will not be possible to use solid oxide electrolytes as a catholyte for two reasons: their low ionic conductivity and the difficulties during processing. The first commercialized concepts may therefore either contain gel electrolytes or solid electrolyte components mixed with gel electrolytes. The CAM, coated onto an aluminum current collector, requires a sufficient porosity for the wetting with gel

electrolyte. The proportion of gel electrolyte in the cathode is approx. between 20–30 vol.% of the cathode.

Separator

Experts confirm the possibility of oxide solid electrolytes (oxide SE) with layer thicknesses below 30 μm (even 10μm are mentioned [169]). Currently, the most promising oxide electrolyte is the garnet-type (LLZO): Due to its mechanical stability and additionally its electrochemical stability against Li metal, the material can be used on the anode side without any protective layers. Additives in the material increase its flexibility and therefore make it less stiff. Ionic conductivities above 1 mS/cm at room temperature for the garnet-type are sufficient to enable the use as a SE separator. However, it is also possible to use NASICON-type oxides due to their advantages in ionic conductivity. In this case, a protective layer would have to be applied between the anode and the SE separator to protect the material from the Li metal anode (e.g. LLZO layer < 5 μm).

Cell Assembly

The limited flexibility of the oxide separator makes rolling up the material in a round cell almost impossible. The limited flexibility of sintered oxide layers limits the use of typical electrode assembly procedures (winding, Z-folding, stacking) to stacking techniques which do not require any sheet bending. Current prototype cells have fewer than five layers (with ceramic separators). In the next two years, this number might be increased to 10, and subsequently even more. The dimensions of the sheets installed in prototype cells so far have dimensions of 70 x 85 mm [137].

Cell production

In contrast to state-of-the-art LIB production, the process of stacking active materials and solid electrolytes during electrode manufacturing is not straight forward. This particularly concerns the handling of the interfaces between the layers. In addition, both the "*in-situ* Li anode approach" as well as the "Li thin film approach" require changes in the production on the anode side compared to currently used graphite anodes. Due to the development stage of oxide solid-state batteries, there is not yet an established production process.

Anode

The Li metal anode can be manufactured by different processing routes (Section 3.1.2). None of them have so far commercially established themselves. In case tailored current collectors or host structures are used, a process for the structuring

Figure 15: Structure and components of the LiOx-concept: Oxide SSB with Li metal anode.

Current collector

Li metal anode

Solid oxide electrolyte

Cathode: NMC + gel electrolyte
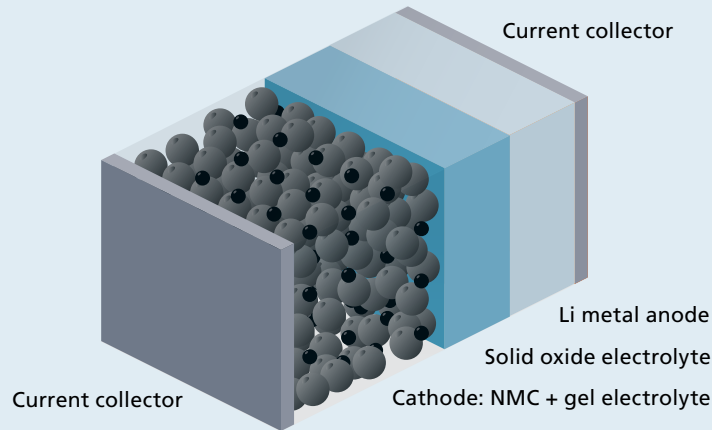
Current collector

or coating of current collectors needs to be introduced. Oxides in particular offer the possibility of applying the Li layer directly to the self-standing SE. This production method has no obvious advantages (in processing or in costs) and will probably not find its way to commercialization. In addition to process parameters such as the pressure applied when joining the parts or prior surface treatment of the foil or SE separator can also effect the cycle stability [131]. "Anode-less" approaches, in which lithium is plated *in-situ* on the current collector during formation, are very promising. Thereby, the anode production steps can potentially be omitted [133]. However, there are still many challenges regarding lithium plating (Section 3.1.2). A working *in-situ* anode preparation is claimed along with a ceramic separator for prototype cells [137].

Cathode

In the hybrid cell concept with an incorporated gel electrolyte, significantly different processing steps are required than in a cell concept consisting of pure solid electrolyte. A plausible process route is the coating of CAM on an aluminum current collector with a slurry manufacturing process, followed by an annealing process. Due to the expense of electrolyte filling after stacking (and subsequent degassing etc.), the gel electrolyte is likely to be layered on top of the CAM and pressed into the structure of the cathode material to achieve complete wetting.

Separator

In the near future, the oxide separator could be produced primarily by wet chemical processing routes (Section 3.1.3). The targeted layer thickness of 10 µm has so far not been realized. The production of layers with a thickness of 25 µm has been demonstrated on laboratory scale [27, 140, 151, 169]. After the

layer formation, however, a further sintering step has to be carried out. The process control can have a decisive influence on the later properties of the SE separator. After sintering, the material is brittle. The subsequent production steps have to be adapted to the material properties and a dry room with low residual moisture is needed to prevent the decrease in ionic conductivity due to the formation of Li_2CO_3 on the oxide surface [184].

When using a NASICON-type SE, an additional process step for the LLZO protection layer towards the anode has to be applied. This can be done dry-chemically in the future.

Cell Assembly

If an approach consists of a wet processing of the separator and a subsequent lamination of the cathode layer, SE separator (with associated cathode) and anode have to be stacked in a single layer stacking process. To reduce interface resistances between the components, the stacks have to be (hot-)pressed [131]. Electrolyte fillings and degassing steps are completely omitted and the formation and aging steps may be significantly shortened, thus saving costs. For cell concepts with Li-foil anodes, the formation may even be omitted completely.

Key performance indicators

Energy density

Li metal-based SSB can achieve higher energy densities compared to state-of-the-art LIB. Since oxide materials have a high density, the advantage is particularly evident in the volumetric energy density (up to 1000 Wh/l) and only slightly observable in the gravimetric energy density (320 Wh/kg). This leads

Table 13: Comparison of KPIs between LIB and the LiOx-concept, today and in future cells (values shown in italics are company announcements/goals):

KPI	Typical automotive LIB		Cell Concept 1:
	2021/22	**2030**	**Li metal | Oxide SE | NMC+Gel**
Energy density	230–300 Wh/kg	310–350 Wh/kg	Company information:
	600–750 Wh/l	750–950 Wh/l	*350–400 Wh/kg* [137, 182]
			1000 Wh/l [137]
			Own calculations:
			approx. 320 Wh/kg
			approx. 1000 Wh/l
Price	90–175 EUR/kWh	45–105 EUR/kWh	*65 EUR/kWh* [185]
Fast charging	High Energy	No forecast possible	High Energy:
	1–1.5 C [186]		*1–1.2 C* [182]
			Fast Charging:
			4 C [187]
Lifetime	800–1500 cycles	No forecast possible	*> 1000 cycles* [182]
Safety	Flammable,	No forecast possible	Nonflammable SE separator but flammable
	thermal runaway possible		gel-electrolyte and reactive Li metal anode

to increases of up to 30-40 % for volumetric energy density and around 5-25 % of gravimetric energy densities in comparison to state-of-the-art LIB, which have been on the market since 2021 (calculations and assumptions described in Section 4.7). Company announcements of gravimetric energy densities exceed our own calculations, while the published volumetric energy densities reproduce the calculated values well.

Price

Since no scale up of the SSB production has taken place yet, a future price comparison with LIB is difficult. Prices for materials are discussed in Section 3.3. For the cell concept in particular, the later commercialization of *in-situ* anodes could lead to cost savings. All in all, prices are expected to be higher than those of LIB. A price of 65 EUR/kWh was recently announced for a solid oxide battery cell [185]. However, since no further details of the cell concept are specified, this value should be treated with caution.

Fast charging

High charging rates can accelerate dendrite growth, which may also under some circumstances stress the oxide layers. Another limitation is the moderate ionic conductivity of oxides, which is lower than that of sulfides. Fast charging oxide SSB concepts have already realized charge rates of around 4 C for a one-layer prototype for 400 cycles (10-80 % state of charge) [187]. 1 C has been realized in prototype cells with over 1000 cycles [188].

Lifetime

The high chemical stability of oxides means there are minimal side effects associated to the SE material and hence few chemical ageing effects. The volume change of active materials or other mechanical impacts on the cell may result in the fracture of the brittle SE layers. This could lead to increased contact resistances and hence reduced performance, and secondly to the opening of pathways for Li-dendrite growth. However, 800 cycles of a prototype cell with 4 layers and over 1000 cycles with a one-layer prototype cell have already been demonstrated (with 1C dis-/charging) [182].

Safety

Depending on the electrolyte class, the oxide separator can reduce a thermal runaway to a minimal reaction (perovskite-type) or even prevent it completely with external heating (garnet-type). This significantly increases safety [35]. Furthermore, combustible binders can be eliminated from the anodes. In theory batteries with *in-situ* anodes could be completely discharged and therefore no combustible Li metal is left on the anode side, which would make it safe even during dismantling. In practice, however, this has not yet been demonstrated. Remains of Li metal at the anode in a discharged cell is highly reactive. Compared to all-solid-state batteries (ASSB) the gel electrolyte is still flammable. In comparison to state-of-the-art LIB, advantages for the SSB in terms of safety are expected.

Further Aspects

The cell voltage of the LiOx-concept is about 3.8 V with the Li metal anode and an NMC cathode (assumed: NMC-811). Replacing the CAM with LCO could raise this voltage up to 3.9 3.95 V. High voltage cathodes such as LMNO increase the cell voltage to 4.6 V. At cell voltages above 4 V, the first component

to reach its electrochemical limit is the gel electrolyte. The materials used for the garnet-type solid-state electrolytes can be rated as non-critical in terms of availability; whereas germanium, which can be considered a rare element, may be used for NASICON-type batteries, depending on the chemical composition. The energy consumption for oxides, on the other hand, is high due to the high temperatures required during processing.

Open Challenges

Oxide cell concepts as described here are still being developed in prototype status. So far, all steps for the material production have been made on very small pilot production lines involving many manual steps. Therefore, a major challenge will be to upscale the required process steps. Additionally, it had not been possible so far to realize cells with more than 10 layers. Stacking and cell assembly is technically difficult and another big challenge for scale-up.

For the SE separator layer, there is currently no information on layer thicknesses for large-scale production. Furthermore, high-charging rates are difficult to handle with lithium metal anodes, because of facilitated dendrite formation and inhomogeneous deposition. The use of *in-situ* lithium metal anodes seems very promising. Since lithium is plated directly from the cathode onto the current collector, there is no excess lithium. However, this could become problematic if lithium losses occur as a result of side-reactions, such as SEI formation.

Concept Variations

Si anode
Besides the Li metal anode, there are other another possibility is to use a silicon graphite anode. Here, a disadvantage is a reduction of the theoretically available capacity. An advantage on the other hand is the possible use of established anode production methods as well as the avoidance to work with reactive Li metal. However, the implementation of this concept is questionable. The oxide separator cannot realize its full potential (compatibility with Li metal). Published manufacturer data today present a concept with Si anode that enables 440 - 485 Wh/l and lifetimes of over 1000 cycles. In addition, it should be fast-chargeable (up to 4 C) and can be operated at low temperatures down to -30 °C [181].

Hybrid concept with robust gel electrolyte
Another solution approach is the use of a robust gel composite with nanowires out of oxide materials. This should enable a production process similar to state-of-the-art LIB as well as the opportunity to use Li metal anodes [189]. Until now, only symmetric cells (without anode and cathode material) have been demonstrated in laboratory scale.

ASSB with oxide catholyte:
Obviously, the further development of the hybrid cell concept could be an ASSB concept with pure oxide catholyte. This causes particular challenges for the processing of the composite cathode material made of oxide material and CAM.

To produce composite electrolytes with a solid catholyte, a co-sintering or annealing step with the active material and the electrolyte is necessary. Temperatures above 600 °C are needed. A coating of the active material particles can be applied to protect against thermal stress of the material. Later on, aerosol decompositions of powder direct on the cathode layer are discussed. This allows for the individual layers to become thinner and also to avoid high temperature sintering. Then, only a tempering of around 600 °C is required to produce the connection between cathode and SE separator (no sintering of the separator itself necessary) [131].

Due to the lack of gel electrolyte, this concept has considerable advantages over hybrid oxide concepts, especially in terms of safety. The current disadvantages, however, are the highe

ASSB with sulfide catholyte
The concept should combine the advantages of the oxide material as a SE separator and the good ionic conductivity of the sulfide material. In the long term, this could lead to a high performance cell concept. Without any further effort, Li metal anodes as well as NMC can be installed as cathode material. This would increase the energy density while at the same time enabling high charge and discharge rates because of good ionic conductivity in the cathode. A concept with both electrolyte systems combines the challenges of both material systems. In addition, there is no information on the contact surface resistance between oxide and sulfide. The cycle lifetime of such cell concepts is also difficult to predict.

It is therefore not possible to clearly foresee whether the cell concept can deliver its hoped-for performance. However, if it does and solid-state batteries become an increasing

Summary and conclusions

The oxide cell concept with a Li metal anode and an NMC/NCA cathode with gel electrolyte is a precursor of an all-solid-state battery approach. Due to the stability of the oxide compared to lithium, it represents a promising concept. However, as the production of oxide materials is challenging, the commercialization and the associated scale-up is problematic. The anode half-cell, consisting of an oxide separator and a Li metal anode, is technically very promising. It is questionable whether an oxide catholyte will really prevail on the cathod.

4.4. Sulfide Electrolyte SSB with Li anode (LiSu-concept)

Concept

Two promising solid-state battery (SSB) concepts based on sulfide solid electrolyte (sulfide SE) are being developed, which could come to market in medium term. Both contain a layered transition metal oxide-like NMC or NCA as cathode active material (CAM). The main distinction of the concepts is their anode active material. The first concept contains a lithium metal anode, the second concept contains a silicon-based anode, such as for example a carbon-silicon composite. Further, hybrid concepts with, for example, an oxide or polymer electrolyte are investigated, as well as concepts with conversion type cathodes, like sulfur or iron sulfide (FeS_2). However, especially the latter is still far from market introduction. Therefore, this roadmap report focuses on the first named concepts, starting with the cell based on a lithium metal anode.

Structure

Anode

This cell concept comprises a Li metal anode on a current collector, either flat or structured, e.g. Cu-, Ni- or stainless steel foil or –mesh. Li metal anode concepts are discussed in Section 3.1.2. Most common anodes are thin lithium foils (<30 µm), which are applied directly on the current collector. In order to stabilize the sulfide electrolyte against the Li metal, a lithium-ion conducting coating (e.g. LLZO) can be applied between the lithium and the solid electrolyte to prevent direct contact. This coating may be a micro-layer of densified (oxide-) particles. The coating layer has to be stable and thin at the same time, to maximize cycling stability and energy density.

Cathode

The CAM in this cell concept is a high-energy layered oxide, such as nickel-rich NMC (e.g. NMC-811) or NCA, as in current state-of-the-art LIB. The cathode consists of a mix of CAM, a sulfide catholyte, as well as organic binders and conductive agents. Due to reasons of chemical stability, the CAM-particles may be coated by a micro- or nano-layer of an ionic conductive material, e.g. $LiNbO_3$. Depending on the manufacturing process, the cathode will have a finite porosity, i.e. an open volume which is not filled with any of the materials mentioned. The catholyte needs to ensure high lithium-ion conductivity in the whole cathode, therefore high ionic conductivity values are required, especially for applications requiring fast charging. In addition, sufficient contact between active material and SE particles is required. Respective cathodes may hence consist of 20 to 30 vol.% SE, comparable to the pore volume of cathodes in liquid electrolyte-based LIB filled with electrolyte. Promising catholyte materials are

crystalline materials of the argyrodite or LGPS sub-class, as well as highly conductive LPS glass-ceramics, such as $Li_7P_3S_{11}$. The cathode material mix is coated onto an aluminum current collector.

Separator

The separator is a thin sulfide SE layer of few µm to several ten µm. The layer may consist of densified micro- or nanoparticles or even a dense layer of molten/quenched SE. Depending on the structure of the anode, the interface between (coated) Li anode and SE separator may be 2D or 3D.

Today, the argyrodite sub-class as well as sulfide glasses of the LPS sub-class are most promising as commercial SE separator materials. Argyrodites, especially chlorine argyrodites such as Li_6PS_5Cl show high ionic conductivities and higher electrochemical stability than other conducting crystalline materials, like the LGPS sub-class. LPS-glasses show lower ionic conductivities, but if the SE separator is sufficiently thin other criteria, such as the interface stability prevail. The sulfide SE classes are discussed in Section 2.4.2 in more detail.

Cell Assembly

The mechanical stability of the electrode stack, e.g. for handling, is provided by the current collector foils. The cathode- as well as the separating SE-layer cannot be considered to have "free standing" stability. The safety properties with respect to internal short-circuits (e.g. due to dendrites) are introduced by the separating sulfide SE-layer and optionally by additional non-sulfide coatings as mentioned above.

Prototype pouch-cells with an electrode stack size of less than ten stacks have been demonstrated. Automotive grade cells with a capacity of more than 50 Ah are not available yet. The winding of the solid electrolyte is problematic, which is why sulfide-based ASSB in cylindrical form are rather unrealistic. Instead, the cells are processed as pouch or prismatic cells.

Cell production

Anode

There is no well-established industrial process for the production of Li anodes, although manufacturing concepts for the different Li anode-concepts exist (see Section 3.1.2). A controlled production environment with an inert atmosphere may be necessary. Handling lithium metal is costly and requires special safety conditions. In case tailored current collectors or host structures are used, a process for the structuring or coating of current collectors needs to be introduced. Protective coatings

Figure 16: Structure and components of the LiSu-concept: Sulfide SSB with Li metal anode.

Current collector

Li metal anode

Solid sulfide electrolyte

Cathode: NMC + solid sulfide electrolyte

Current collector
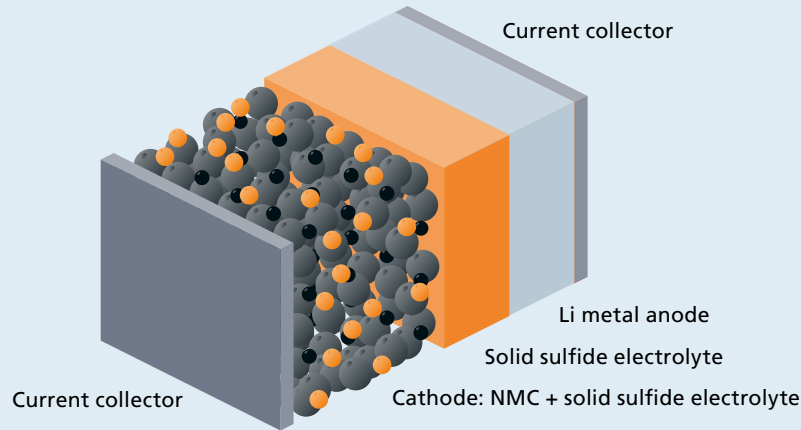
(e.g. LLZO) can be applied via wet processing or gas-phase processes, such as sputtering.

Cathode

The cathode will most likely be produced, as in state-of-the-art LIB, in a wet chemical process. The main difference is the additional sulfide catholyte during slurry mixing as well as the production in a dry or inert atmosphere [131]. Moreover, different solvents and binders have to be applied, since sulfides react with polar solvents, such as N-Methyl-2-pyrrolidone (NMP) used in LIB production [128]. In contrast to oxide electrolytes, no sintering process is necessary because the plasticity of sulfides is sufficient to reach high densities during high-pressure calendering. In the long term, processes based on green solvents or dry roll-to-roll processes are targeted, to exclude expensive and toxic solvents.

Separator

The sulfide separator can be coated as a layer onto the cathode. Initially, wet processing methods will probably dominate, since they are easily transferable from the current LIB technology. In the long term, as for the cathode, dry or green solvent-based processes are favored. Analog to the composite cathode production the sulfide separator needs to be processed in a dry room.

Cell Assembly

In cell assembly, compared to current LIB production, SSB production requires an additional stack-pressing step to improve the interface contacts between the active materials and the SE. Electrolyte filling and degassing steps are completely omitted and the formation and aging steps may be significantly

shortened, which is a cost saver. For cell concepts with Li-foil anodes, the formation may even be omitted completely.

Key performance indicators

Energy density

The LiSu-concept enables slightly higher energy densities than current LIB. Based on own calculations, a cell concept with a 25 µm lithium foil and the argyrodite electrolyte Li_6PS_5Cl with an oxide protective layer can achieve a specific energy density of approx. 340 Wh/kg and a volumetric energy density of approx. 770 Wh/l (Section 4.7). These values are approx. 5-25 % higher than for a state-of-the-art LIB with a graphite anode in 2021. The main challenge will be to combine the high capacities with a long lifetime, which has not been achieved so far. Manufacturer information of gravimetric energy densities reproduce the self-calculated values well. For volumetric energy densities, the manufacturer's specifications are lower than the calculated values.

Price

The LIB price has already reached prices as low as 90 EUR/kWh and is expected to fall to 45 EUR/kWh by 2030. SSB can profit to a certain degree from the price reductions for LIB, since some components and production steps are very similar, especially for the cathode. However, initially SSB will enter the market with decisively higher prices, originating from the implementation of new, initially more expensive materials with smaller or newly established value chains and different production methods. The material costs relevant for pricing are discussed in Section 3.3.

Table 14: Comparison of KPIs between LIB and the LiSu-concept, today and in future cells (values shown in italics are company announcements/goals):

KPI	Typical automotive LIB		Cell Concept 2: Li metal | Sulfide SE | NMC+SE
	2021/22	**2030**	
Energy density	230–300 Wh/kg 600–750 Wh/l	310–350 Wh/kg 750–950 Wh/l	Company/R&D information: *320 Wh/kg* [149] *550 Wh/l* (Li-foil anode) [149] 942 Wh/l (in-situ anode) [136] Calculations (Section 4.7): approx. 340 Wh/kg approx. 770 Wh/l (Li-foil anode)
Price	90–175 EUR/kWh	45–105 EUR/kWh	Initially higher price compared to state-of-the-art LIB likely
Fast charging	High Energy 1–1.5 C [186]	No forecast possible	High Energy: *0.1 C* [149] Fast Charging: Fast charging (> 1 C) today not possible, goal 2 C [149]
Lifetime	800–1500 cycles	No forecast possible	No forecast possible
Safety	Flammable, thermal runaway possible	No forecast possible	No flammable liquid electrolyte but H_2S reaction in moisture environment and reactive Li metal anode

Fast charging

Especially sulfide solid electrolytes are very promising for fast charging applications, because of their high ionic conductivity. However, in combination with lithium metal anodes the realization of high charging rates is problematic and the charging rates of the LiSu-concept are well below 1 C, today. With increasing charging rates, inhomogeneous lithium deposition is increasing, which eases dendrite formation. Dendrites are formed in SSB at even lower critical current densities (approx. 0.3 mA/cm) compared to liquid electrolyte LIB. The critical current density is still far from the fast-charge goal of approx. 10 mA/cm [188]. A possible solution could be the heating of the battery during charging, which on the one hand increases the ionic conductivity of the solid electrolyte. On the other hand, it leads to higher lithium diffusion, which enables a more homogeneous distribution.

Lifetime

SSB may exhibit longer calendar lifetimes. However, challenges and failure mechanisms still exist, especially regarding the lithium metal anode. Decomposition reactions and dendrite formation drastically shorten the lifetime in most approaches. Moreover, volume as well as mechanical changes in the cell and the contact loss between solid electrolyte and active materials reduce the cycle lifetime of the battery. Coatings and further material development can increase the battery's lifetime and make it competitive to LIB, but there are still a lot of R&D necessary.

Safety

Due to the solid electrolyte, SSB may exhibit higher safety, since, compared to liquid electrolytes, most SE are inflammable. They generally comprise fewer volatile compounds, engage in fewer side reactions and are stable at high temperatures. On the other hand, decomposition reactions and dendrite formation portray a safety risk. Even though the SE is thermally stable, at elevated temperatures the cathode active material can release oxygen, which can lead to exothermic reactions with further heat generation. Furthermore, sulfide SE produce toxic H_2S in contact with moisture. Another safety hazard is the Li metal anode due to the reactive lithium.

Further Aspects

The cell voltage of the LiSu-concept is about 3.8V with the Li metal anode and an NMC cathode (assumed: NMC-811). This voltage could be raised up to 3.9-3.95 V by replacing the CAM with LCO. Because of the limited electrochemical window, high voltage cathodes such as LMNO are only possible with further improvements in material compatibility.

The materials criticality of sulfides can be rated as non-critical in terms of availability. Sulfide SE containing expensive materials such as germanium will probably not be used in larger scales, at least not for price-sensitive markets such as the automotive sector.

Open Challenges

In theory, this cell concept exhibits many advantages and especially in terms of energy density it could exceed current LIB. However, there are reasons why it has not yet been commercialized. Even though in the last decade major progress has been achieved, there are still many open challenges.

The biggest bottleneck towards commercialization is the lithium metal anode and its compatibility with the sulfide electrolyte. The SE is being reduced at the lithium anode. The formed SEI is electronically insulating and results in a high interfacial resistance, which limits the battery lifetime and high-performance applications, but enables the cell to operate. Reducing the interface resistance and preventing the growth of lithium dendrites is crucial to compete with current LIB. To stabilize the interface, the most cost-effective and promising approaches are coatings, e.g. with LLZO, and the doping of the SE surface. The production of defect-free SE layers is of very high importance as well, to minimize interface resistance and nucleation sites for dendrite propagation. The use of *in-situ* lithium metal anodes seems very promising. Since lithium is plated directly from the cathode onto the current collector, Li metal can be avoided during processing. The homogeneous plating of lithium on the current collector is very challenging and often tailored current collectors or host structures are used to enable homogeneous Li-layers [136]. Those manufacturing processes have, however, not been established yet. Generally, in-situ lithium anodes still face many challenges and the lamination of lithium foils shows higher market maturity, but plating approaches are theoretically superior and a long-term target.

Sulfides are electrochemically unstable in the presence of high voltage cathode materials such as NMC. This creates a need for cathode coatings (e.g. LiNbO3) to stabilize the cathode-SE interface, which can be further complemented by doping of the SE surface, e.g. by exchanging sulfur with oxygen [66].

As it is challenging to find one electrolyte that shows good properties as a SE separator, as well as catholyte, combining different materials seems to be a promising approach. An example is a sulfide glass of the LPS sub-class as a separator and a member of the LGPS sub-class as catholyte. However, this approach leads to new challenges such as interface resistances between the two electrolyte materials as well as higher processing costs.

Furthermore, the conditions during cell operation have still not been defined, yet. Nowadays, most concepts need external pressure and sometimes even elevated temperatures to achieve high reversibility at the lithium metal anode and to compensate the volume changes of the electrodes [136].

Finally, a big challenge will be the scale-up to mass production. The value chains of the precursor materials required to produce the sulfide electrolyte, still need to be established (especially for Li_2S), as well as low-cost and high-scale production methods, which take the moisture instability of the sulfide electrolyte into account.

Concept Variations

Another cell concept containing Li metal and a sulfide SE applies a lithium-free conversion cathode, such as sulfur or iron sulfide (Fe_2S). Sulfur is a promising CAM, based on its very high theoretical capacity (1672 mAh/g). In combination with Li metal theoretical energy densities of approx. 2650 Wh/kg or approx. 2900 Wh/l are reached on the material level [4]. Moreover, sulfur is an abundant, cheap, non-toxic nonmetal, which has a clear advantage compared to current layered-oxide CAM and makes sulfur-based CAM the most promising next-generation cathode material [190]. However, there are still many fundamental challenges to be solved to implement sulfur-based cathodes, which currently lead to comparatively low practical energy densities [4]. Sulfide SE can solve the problem of side-reactions with common liquid electrolytes and the sulfur cathode. Therefore, using sulfide SE in combination with Li metal and a conversion cathode is a promising future cell-concept, even though there are still many open challenges, such as ensuring sufficient charge transport in the cathode and problems concerning the lithium anode [191].

Conclusion

The LiSu-concept, combining a lithium metal anode with a sulfide SE and high energy, layered oxide cathode, represents an all-solid-state battery concept. Liquid electrolyte is completely omitted, even as a catholyte, taking advantage of the high ionic conductivity of sulfide electrolytes. In recent years, research and industry have made considerable progress, but there are still open challenges, especially regarding the lithium metal anode and the electrochemical stability of the sulfide SE. Price, lifetime and fast charging capability are, today, the KPI with the biggest drawback to state-of-the-art LIB. The underlying challenges have to be solved urgently particularly for automotive applications. However, the potential of the cell concept is high and strongly pushed by the battery and automotive industry.

4.5. Sulfide Electrolyte SSB with Si anode (SiSu-concept)

Concept

Another promising sulfide-based SSB cell concept is being developed that contains a silicon anode active material instead of Li metal (compared to the LiSu-concept in Section 4.4). The silicon-based anode is combined with a layered transition metal oxide such as NMC or NCA as cathode active material (CAM). Although the theoretical cell capacity is lower in comparison with Li anodes, silicon anodes can realize higher charging rates during charging and discharging.

Structure

Anode

This cell concept comprises a silicon/carbon composite anode or a silicon-only anode on a Cu-current collector. Silicon-based anode active material is discussed in Section 2.2. The silicon/carbon composite concept is closer to industrial realization, while recent publications also show promising results for silicon only anodes [192, 193]. Depending on the extent of capacity utilization, the silicon particles may experience a volume expansion of 300 % or more during lithiation. For 3D composite anodes, the electrode structure hence needs to exhibit a high degree of flexibility, e.g. by the use of highly flexible binders or must have a high porosity accommodating the Si volume change, e.g. by utilization of a porous carbon structure. In the case of silicon-only anodes, the electrode might consist of a structured 2D/3D anode, e.g. by utilization of columnar silicon which features an open volume that can accommodate the Si volume change.

Depending on the concept, the silicon electrolyte interface may be realized by particle-particle contact between active material and anolyte in a composite electrode or by direct contact of the structured silicon with the separating solid-electrolyte layer. In contrast to liquid electrolytes, the anolyte does not permeate the whole anode, which limits the contact area. For the composition concept, a volume fraction of 20 to 30 vol.% anolyte in the anode can be expected.

Cathode

The CAM in this cell concept is a high energy layered oxide, such as high nickel NMC (e.g. NMC-811) or NCA, as in current state-of-the-art LIB (Section 2.3). The cathode consists of a mix of CAM, a sulfide catholyte, as well as organic binders and conductive agents. Due to reasons of chemical stability, the CAM-particles may be coated by a micro- or nano-layer of an ionic conductive material, e.g. $LiNbO_3$ particles. Depending on the manufacturing process, the cathode will have a finite porosity, i.e. an open volume that is not filled with any of the materials mentioned. The catholyte needs to ensure high lithium-ion conductivity in the whole cathode, therefore high ionic conductivity values are required, especially for applications requiring fast charging. In addition, sufficient contact between active material and SE particles is required. Respective cathodes may hence consist of 20 to 30 vol.% SE, comparable to the pore volume of cathodes in liquid electrolyte-based LIB filled with electrolyte. Promising catholyte materials are crystalline materials of the argyrodite or LGPS sub-class, as well as highly conductive LPS glass-ceramics, such as $Li_7P_3S_{11}$. The cathode material mix is coated onto an aluminum current collector.
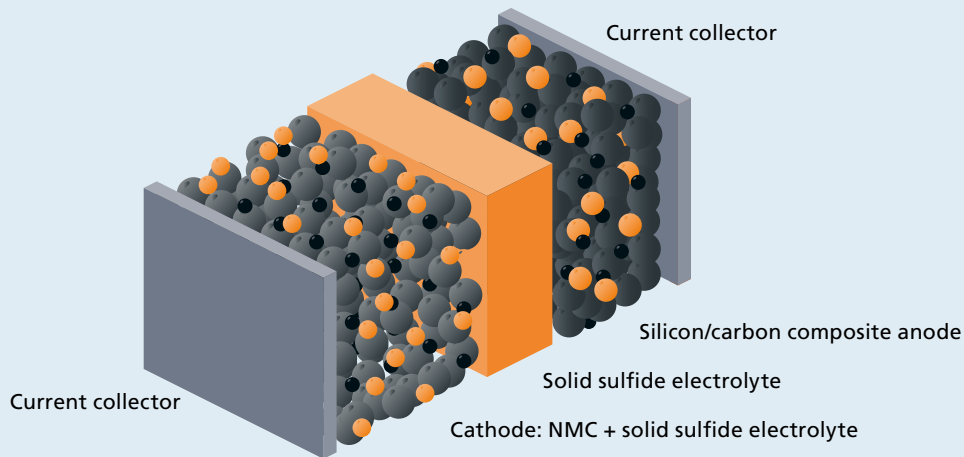
Separator

The separator is a thin sulfide SE layer of a few μm to several ten μm. The layer may consist of densified micro- or nanoparticles or even a dense layer of molten/quenched SE. Depending on the structure of the anode, the interface between (coated) Li anode and SE separator may be 2D or 3D.

Today, the argyrodite sub-class as well as sulfide glasses of the LPS sub-class are most promising as commercial SE separator materials. Argyrodites, especially chlorine argyrodites such as Li_6PS_5Cl show high ionic conductivities and higher electrochemical stability than other conducting crystalline materials, like the LGPS sub-class. LPS-glasses show lower ionic conductivities, but if the SE separator is sufficiently thin other criteria, such as the interface stability prevail. The sulfide SE classes are discussed in Section 2.4.2 in more detail.

Cell Assembly

The mechanical stability of the electrode stack, e.g. for handling, is provided by the current collector foils. The cathode-, anode- as well as the separating SE-layer cannot be considered to have "free standing" stability. The safety properties with respect to internal short-circuits (e.g. due to dendrites) are introduced by the separating sulfide SE-layer and optionally by additional non-sulfide coatings as mentioned above. The microscopic volume change of electrode components during cycling might be very large in this cell concept. Whether or not this translates into a macroscopic volume change on the cell level depends on the density and porosity of the silicon anode, i.e. the capability of the anode structure to accommodate the volume change of silicon (particles). The winding of the solid electrolyte is problematic, which is why sulfide-based ASSB in cylindrical form are rather unrealistic. Instead, the cells are processed as pouch or prismatic cells.

Figure 17: Structure and components of the SiSu-concept: Sulfide SSB with silicon anode.

Current collector

Silicon/carbon composite anode

Solid sulfide electrolyte

Cathode: NMC + solid sulfide electrolyte

Current collector

Cell production

Anode

Composite silicon anodes can be manufactured similar to the electrodes in current LIB, for which a wet chemical process is used [194]. However, instead of a water-based process, organic, nonpolar solvents have to be used, owing to the moisture instability of sulfide solid electrolytes [193, 195]. Hence, expensive solvent recovery will be necessary. Pure silicon anodes, could be produced with wet processes based on polar solvents such as water or NMP [193]. Special electrode concepts such as columnar silicon anodes are currently manufactured by a sputtering process. On the one hand, this process prevents the use of solvents. On the other hand, the deposition speed and thus the throughput of this process is currently not competitive for the required layer thickness of the Si anode.

Cathode

The cathode will most likely be produced, as in state-of-the-art LIB, in a wet chemical process. The main difference is the additional sulfide catholyte during slurry mixing as well as the production under dry or inert atmosphere [131]. Moreover, different solvents and binders have to be applied, since sulfides react with polar solvents, such as N-Methyl-2-pyrrolidone (NMP) used in LIB production [128]. In contrast to oxide electrolytes, no sintering process is necessary because the plasticity of sulfides is sufficient to reach high densities during high-pressure calendaring. In the long term, processes based on green solvents or dry roll-to-roll processes are targeted, to exclude expensive and toxic solvents.

Separator

The sulfide separator can be coated as a layer onto the cathode. Initially, wet processing methods will probably dominate, since they are easily transferable from the current LIB technology. In the long term, as for the cathode, dry or green solvent-based processes are favored. Analog to the composite cathode production the sulfide separator needs to be processed in a dry room.

Cell Assembly

In cell assembly, compared to current LIB production, SSB production requires an additional stack-pressing step to improve the interface contacts between the active materials and the SE. Electrolyte filling and degassing steps are completely omitted and the formation and aging steps may be significantly shortened, which is a cost saver.

Key performance indicators

Energy density

According to our own calculation, a cell concept based on a porous silicon/carbon composite anode with a thickness of 42 μm and the argyrodite electrolyte Li_6PS_5Cl can achieve a specific energy density of approx. 270 Wh/kg and a volumetric energy density of approx. 650 Wh/l (Section 4.7). These values are competitive with actual state-of-the-art lithium-ion batteries. However, it is not able to reach the values of the LiSu-concept, which contains a lithium metal anode. Manufacturer information of gravimetric and volumetric energy densities are larger than the self-calculated values.

Table 15: Comparison of KPIs between LIB and the SiSu-concept, today and in future cells (values shown in italics are company announcements/goals):

KPI	Typical automotive LIB		Cell Concept 3: Si-based anode | Sulfide SE | NMC+SE
	2021/22	**2030**	
Energy density	230–300 Wh/kg	310–350 Wh/kg	Company information:
	600–750 Wh/l	750–950 Wh/l	*320 Wh/kg* [149]
			740 Wh/l [149]
			Calculations (Section 4.7):
			approx. 270 Wh/kg
			approx. 650 Wh/l
Price	90–175 EUR/kWh	45–105 EUR/kWh	Initially higher price compared to state-of-the-art LIB likely
Fast charging	1–1.5 C [186]	No forecast possible	*2 C* [149]
Lifetime	800–1500 cycles	No forecast possible	No forecast possible
Safety	Flammable, thermal runaway possible	No forecast possible	No flammable liquid electrolyte but H_2S reaction in moisture environment

Price

The LIB price has already reached prices as low as 90 EUR/kWh and is expected to fall to 45 EUR/kWh by 2030. SSB can profit to a certain degree from the price reductions for LIB, since some components and production steps are very similar, which could be advantageous towards market introduction. This aspect is particularly the case for this cell concept, since silicon carbon composites and NMC cathodes are also used in current LIB. This is a benefit compared to the LiSu-concept with a not well-established Li metal anode processing. However, initially SSB will enter the market with decisively higher prices, originating from the implementation of new, initially more expensive materials with smaller or newly established value chains and different production methods. The material costs relevant for pricing are discussed in Section 3.3.

Fast charging

Especially sulfide solid electrolytes are very promising for fast charging applications, because of their high ionic conductivity. Silicon currently is less problematic compared to lithium metal anodes regarding fast charging, especially dendrite formation at high charging rates is reduced (but not fully solved) compared to the LiSu-concept. Based on company cell tests, today, charging rates of 2 C are achieved for this cell concept with composite anodes containing 50 % silicon [196]. Nevertheless, there are still challenges regarding fast charging, especially connected with the 3D volume changes in composite anodes, which are even more critical than the 1D volume changes of lithium metal. To enable cell operation despite the volume changes, in most approaches high pressure has to be applied to ensure sufficient interface contact [192, 193].

Lifetime

Sulfide solid electrolytes show a higher electrochemical stability towards silicon compared to current organic electrolytes. Through the use of sulfides, a stable SEI can be formed and hence continuous loss of active material during cycling can be avoided. However, the volume changes of silicon, potentially leading to particle cracking or other mechanical defects in the anode or other battery components, have to be further optimized to ensure comparable lifetimes to current state-of-the-art batteries. Advanced concepts enabling 2D silicon/SE interfaces (e.g. columnar silicon or pure silicon anodes) can limit the volume change to one dimension. It still has to be evaluated, if they are suitable for commercial application and more R&D efforts will be necessary.

Safety

Due to the solid electrolyte, SSB may exhibit increased safety, since, compared to liquid electrolytes, most SE are inflammable. They comprise fewer volatile compounds, engage in fewer side reactions and are stable at high temperatures. The large volume changes of the Si anode during cycling can be a safety problem, when leading to fractions and unwanted side reactions in the cell. Furthermore, even though the SE is thermally stable, the cathode active material can release oxygen at elevated temperatures, which can result in exothermic reactions with further heat generation. Furthermore, sulfide SE produce toxic H_2S in contact with moisture.

Further Aspects

The cell voltage of the SiSu-concept is about 3.4 V with the silicon/carbon anode and an NMC cathode (assumed: NMC-811). This voltage could be raised up to 3.5–3.55 V by replacing the CAM with LCO. Because of the limited electrochemical window, high voltage cathodes such as LMNO can only be implemented, if further improvements in material compatibility are made.

The materials criticality of sulfides can be rated as non-critical in terms of availability. Silicon as an anode material can be classified as absolutely uncritical due to the very large raw material deposits. Sulfide SE containing expensive materials such as germanium will probably not be used on larger scales, at least not for markets as price-sensitive as the automotive sector.

Open Challenges

While the solid electrolyte can solve some of the issues of the silicon anode, which are present with liquid electrolytes, the cell concept with a solid sulfide electrolyte still faces many challenges.

The biggest bottleneck is the large volume changes of silicon. Especially for composite electrodes with 3D interfaces, the 3D volume change puts stress on the whole cell and especially the anode/electrolyte interface, which reduces the lifetime of the battery. The challenges can be mitigated by developing silicon anodes with 2D interfaces to the solid electrolyte, which show an only one-dimensional breathing mechanism [192, 193]. However, these concepts are still in the early research phase. They need to be scaled-up and, so far, require high external pressures; therefore, they can only be considered as long-term solutions. Moreover, the solid electrolyte can decrease SEI formation and Li-loss, but not completely inhibit it, which means that excess lithium e.g. by prelithiating silicon needs to be added.

Just as in the LiSu-concept, the cathode/electrolyte interface is a challenge, due to the electrochemical instability of sulfides in the presence of high voltages. This creates a need of cathode coatings (e.g. LiNbO3) to stabilize the cathode-SE interface, which can be further complemented by doping the SE surface, e.g. by exchanging sulfur with oxygen [66].

When it comes to developing suitable electrolytes there has been tremendous progress in the last decade. However, there is still room for improvement, especially with regard to electrochemical stability. As it is challenging to find one electrolyte that shows good properties as a SE separator, as well as anolyte and catholyte, combining different materials seems to be a promising approach. An example is a sulfide glass of the LPS sub-class as a separator and a member of the LGPS sub-class as a catholyte. However, this approach leads to new challenges such as interface resistances between the two electrolyte materials as well as higher processing costs.

Finally, a big challenge will be the scale-up to mass production. The value chains of the precursor materials, required to produce the sulfide electrolyte, still need to be established (especially for Li_2S), as well as low-cost and high-scale production methods, which take the moisture instability of the sulfide electrolyte into account. Nevertheless, the silicon-based cell concept seems closer to market than the LiSu-concept based on a Li metal anode, since production methods and fast charging capability are closer to market maturity.

Conclusion

The SiSu-concept combining a silicon-based anode with sulfide SE and a high energy, layered oxide cathode active material represents a promising cell concept for high energy density applications. The biggest challenge is the high volume change of the silicon during de-/lithiation, which especially limits the lifetime of the battery. Next to the lifetime, the price will be a critical KPI to determine if the concept can compete with current LIB. Fast charging is less challenging than for Li metal-based cell concepts and could be an advantage in competition to other SSB concepts. Finally, the use of a silicon-based anode overcomes or eases many of the problems, which lithium metal anode-based concepts face. Consequently, this cell concept can be considered close to market maturity.

4.6. Polymer Electrolyte SSB (LiPo-concept)

Concept

The cell concept discussed in the following is based on an already proven technology: a lithium metal anode is paired with one or more solid polymer electrolytes and an LFP cathode (LiPo-concept). The resulting battery has a moderate energy density on the pack level and requires temperature management to maintain an operating temperature well above room temperature (commonly 50–80 °C). In fact, this is the only solid-state battery concept which can already be produced with annual production capacities of up to 1.5 GWh [180].

Structure

Anode

The first commercialized processing route to integrate Li metal anodes into the cell is the application of thin lithium foils (< 50 μm). The lithium metal can be used as anode material and current collector at the same time, for which it is connected with copper contacts. In this way the gravimetric energy density on the anode side is optimized by minimizing the amount of copper and therefore inactive weight. This approach of processing lithium foils for polymer SSB is the foundation for the annual production capacity of > 1 GWh [180]. An example of another approach is the anode free in-situ concept (Section 3.1.2).

Cathode

Due to the limited electrochemical stability window of most polymer SE, lithium iron phosphate (LFP) cathodes, with their relatively low potential, are a logical choice for this cell concept. Further advantages of LFP are the cycle stability and the low price. The comparatively low energy densities of LFP battery cells are the most important drawbacks of this cathode material. The polymer solid electrolyte can be mixed into the LFP to form the composite cathode and to achieve a good cathode-catholyte interface. An exemplary weight ratio of this composite is 65:20:15 (LFP/SE/carbon black) [90] . Cathodes with higher potential, such as NMC or NCA, are so far not compatible with this cell concept due to the limited electrochemical stability with the electrolyte (Section 2.6). Commonly, the current collector used on the cathode side is made of aluminum.

Separator

In the presented cell concept, a solid polymer electrolyte is used as a separator. As discussed in Section 2.4.3, the electrolyte can be made from different material combinations, always consisting of at least one polymer matrix and one type of lithium salt. The most used and investigated polymer SE are based on PEO and LiTFSI. The addition of nanofillers or the combination with another polymer matrix can optimize important properties such as ionic conductivity or mechanical stability, in particular with respect to the resistance to dendrite formation. Furthermore, novel polymer matrices, such as single-ion conducting electrolytes, are investigated. For the following discussion, a PEO-based solid electrolyte was assumed, if not specified otherwise.

Cell Assembly

The cell can be produced as a prismatic or pouch cell. The microscopic volume changes of the electrodes are mitigated by the polymer SE, which reduces the requirements for the casing. Even though the polymer SE is flexible, it remains unclear whether the development of a rolled-up cell is possible. The resistance against dendrite formation is introduced by the mechanical stability of the electrolyte, which is therefore a crucial property in this concept. When the lithium anode simultaneously functions as the current collector, no copper foil is used that introduces "free standing" stability. The minimum thickness of the lithium anode required to ensure the stability of the electrode stack remains unclear.

Cell Production

Anode

For the production of lithium foils, the extrusion process shows the highest maturity (see Section 3.1.2) and is already applied for polymer SSB. However, reducing the thickness of the lithium foil below 30 μm is still an open challenge, intensively researched, to further improve polymer SSB. Handling lithium metal requires a controlled production environment with an inert atmosphere and special safety conditions. The control of the SE-anode interface during the production is critical [82].

Cathode

The LFP cathode can be produced by different wet or dry processes. The LFP cathode active material (CAM) can be mixed with the solid polymer electrolyte, carbon black and a solvent into a slurry, which is then coated on the aluminum current collector and dried [90]. Alternatively, the cathode can be produced by an extrusion process with little or no solvent [197]. Another approach is the mixing of the components into a powder and hot-pressing it onto the current collector. Finally, the cathode is calendared to increase its compactness to achieve higher energy density.

Figure 18: Structure and components of the LiPo-concept: Polymer SSB with Li metal anode.

Current collector

Li metal anode

Solid polymer electrolyte

Cathode: LFP + solid polymer electrolyte

Current collector
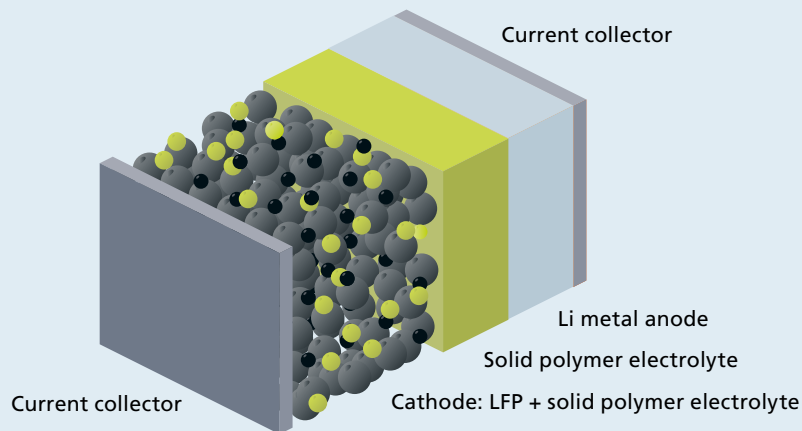
Separator

The manufacturing method of the polymer SE depends on its composition. To achieve high productivities, polymer films can be produced by extrusion, however, with limitations in respect to their thickness (tens of microns). Alternatively wet-chemical processing routes can be used. The combination of different polymers and the integration of fillers can be achieved for example by dry blending the respective components [82].

Cell Assembly

The production of solid polymer batteries could be performed with similar processes as the manufacturing of conventional liquid electrolyte LIB. Some production steps, however, can be shortened or removed, like the formation and the electrolyte filling. The battery cell production can be performed solvent-free and based on roll-to-roll processes [180], which allows for a high productivity and cost-effective large-scale manufacturing. To form the cell, the electrodes and the SE separator are manufactured and laminated together.

Key performance indicators

Energy density

The energy density of a PEO-based Li|Polymer|Polymer/LFP cell in 2021 was around 255 Wh/kg and 380 Wh/l [144], with room for improvements through the use of novel polymer SE [90, 200]. This is competitive to conventional liquid electrolyte cells with high voltage NMC cathodes and moderate energy densities, while outperforming liquid electrolyte LFP cells significantly. According to our own calculations, theoretical energy densities of 300 Wh/kg and 540 Wh/l are feasible for this cell concept. However, the energy density of the

polymer SSB drops on the module and pack level, due to the required heating system. Currently a volumetric energy density of 230 Wh/l is achieved on the module level and expected to increase towards 250–300 Wh/l in the next few years. This is lower than the energy density of about 350 Wh/l of the module of conventional prismatic or pouch LIB.

Price

The production of the presented polymer battery cell can be performed based on dry extrusion processes. This eliminates the need for energy-intensive drying steps, offering cost saving potential compared to conventional battery production. For SSB in general, the electrolyte filling can be omitted. Furthermore, the formation step might be substantially shortened, which would further reduce the cost of production. Additional precautions have to be taken into account when processing lithium metal. PEO and other commonly used polymers can already be produced for a low price, while the cost for novel polymer electrolytes strongly depends on the materials in use and, therefore, cannot be estimated in general. The price of lithium is crucial for the LiPo-concept, as it can otherwise be produced based on low-cost materials (see Section 3.3). When taking these aspects into account it is not unlikely that the production costs of the cell-concept, when established and scaled up, can undercut the price for producing conventional batteries, which could fall below 90 EUR/kWh in the next decade.

Table 16: Comparison of KPIs between LIB and the LiPo-concept, today and in future cells (values shown in italics are company announcements/goals):

KPI	Typical automotive LIB		Cell Concept 4: Li metal | Polymer SE | LFP+SE
	2021/22	**2030**	
Energy density	230–300 Wh/kg	310–350 Wh/kg	Company information:
	600–750 Wh/l	750–950 Wh/l	*255 Wh/kg* [144]
			380 Wh/l [144]
			Calculations (Section 4.7):
			approx. 300 Wh/kg
			approx. 540 Wh/l
Price	90–175 EUR/kWh	45–105 EUR/kWh	Competitive prices in the long term possible.
Fast charging	High Energy	No forecast possible	High Energy:
	1–1.5 C [186]		*C/4* [180]
			Fast Charging:
			1 C [198]
Lifetime	800–1500 cycles	No forecast possible	*4000 cycles* [199]
Safety	Flammable, thermal runaway possible	No forecast possible	▪ Dendrite formation can be prevented by mechanically stable polymer separators. ▪ High flammability of Li metal is a risk factor. ▪ High thermal stability of SE.

Fast charging

The LiPo-concept is not built for fast-charging. The limited ionic conductivity and commonly low cationic transference number of polymer SE hinder high charging rates. Currently a charging rate of C/5 is established and a rate of C/4 might be achieved in the short term [180]. At rates above C/2 the lifetime drops rapidly. However, some prototypes achieved already charging rates of 1C and beyond for a small number of circles [90, 198] or at high temperatures [107], indicating further potential for improvement. Nevertheless, the presented cell concept cannot be considered as competitive in respect to fast-charging with liquid electrolyte LIB.

Lifetime

The formation of dendrites, which strongly depends on the dis-/charging rates of the battery, can limit the lifetime of the polymer battery. Claims for this concept reach up to 4,000 cycles, with a constant capacity, depending on the application of the battery [199]. The battery cell can also fail when the contact at the interfaces is damaged, which can occur due to the microscopic volume changes of the components under cycling. Due to the flexibility of the polymer electrolyte, achieving a good contact interface between electrode and electrolytes is feasible; even though liquid electrolytes have a natural advantage in this aspect. Furthermore, the volume expansion of the lithium metal under cycling is mitigated by the flexible electrolyte and accounted for in the design of the module. Chemical reactions between the solid electrolyte and the cathode can promote gas evolution at the interface, which reduces the contact area, and, therefore, has to be prevented.

Safety

The absence of liquids in the presented concept is beneficial in terms of cell safety, as there is no risk of leakage in contrast to conventional batteries. Furthermore, the thermal stability of the battery cell is considerably high and only limited by the melting point of lithium metal. However, the use of lithium metal comes in general with safety concerns due to its high flammability and the tendency to form dendrites under cycling. To prevent the latter from causing short circuits, the mechanical stability of the electrolyte is key. For the polymer SSB used in applications in the past years, no final assessment considering their safety compared to state-of-the-art LIB can be given.

Further Aspects

The cell voltage of the LiPo-concept is about 3.3 V. Variations of the concept could increase the voltage, e.g., to 3.8 V if the LFP cathode can be replaced by NMC. One of the main differences of the presented concept and liquid electrolyte LIB, is found in the temperature requirements. While conventional LIB require cooling of the cell to prevent a thermal runaway, this concept relies on constant heating of the cell for maintaining an optimal operating temperature of 50–80 °C to provide reasonable ionic conductivities. While the battery cooling of LIB is only required during the active usage (charging or discharging), the heating of the SSB-cell is required continuously to ensure

that no long warm-up phases are needed, before the battery can be used.

Depending on the processing techniques used, the amount of solvent required can be significantly reduced compared to the production of conventional liquid electrolyte LIB. Furthermore, since the cell can be manufactured with no critical materials except lithium, the environmental impact can be kept relatively low.

Open Challenges

To further improve the polymer SSB discussed herein and to pave the way for wide commercialization, several challenges still have to be addressed. The high operating temperature of the battery, as the main drawback of the concept, has to be improved by lowering it as close as possible to room temperature. In this way, the temperature management system does not have to work and consume energy continuously and EV with this battery do not have to be plugged-in when not used for a longer time period. Furthermore, the energy density at module level can be optimized in this way.

The electrolyte can be further improved to increase the ionic conductivity, which can improve the fast-charging ability and lower the operating temperature. The use of novel polymer electrolytes can optimize the cationic transference number (as discussed in Section 2.4.3), which would reduce internal resistances and improve the lithium plating, leading to a positive impact on the achievable charging rates and the cycling lifetime. To enable higher charging rates, the electrolyte's robustness against dendrite formation has to be ensured.

The striking advantage of this concept is to achieve many benefits commonly associated with solid-state electrolytes, while being able to maintain a low price. However, to prove the competitiveness of this concept compared to conventional LIB (low cost) on the one hand and inorganic SSB (promise for high energy densities) on the other, both KPI have to be improved in the long run. Therefore, a cost-effective production mechanism has to be established on a large scale.

The cost of the cell is strongly dependent on the prices for the electrode materials. Therefore, a good recyclability of the cell is highly desirable and especially the regaining of lithium metal and the lithium salts can be considered as the most important challenges in the presented cell concept. The cathode active material LFP is considered to have good recyclability, however, due to its low price, the economic value of its recycling is comparatively low.

Concept Variations

The herein presented concept can be varied by different approaches. The solid polymer electrolyte was not further specified in this section: different material combinations can have a strong impact on the properties of the lithium metal polymer battery. The most intriguing approach for moving beyond the herein presented concept is found in the replacement of the cathode. If the electrochemical stability of the electrolyte can be guaranteed for higher potential cathodes than LFP, such as NMC, NCA or $LiMnPO_4$, the energy density can be improved drastically. The adoption of $LiFe_{1-x}Mn_xPO_4$ (LFMP) could be aspired as an intermediate step in this direction [201]. If an electrolyte with good ionic conductivity at room temperature can be developed simultaneously, a polymer SSB with a very high energy density on the pack level can be produced.

This concept can be further modified by using solid composite (inorganic-organic) or hybrid (liquid-solid) electrolytes, to overcome some of the challenges described above.

Conclusion

The presented lithium metal polymer SSB has the potential to be competitive as a low-cost and high energy-density battery, when the ionic conductivity at lower temperatures can be improved for polymer SE. The concept is already implemented in applications and produced on a GWh-scale. Room for improvements are especially found in modifying or replacing the solid electrolyte used.

4.7.   Energy Density of Cell Concepts

As discussed in Section 2.4, all material classes of SE feature different properties in terms of material performance, compatibility and processability. A holistic evaluation and comparison of respective cell concepts is not yet possible. However, the potential performance of the promising SSB concepts discussed can still be evaluated in terms of estimated volumetric and gravimetric energy densities, assuming that the respective material compatibilities, conductivity and manufacturing processes meet the requirements for their use in batteries. The realizable energy density of SSB is one of the main arguments for the future market penetration of the batteries.

Calculation of SSB energy densities

For the calculation of energy densities, we used a calculation tool that allows the modelling of energy densities based on active and passive material parameters and basic cell design such as electrode design, cell format, size and other design characteristics of housings and sealings. For the quantification, we used a 500x100 mm² pouch-type cell with a thickness of 10 mm, commonly found in passenger electric vehicles today.

Assumptions

Since final material parameters and performances are not known yet, we evaluated two different cell configurations for each SSB concept: a base version and an advanced version, which differ in the assumptions for material performance (e.g. cathode active material) and SE-layer-thickness. The assumptions are summarized below.

A Cu-current collector of 9 µm and an Al-current collector of 12 µm was assumed for the anode and cathode, respectively, for the oxide and sulfide SSB. These thicknesses can be considered as rather conservative. For the polymer concept, it was assumed that the Li metal foil is free-standing and serves as a current collector itself.

For the base versions of the calculated cells, a separating solid electrolyte of 30 µm, for the advanced versions a layer of 20 µm was assumed. For the base version of the LPS-based cell, an additional ceramic separating layer of 5 µm between the lithium metal and the LPS SE was assumed. A remaining porosity of 5 vol.% was estimated for the separating layer for all SE materials.

For the base versions featuring a Li metal anode, an initial Li-layer-thickness of 25 µm, for the advanced versions, a layer-thickness of 10 µm was assumed. For the polymer SE-based cells, an initial Li-thickness of 40 µm for the base and of 30 µm for the advanced version was presumed (with no additional current collector).

The base version of the Si-based SSB was calculated assuming a specific capacity of 1500 mAh/g, the advanced version assuming a specific capacity of 2500 mAh/g for the anode active material (AAM). A weight ratio of 7:1:1:0.7 referring to AAM:anolyte:binder:conductive additive was estimated. Note that for the Si anodes, a certain build-up of SEI in the first cycle was assumed which leads to the loss of about 15 mol.% of the lithium delithiated from the cathode in the first charging process. These numbers are based on results taken from Si-materials in liquid electrolyte set-ups and could be significantly smaller in case of solid electrolytes.

At the cathode side, a coating thickness of 75 µm for the base and of 80 µm for the advanced version was assumed. These values are reached in state-of-the-art LIB and could be increased if even higher energy densities at a moderate power density are desired. With respect to the cathode active materials (CAM) LFP, NMC811 and a future high nickel NMCA-type was considered, corresponding to a cathode loading between 2.7 and 4.4 mAh/cm². A volume ratio of 6:2.5:1:0.6 referring to CAM:catholyte:binder:conductive additive was assumed. For all cell concepts featuring a solid catholyte, a final cathode porosity of 10 % was assumed.

Results

The advanced cell concepts have a calculated capacity of 120 to 140 Ah. The volumetric energy density, as shown in Figure 19, was calculated for a charged and therefore expanded cell, due to the increased volume of lithiated Si-particles or the Li metal anode layer. Note, that these numbers assume a working electrochemistry in the cells, which is at present not given for all material combinations considered, due to chemical instabilities or poor kinetic properties.

With all electrolyte classes under investigation (oxides, sulfides, polymers) theoretical energy densities of more than 1100 Wh/l are possible in well optimized cell designs and with the highest energy cathode active materials. The optimized volumetric energy densities of the different concepts are so close because the volume distribution of the cell components are similar for all materials. The concepts, however, strongly differ in terms of specific energy, which is a result of the very different density of oxide, sulfide and polymer SE materials. Still, specific energies

Figure 19: Calculated energy densities and specific energy for different SSB concepts in a base and an advanced configuration.
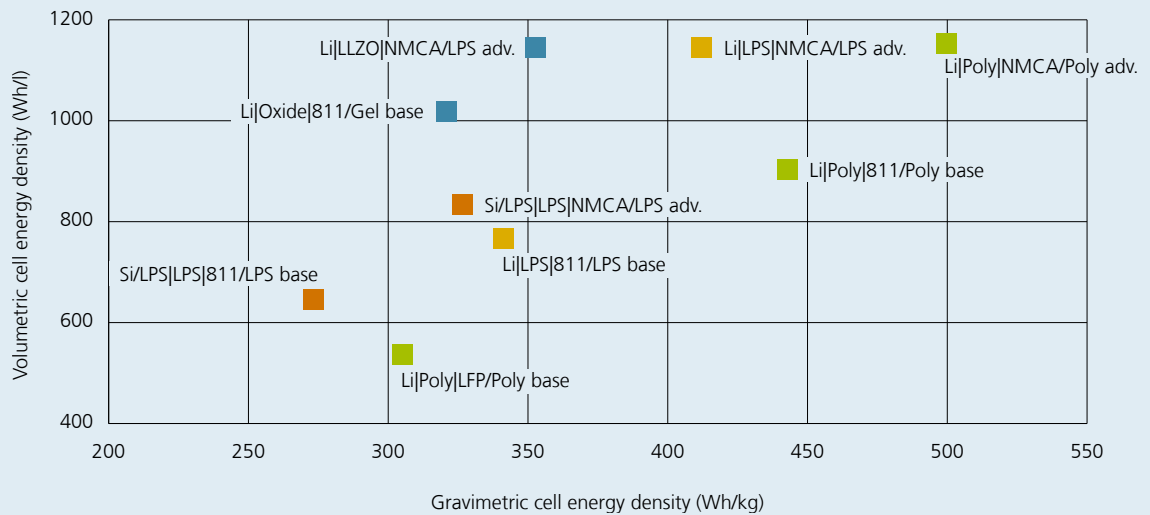
of more than 300 Wh/kg are possible even for the base versions of all concepts featuring a lithium metal anode. These values exceed the state-of-the-art for liquid electrolyte-based LIB.

From the perspective of energy density, concepts featuring a silicon anode lag behind. This has two main reasons: (1) The assumption that a certain amount of lithium, introduced to the cell only by the cathode, will be consumed in irreversible reactions, e.g. at the Si/SE-interface and (2) the redox potential of silicon vs. lithium, which effectively leads to a lower cell voltage of 300 to 400 mV as compared to the Li anode concepts.

All calculations were done for LLZO, LPS and PEO-based electrolytes. The calculated energy densities refer to the cell concepts presented in Sections 4.3 to 4.6. Since the specific weight also of other oxides, sulfides and polymers is similar to these exemplary materials, the trends observed for the calculated energy densities and specific energies can also be transferred to other SE materials of the same classes.

4.8. Industry Perspective

Besides the polymer electrolyte-based solid-state battery (e.g. by BlueSolutions) [180], SSB microbatteries with oxide thin film electrolytes are on the market already. However, the latter will not be considered further herein, as the main demand for the cells (e.g. xEV) cannot be supplied by these cell concepts.

In addition to the SSB already on the market, there are a large number of announcements for further cell systems under development. Various cell manufacturers as well as automotive OEM are investing in the technology and have set ambitious milestones for the next 10 years. These announcements by different companies are listed in Table 14 in a timeline, without an assessment of feasibility.

Public announcements about the solid-state strategy of Asian players are rare. It can be assumed, however, that there are a number of Asian companies active in the development of solid-state batteries in addition to the companies mentioned below.

Players with R&D activities

Overview of individual announcements
Stellantis and Honda announced the date of integration of solid-state battery prototypes in their R&D roadmaps for 2026 and 2030+, respectively. Blackstone Technologies built up their production facility for a polycrystalline solid electrolyte, which will be printed in 3D. They plan to reach a production capacity of 500 MWh in 2022. StoreDot develops a composite solid-state battery by synthesizing organic and inorganic components by 2028. In all these announcements the solid-state electrolyte, on which the SSB will be based, is not revealed.

Oxides
Cell maker ProLogium and car manufacturers are teaming up to put a solid-state battery in a commercial vehicle (VinFast) or Prototypes (Mercedes-Benz) by 2023 [216, 217]. For this goal, production capacities of 1 to 2 GWh are planned to be built up in 2022 [202, 204]. A battery with ceramic separator and a capacity of 2,5 kWh was demonstrated together with scooter manufacturer Gogoro in 2022 [203]. In another cooperation between carmaker VW and cell manufacturer Quantum Scape, market-ready batteries for the automotive sector are to be developed by 2025. In 2024, Quantum Scape wants to have built up a production capacity of 1 GWh, which is to be expanded to 20 GWh by 2026 [137, 205]. Quantum Scape itself describes the electrolyte material as a ceramic material and demonstrated already prototype cells with Li anodes. Due to the potential proximity to oxide materials,

the announcements are classified as oxides. Qing Tao Energy Development and Ampcera are also working on solid oxide electrolytes. Quin Tao announced a production capacity from 1 GWh in 2020 and a second production facility with an optional capacity of 10 GWh in 2022 [206].

Sulfides
Most SSB-related company announcements are based on sulfide electrolytes. Especially established cell manufacturers such as CATL, LGES, Panasonic, SDI and SKI are aiming for a development of cells within this class of materials. In 2020, SDI introduced a prototype cell with in-situ Li-metal anode and started the construction of a pilot production plant in 2022 [136, 208]. According to the company's own roadmap, CATL plans to be the first SSB cell manufacturer, by developing a sulfide solid-state battery ready for market introduction by 2025, followed by SDI (2027), SKI (2029) and LGES (2030+) [205]. The cooperation between Toyota and Panasonic presented a prototype of a car equipped with a solid-state battery in 2021. Although no technical data was published on this battery, it can be assumed that a sulfide electrolyte was used [40, 59]. They plan to bring the solid-state battery to the market by 2025. In addition, Solid Power plans to develop a prototype car with a solid-state battery before 2025 and a series-produced solid-state battery for passenger cars by the end of the decade in collaboration with BMW and Ford. Since 2018, Hyundai has also taken a financial stake in Solid Power [218]. Additionally, Solid Power plans to develop a 100 Ah cell with a Si anode by 2026 and a 100 Ah cell with a Li metal anode by 2028. Furthermore, a large number of other companies are involved in the development of sulfide solid-state batteries, such as Mitshu Kinzoku ACT (electrolyte production), Hitz Hitachi Zasen, NEI Corporation, idemitsu and ATL (thiophosphate separator).

Polymers
Polymer SSB have already entered the market. Bollore developed a passenger car with a solid-state battery (BlueCar) in 2011. In addition, buses equipped with solid-state batteries were launched in 2020 together with Mercedes. Car manufacturer NIO, together with WeLion New Energy Technology, plans to launch a polymer battery with a Li metal anode and a NMC cathode by 2022 [205, 219]. In addition, the start of construction of a Production plant was announced, which will initially produce 20 GWh of hybrid solid-state batteries with liquid electrolyte as well as ASSB. An expansion to 100 GWh is targeted [212]. Furthermore, Factorial Energy presented a cell with a solid separator and liquid electrolyte and a Li metal anode that achieved 40 Ah capacity in 2021 [220]. The OEM Hyundai-Kia, Mercedes-Benz and Stellantis already invested in Factorial Energy. Mercedes-Benz and Factorial Energy scheduled a small series to enter the market for automotive applications by the end of 2026 [221]. Other cell announcements include the start-up SES, which plans to develop a prototype car together with GM and Hyundai by 2023 and reach market maturity by 2030

[218]. GM also invested in Soelect which is developing non-PEO-based polymer electrolyte membranes along with Li anodes [222]. Furthermore, the company Ionic Materials is developing a polymer battery with Renault-Nissan-Mitsubishi. SES is relying on a hybrid cell concept with a LCO or NCA cathode active material and a Li metal anode. Ionic Materials is only known to use a Li metal anode. Hydro Quebec plans to start production between 2025 and 2027, initially launching polymer electrolytes with a Li metal anode and an LFP cathode. Later, the LFP cathode will be replaced with NMC and the polymer electrolyte will be replaced by a composite electrolyte with ceramics components [214]. Other companies known to be developing solid polymer batteries include Beijin Shenzhou Judian New Energy, Fujian Super Power New Energy and BrightVolt.

Table 17: SSB-related company announcements (blue shading: oxide SSB, orange shading: sulfide SSB, green shading: polymer SSB, white shading: SSB-type not known):

Company	Time Horizon	Announcement	Source
ProLogium (Cells)	2022	1–2 GWh production capacity	[202]
ProLogium (Cells), Gogoro (OEM)	2022	2,5 kWh Prototype SSB for Scooter	[203]
ProLogium (Cells), VinFast (OEM), Mercedes-Benz (OEM)	2023	Market maturity for automotive application	[202, 204]
Quantum Scape (Cells)	2024	1 GWh production capacity	[137]
Quantum Scape (Cells), VW (OEM)	2025	Prototype in car	[205]
Quantum Scape (Cells)	2026	20 GWh production capacity	[137]
Qing Tao (Cells)	2020	1 GWh production capacity	[206]
Qing Tao (Cells)	2022	Factory with up to 10 GWh optional production capacity	[206]
SDI (Cells)	2020	Prototype Cell with in-situ Li metal anode	[136]
Panasonic (Cells), Toyota (OEM)	2021	Prototype in car	[205, 207]
Ampcera (Cells)	2021	Solid electrolyte commercially available	[205]
SDI (Cells)	2022	Construction of a pilot production plant	[208]
Solid Power, BMW (OEM), Ford (OEM)	Before 2025	Prototype in car	[209]
Panasonic (Cells)	2025	SSB development finished	[205]
Panasonic (Cells), Toyota (OEM)	2025	Market maturity for automotive application	[205, 207]
CATL (Cells)	2025	Development of Thiophosphate separator for sulfide SSB	[205]
Solid Power (Cells)	2026	100 Ah Si anode Cell	[149, 210]
SDI (Cells)	2027	SSB development finished	[205]
Solid Power (Cells)	2028	100 Ah Li metal Cell	[149, 210]
SKI (Cells)	2029	SSB development finished	[205]
Solid Power, BMW (OEM), Ford (OEM)	End of decade	Market maturity for automotive application	[209]
LGES (Cells)	2030+	SSB development finished	[205]
Bollore (Cells), Mercedes-Benz (OEM)	2020	Ceitavo Bus with 441 kWh LMP battery	[199]
Factorial Energy (Cells)	2021	Prototype 40Ah ASSB	[211]
WeLion New Energy Technology (Cells), NIO (OEM)	2022	SSB development finished	[205]
WeLion New Energy Technology (Cells)	2022	20 GWh production capacity, later on a expansion to 100 GWh	[212]
SES (Cells), GM (OEM)	2023	Prototype in car	[213]
Ionic materials (Cells) Nissan-Renault-Mitsubishi (OEM)	2025	Prototype in car	[213]
Hydro Quebec (Cells)	2025	SSB development finished	[214]
Ionic materials (Cells), Hyundai (OEM)	2030 +	Market maturity for automotive application	[213]
Blackstone Resources (Cells)	2022	500 MWh production, polycrystalline material	[199]
Stellantis (OEM)	2026	Prototype in car	[213]
StoreDot (Cells)	2028	Composite out of organic and inorganic materials	[215]
Honda (OEM)	2030	Market maturity for automotive application	[213]

5. Roadmap

5.1. Materials to Cell Roadmap

The first part of the solid-state battery (SSB) Roadmap "Materials to Cell" considers the components required for solid-state batteries, the most promising materials, as well as current challenges and how and when these could be resolved. The second step regards promising combinations of these components into cell concepts and estimates when these concepts might reach the phase of pilot production considering the existing challenges. All assessments regarding market entry and technological maturity are based on the expert consultations held as part of this roadmap study. The following sections discuss the most important points for each component and cell concept.

Anode

Battery cells using lithium metal anodes have the highest energy density and lithium metal is therefore considered the ideal anode material. Current challenges to using lithium metal include its high reactivity and thus limited stability in contact with other battery components such as the solid electrolytes as well as difficulties with handling lithium metal during production. Although Li anodes are already being used in polymer-based SSB on the market, their maturity is quite low compared to other anode materials. Their high technological potential combined with huge market interest is likely to result in broader market implementation in the future.

Alternatively, silicon anodes are also considered promising for the use in SSB, as they can achieve high energy densities (although lower than Li anodes). Silicon anodes are already more mature than Li anodes and are increasingly applied in liquid electrolyte LIB, which supports the development efforts. From a market perspective, silicon anodes can thus be considered more promising in the short to medium term for certain SSB.

Solid Electrolytes

Solid electrolytes are the core component of solid-state batteries, and distinguish SSB from liquid electrolyte LIB. Oxides, sulfides and polymers are the three solid electrolyte classes currently considered the most promising. All of them are subject to challenges and bottlenecks that are limiting or hindering their widespread market implementation at present.

Oxide Electrolytes

Oxide electrolytes face processing challenges due to their brittleness and high sintering temperatures, which makes cost-efficient processing of thin and homogeneous oxide electrolyte films difficult using the current processing techniques. Technological advances that will facilitate the processing of oxides are anticipated in the medium term. Furthermore, the ionic conductivity of oxides is typically too low for them to be used as the catholyte in SSB. This is why hybrid cell concepts containing liquid/gel electrolytes are considered more likely in the medium term. In the longer term, the use of sulfide electrolyte catholytes might be possible to enable all-solid-state batteries. Another challenge is the limited stability of some oxide electrolytes in the presence of lithium anodes, which might be overcome by applying special coatings in the medium term.

Sulfide Electrolytes

There is currently a limited availability of materials for sulfide electrolytes. Many potential materials are only available at gram-scale for R&D purposes at exorbitant prices. In the medium term, a scale-up of the most promising materials is expected, which would lead to decreasing prices. Furthermore, sulfides exhibit only limited stability in the presence of high-potential cathode active materials (CAM), such as NMC and NCA. CAM coatings, or doping the sulfide electrolytes at the interface are considered viable options to increase stability. The interface between sulfide electrolytes and the Li anode also poses a challenge for two reasons. First, sulfides are chemically unstable in contact with Li, and coating or doping the electrolyte at the interface is needed to increase stability. Second, the formation of dendrites has to be prevented, which could probably also be achieved by a suitable interface modification.

Polymer Electrolytes

Polymer electrolytes exhibit a limited ionic conductivity in general and especially at room temperature. For this reason, heating systems are currently required for the battery pack, which limits the applications for such SSB. The generally low ionic conductivity also limits the charging and discharging rates. Advances in materials R&D are anticipated to yield polymer electrolytes with higher ionic conductivities that might

enable room temperature applications. Polymer electrolytes are electrochemically unstable in the presence of high-potential cathode materials, such as NMC or NCA. However, these cathode active materials are currently the most promising option to achieve higher energy densities. Coatings or the development and use of more stable polymer electrolyte systems could increase the compatibility. Another challenge for polymer electrolytes is low dendrite resistance on the anode side. As the polymer electrolytes exhibit only limited mechanical stability, dendrites can easily penetrate the polymer separators. Dendrite resistance can, however, be increased by coatings that lead to an even deposition of lithium on the anode during charging.

Cathodes

The most promising cathode active materials for high energy density SSB cells are Ni-rich layered oxides (NMC, NCA). These materials are well established in state-of-the-art LIB manufacturing processes. Their broad use is currently hindered by their limited compatibility with many solid electrolyte materials. In many cases, however, coatings on the CAM particles are sufficient to enable stable operation.

Lithium iron phosphate (LFP) as a CAM with lower costs and a lower electrochemical potential (compared to NMC/NCA) already plays a significant role in polymer-based SSB on the market. LFP (and potentially also LFMP) is considered to play an important role in the future for medium-priced and medium-performance applications, also due to its high compatibility with most solid electrolytes.

In the longer term, alternative materials such as LMNO or sulfur might play a role for the highest-performance, or lowest-cost applications, respectively.

Cell Concepts

Polymer Electrolyte-Based Cell Concepts
Polymer electrolyte-based SSB have been on the market for several years. The commercial polymer SSB consist of lithium anodes, one or more polymer electrolytes and LFP as the cathode active material. The polymer electrolyte serves as the catholyte and is intermixed with the particle-based LFP CAM. This type of polymer SSB is expected to improve its

performance in the coming years, mainly due to improved properties of the polymer electrolytes.

Replacing the LFP CAM by an NMC/NCA active material would lead to another cell concept with potentially higher energy density. Significant improvements will be required in the stability of the polymer electrolytes in the presence of the relatively high potential NMC CAM to achieve operational stability. Pilot production could start between 2025 and 2030.
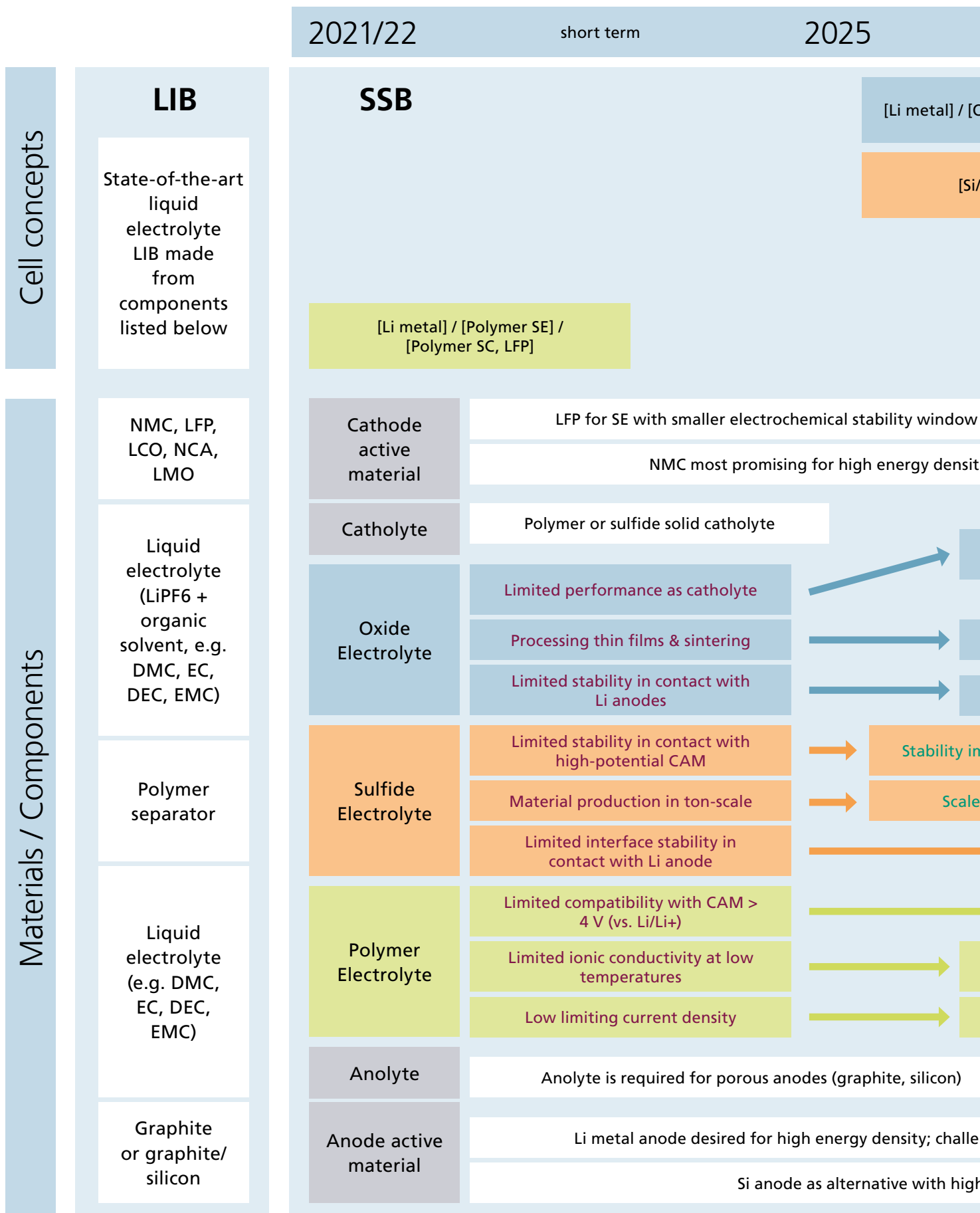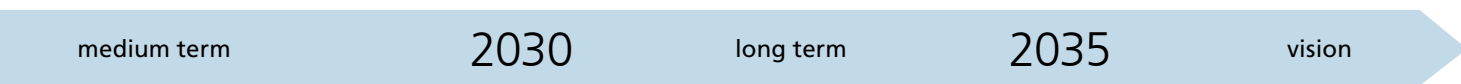
Sulfide Electrolyte-Based Cell Concepts
Sulfide electrolyte-based SSB are not on the market yet, but strong R&D efforts are currently on-going. The cell concept consisting of a silicon/graphite anode, a sulfide anolyte, electrolyte, and catholyte, and an NMC cathode active material is currently considered the closest to market among the sulfide-based SSB. Due to the high maturity of the silicon/graphite-based anode active material and established processing methods, fewer challenges are expected compared to lithium anode-based SSB, and pilot production might start in 2025 or shortly after. The second very promising sulfide-based SSB concept contains a lithium metal anode instead of the silicon/graphite one. Less experience with Li processing and the lower chemical stability of Li in contact with the sulfide electrolytes make this concept more challenging, but its higher energy density offers an important advantage. Pilot production is expected to start shortly before 2030.

Oxide Electrolyte-Based Cell Concepts
Oxide electrolyte-based SSB are currently on the market in microbatteries, but not yet on a large scale. Similar to sulfide electrolyte-based SSB, strong R&D efforts are ongoing. The most promising cell concept consists of a lithium metal anode, an oxide electrolyte separator, a gel catholyte, and an NMC cathode active material. Due to the limited ionic conductivity of the oxide electrolytes and challenges due to the required high-temperature processing, the gel catholyte is needed at present to enable sufficiently high ionic conductivity at the interface between CAM and electrolyte, making this a hybrid cell concept. Pilot production for this cell concept is expected by the middle of this decade. Further developments in sulfide electrolytes might lead to a cell concept with oxide-based separating electrolytes and sulfide catholytes replacing the gel electrolyte, but this is not expected to go into production within the next ten years.

Figure 15: Materials to Cell Roadmap

		LIB	**SSB**	2021/22 short term 2025

				[Li metal] / [C

[Si/

Cell concepts

LIB	State-of-the-art liquid electrolyte LIB made from components listed below

[Li metal] / [Polymer SE] / [Polymer SC, LFP]

Materials / Components

NMC, LFP, LCO, NCA, LMO	Cathode active material	LFP for SE with smaller electrochemical stability window
		NMC most promising for high energy densit

	Catholyte	Polymer or sulfide solid catholyte

Liquid electrolyte (LiPF6 + organic solvent, e.g. DMC, EC, DEC, EMC)	Oxide Electrolyte	Limited performance as catholyte
		Processing thin films & sintering
		Limited stability in contact with Li anodes

Polymer separator	Sulfide Electrolyte	Limited stability in contact with high-potential CAM	Stability in
		Material production in ton-scale	Scale
		Limited interface stability in contact with Li anode	

Liquid electrolyte (e.g. DMC, EC, DEC, EMC)	Polymer Electrolyte	Limited compatibility with CAM > 4 V (vs. Li/Li+)
		Limited ionic conductivity at low temperatures
		Low limiting current density

	Anolyte	Anolyte is required for porous anodes (graphite, silicon)

Graphite or graphite/ silicon	Anode active material	Li metal anode desired for high energy density; challe
		Si anode as alternative with high

Oxide SE] / [Gel or Oxide/Gel catholyte, NMC]

[Li metal] / [Oxide SE] / [Sulfide SC, NMC]

C] / [Sulfide SE] / [Sulfide SC, NMC]

[Li metal] / [Sulfide SE] / [Sulfide SC, NMC]

[Li metal] / [Polymer SE] / [Polymer SC, NMC]

(e.g. polymers)

ies

CAM >4.2 V vs. Li/Li+ (e.g. LMNO) for highest energy densities

Liquid/gel or sulfide electrolyte as catholyte → Sulfide or oxide SE as catholyte

Improvements in processing

Stability improved by coatings

mproved by coatings or SE doping

-up of materials production

Stability improved by coatings or SE doping & further material developments

Novel polymer SE or coatings

Polymer SEs with higher ionic conductivity at low temperatures

Single-ion conductors

nges in fabrication and compatibility with solid electrolytes

her maturity but lower energy density

Legend

5.2. Cell to Application Roadmap

The second part of the SSB Roadmap "Cell to Application" starts from the cell level and discusses different SSB cell concepts compared to the benchmark of liquid electrolyte LIB. Challenges when integrating SSB into battery packs are discussed as well as potential fields of application for different types of SSB. Finally, market size estimations are made for SSB in the context of the total LIB market. All assessments of current SSB energy densities, integration challenges, fields of applications and time of implementation as well as market size are based on the expert consultations carried out within the frame of this study. LIB KPIs and market size were estimated using market and LIB models of Fraunhofer ISI. Future SSB energy densities were calculated (Section 4.7) and represent an estimate of what might be achievable without considering technical details, such as compatibilities between components and processing challenges.

SSB Cell Concepts and their Potential Energy Densities

Polymer Electrolyte-Based Cell Concepts

The polymer SSB cell concept consisting of a lithium anode, one or more polymer electrolytes and LFP as the cathode active material has already been on the market for several years. Typical energy densities of 240 Wh/kg and 360 Wh/l can be currently achieved with this concept.

Replacing the LFP CAM by an NMC/NCA active material could lead to another cell concept with potentially significantly higher energy densities of up to 440 Wh/kg and 900 Wh/l with NMC811, and even up to 500 Wh/kg and 1150 Wh/l with a potential future high capacity NMCA-type active material and further improvements in the cell. However, significant improvements in the stability of the polymer electrolytes in contact with the relatively high potential of NMC/NCA-type CAM will be required to achieve operational stability.

Sulfide Electrolyte-Based Cell Concepts

Of the sulfide-based SSB, the cell concept consisting of a silicon/carbon anode, a sulfide anolyte, electrolyte and catholyte, and an NMC cathode active material is currently considered closest to market. Energy densities of 275 Wh/kg and 650 Wh/l are estimated. Replacing the silicon/carbon anode with a Li anode would lead to an increased energy density of 340 Wh/kg and 770 Wh/l. Further developments using high-capacity NMCA-type CAM, as well as further improvements in cell design could lead to energy densities of up to 325 Wh/kg and 835 Wh/l with a Si anode, and 410 Wh/kg and 1150 Wh/l with a Li anode.

Oxide Electrolyte-Based Cell Concepts

Currently, the most promising oxide-based SSB cell concept consists of a lithium metal anode, an oxide electrolyte separator, a gel catholyte and an NMC cathode active material. It is estimated that this concept could achieve energy densities of 315 Wh/kg and 1020 Wh/l with NMC811 as the cathode active material. Further improvements in cell design and the use of high-capacity NMCA-type CAMs could lead to energy densities of 350 Wh/kg and 1140 Wh/l.

Key Performance Indicators of SSB and LIB

The individual KPI of LIB and SSB are interdependent, implying that good values in one KPI usually come at the cost of another KPI. For example, if high charging rates are desired, the battery has to be designed accordingly, which will automatically lead to a reduction in its energy density. Vice versa, a battery with maximum energy density will not be compatible with high charging rates. Consequently, the values in the roadmap have to be seen as maximum values for batteries that are optimized for high energy densities. How the KPI develop in future will depend on the answers to the questions raised in Section 4.1.

Energy density

High energy density LIB currently exhibit energy densities in the range of 230 to 300 Wh/kg and 600 to 750 Wh/l. These are not matched by the energy density of the only SSB concept currently on the market on a larger scale (polymer SSB, 240 Wh/kg, 360 Wh/l). Optimizations might further increase the energy density of this concept, but it is still not likely to match state-of-the-art LIB energy densities. Other SSB concepts

are more promising in this regard (as indicated above and in the roadmap), but state-of-the-art LIB are a moving target and their energy density is likely to increase to 250 to 330 Wh/kg and 650 to 850 Wh/l by 2025, to 310 to 350 Wh/kg and 750 to 950 Wh/l by 2030, and to 320 to 360 Wh/kg and 800 to 960 Wh/l by 2035 due to implementing similar improvements in cell design and active materials (e.g., highest capacity NMCA-type and Si-based anodes) as discussed for SSB. If successfully commercialized in time, the energy density of several SSB concepts could compete with liquid electrolyte LIB in the medium term, and even surpass them in some cases, as discussed above. In the long term, all SSB concepts containing Li anodes and high-capacity cathode active materials have the potential to surpass the assumed KPI of liquid electrolyte LIB and thus dominate the high energy density battery field with values up to 500 Wh/kg and 1150 Wh/l at cell level. This means that energy densities with SSB might potentially double in the coming decade compared to today's commercially available LIB technology.

Fast charging

Fast charging of SSB requires the adjustment of the design of the battery cell for this purpose, which comes at the cost of a lower energy density. Furthermore, not all SSB will be suitable for fast charging due to low ionic conductivities of the SE that limit the charging rate. Especially for polymer-based SSB, fast charging seems critical, as current polymer SSB exhibit typical charging rates of only 1/5 C. State-of-the-art LIB currently have an advantage in the context of fast charging over SSB. However, future generations of sulfide or oxide SSB might be designed specifically for fast charging and could outperform liquid electrolyte LIB due to their larger operating temperature range. The ionic conductivities, however, have to be optimized for fast charging as well, as they are partially responsible for cell performance.

Safety

Safety data are not available for most SSB concepts as they are still in the R&D stage. In general, SSB are considered to be safer than liquid electrolyte LIB, as they do not contain flammable liquids and have a larger operating temperature range. On the other hand, the Li metal anode utilized in many SSB concepts poses a potential safety risk due to its high chemical reactivity. Realistic assassments can only be made once market-ready SSB cell designs are available.

Lifetime

Similar to the issue of safety, there is not much information available on the cycle life and calendric lifetime of most SSB concepts. The hopes are that SSB exhibit improved lifetimes compared to liquid electrolyte LIB, as the components and interfaces have a higher stability than the organic solvents used in liquid-electrolyte LIB. Realistic assessments, however, can only be made once data on market-ready SSB are available.

Price

As most SSB concepts are still in the R&D stage, statements about future prices are highly speculative and based not only on material and processing costs, but also on corporate strategies. The current price for state-of-the-art LIB ranges between 90 and 180 EUR/kWh and is expected to drop to as low as 45 EUR/kWh in the coming decade, according to some OEM announcements. However, this price should be considered a lower limit that requires optimistic developments for (raw) materials costs, energy prices, smart fabrication technologies and vanishing margins which are profitable only at very large production scales. Initially, SSB will certainly be more expensive than liquid electrolyte LIB due to smaller production volumes for both materials and cells, and (partially) new production technologies. With increasing production volumes, the costs for SSB are likely to decrease.

SSB System Level

Integrating SSB cells into battery modules/packs poses some SSB-specific challenges. As most SSB concepts work with lithium or silicon as the anode active material, significant volume changes occur inside and potentially outside cells during cycling. At the same time, external pressure on the battery cells is required to ensure good interfacial contacts between the individual (solid) components at all times and to allow for homogeneous lithium deposition (in case of Li anodes) during charging. Applying constantly high pressure to the cells while compensating volume changes at the same time poses a major challenge for the mechanical systems of SSB packs. Due to their soft mechanical properties, polymer electrolytes can compensate volume changes to a higher degree than oxide or sulfide SE, which eases the requirements concerning external mechanical pressure.

Safety aspects of SSB can pose challenges as well, especially in the case of Li anodes, as Li is a highly reactive metal. Furthermore, some sulfide electrolytes can form the toxic gas H_2S in the presence of water, so proper encapsulation of the SSB cells has to be ensured.

The current generation of polymer SSB requires operating temperatures between 50 and 80 °C and hence a heating system at pack level. Although it is not difficult to implement the heating system, which replaces the cooling system in liquid electrolyte LIB, the constant energy consumption this requires to keep the battery operational is disadvantageous for most applications. Developments to reduce the operating temperature of polymer SSB are ongoing. Due to their larger operating temperature range, non-polymer SSB (and possibly also polymer SSB in the long term) require a smaller cooling system than liquid electrolyte LIB.

SSB Applications

Polymer SSB
Among the potential solid-state batteries, only polymer-based SSB are already on the market today on a larger scale. The biggest drawback of the current generation of polymer SSB is the operating temperature of 50–80 °C, which requires a heating system and thus constant energy consumption to keep the battery ready for use. This requirement currently limits the applications to systems that are in regular use with only small idling periods outside the charging periods. At the moment, the main application for this type of SSB is, to the best of our knowledge, electric buses. Further applications suitable for the boundary condition of constant heating are envisaged in the near future, such as automated guided vehicles (AGV) or other industrial applications. Stationary storage is also considered a promising application by some experts. By the end of the decade, with further developments in polymer SSB technology, passenger cars and trucks are considered promising applications, too.

Sulfide SSB
Sulfide-based SSB are expected to be in applications on the market on a larger scale by the end of this decade. The first envisaged large-scale applications are passenger cars, which stand to benefit from the high energy densities involved. At the same time, drones could also become an important application for sulfide SSB. On the other hand, some experts expect the consumer market (including power tools) to be the starting point for this technology, as the requirements and testing procedures are typically less stringent, or at least faster than in the automotive industry. Passenger cars would then follow and benefit from the experiences made with consumer technologies. The general opinion is that automotive applications will be the most important application sector and a major driver of this technology. Once sulfide SSB are established and costs decline, further applications such as trucks and stationary storage are conceivable. In the long term, electric passenger aviation might be another interesting application for sulfide SSB.

Oxide SSB
Oxide-based SSB are expected to develop in parallel to sulfide SSB with similar application scenarios. Due to their (expected) high stability, even in harsh environments, industrial applications in heavy duty machinery are anticipated. However, the big driver will be automotive applications that are expected to come to market at the end of this decade (similar to sulfide SSB applications). The success in the automotive sector will determine further applications, such as trucks and stationary storage applications, depending on performance and price. Military applications could also drive development, especially in the early stages.

SSB Market Size

At this stage of development, any estimation of the future production capacity of solid-state batteries is highly speculative and will depend heavily on technological developments and corporate strategies. Nonetheless, such estimations can be helpful to assess the SSB market size in the context of the overall LIB market.

According to expert estimations, currently, polymer SSB are expected to have an annual production capacity of less than 2 GWh. This capacity is expected to increase to 2–15 GWh by 2025 and to 10–50 GWh by 2035. The large margins indicate the high level of uncertainty. Sulfide SSB that are not yet on the market on a larger scale are expected to have a market capacity of 0–5 GWh in 2025, growing to 20–50 GWh by 2035. A slightly smaller market is anticipated for oxide SSB, with a market capacity of 0–1 GWh in 2025, growing to 10–20 GWh by 2035.
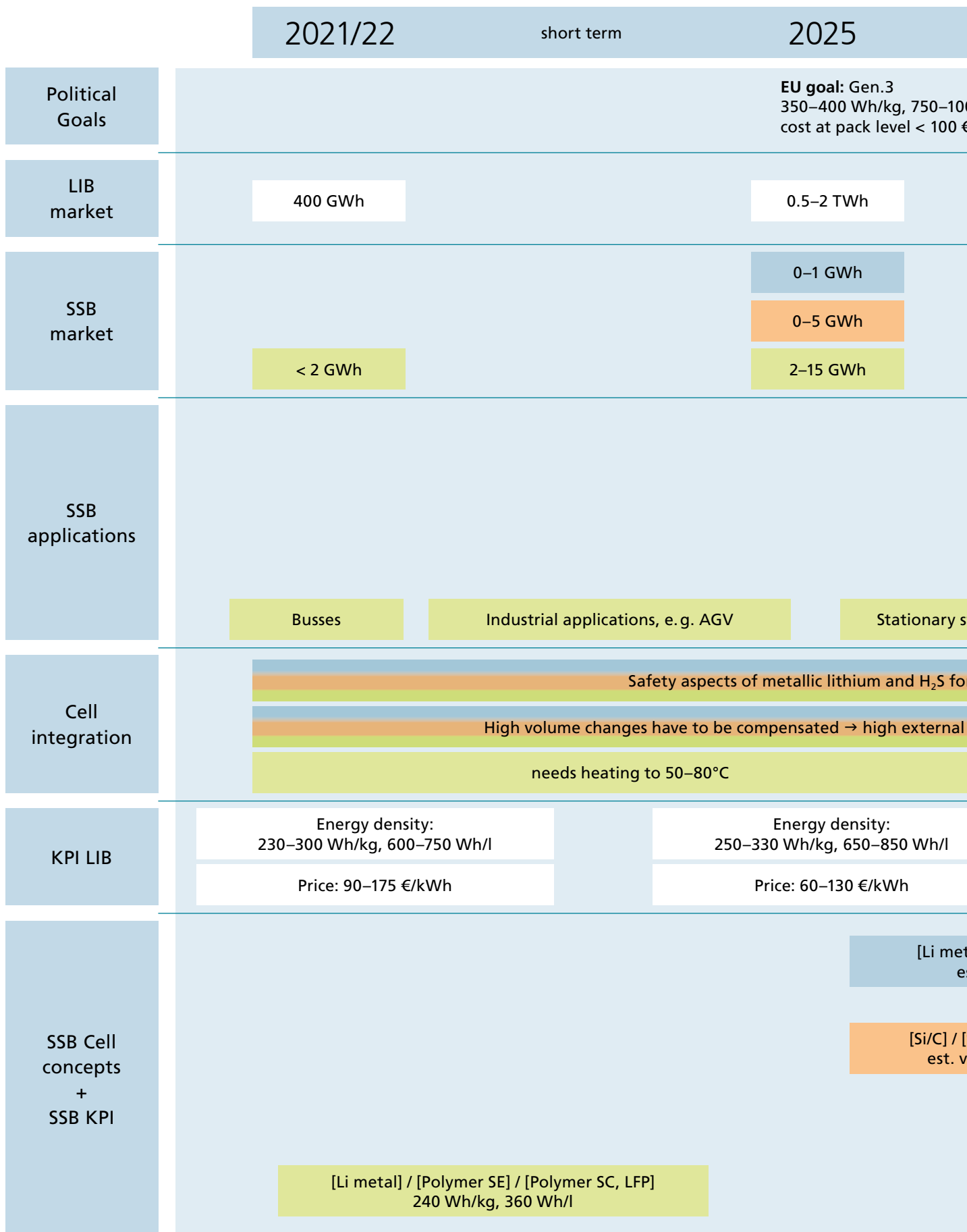
The overall LIB market is expected to grow from its current size of 400 GWh to 0.5–2 TWh by around 2025, 1–6 TWh by 2030 and 2–8 TWh by around 2035. This strong market growth is mostly based on established technologies, i.e., liquid electrolyte LIB. Solid-state batteries, which currently have a share of less than half a percent of the total LIB market, are expected to increase their share to one percent or more by 2035. These estimations show that liquid electrolyte LIB will dominate the market for the forseeable future, and SSB are expected to need time to evolve into a major technology on the world market.

Political Goals

Various countries and their funding agencies have set development goals for lithium-ion batteries and solid-state batteries. We consider the EU goals for Li-ion batteries for mobility applications as an example [223]. The goals for generation 3 LIB ("*High capacity/high voltage stable active cathode materials combined with high-capacity anodes and new liquid electrolytes (additives, composition, etc.), separators with reduced thickness and cost, NMP free processing, etc.*" [223]) are a gravimetric energy density of 350–400 Wh/kg and a volumetric energy density of 750–1000 Wh/l at cell level. The cost target at pack level is below 100 EUR/kWh and the expected market entry is 2025 and beyond. For generation 4 LIB (4: "*Solid state electrolyte Li-ion:(organic,inorganic, hybrid)*", 4a: "*NMC cathode + C/Si composites + Solid electrolyte*", 4b: "*NMC cathode + Li metal + Solid electrolyte*", 4c: "*High voltage cathode + Li metal + Solid electrolyte*" [223]), the goals are a gravimetric energy density of 400+ Wh/kg (500+ for Gen. 4b & 4c) and a volumetric energy density of 800+ Wh/l (1000+ for Gen. 4b & 4c) at cell level. The cost target at pack level is below 75 EUR/kWh, and the expected market entry is 2030 and beyond, depending on the corresponding technology.

We consider these goals rather ambitious, especially in terms of energy density. Based on the results of this study, all these goals could potentially be fulfilled by SSB, but in the longer term. Similar reservations apply to the price goals for SSB (Gen. 4).

Figure 16: Cell to application Roadmap

	2021/22	short term	2025
Political Goals			**EU goal:** Gen.3 350–400 Wh/kg, 750–100... cost at pack level < 100 €...
LIB market	400 GWh		0.5–2 TWh
SSB market	< 2 GWh		0–1 GWh / 0–5 GWh / 2–15 GWh
SSB applications	Busses	Industrial applications, e.g. AGV	Stationary s...
Cell integration		Safety aspects of metallic lithium and H₂S fo... / High volume changes have to be compensated → high external... / needs heating to 50–80°C	
KPI LIB	Energy density: 230–300 Wh/kg, 600–750 Wh/l Price: 90–175 €/kWh		Energy density: 250–330 Wh/kg, 650–850 Wh/l Price: 60–130 €/kWh
SSB Cell concepts + SSB KPI	[Li metal] / [Polymer SE] / [Polymer SC, LFP] 240 Wh/kg, 360 Wh/l		[Li met... es... / [Si/C] / [... est. v...

| medium term | **2030** | long term | **2035** | vision |

00 Wh/l
/kWh

EU goal: Gen.4
400–500+ Wh/kg, 800–1000+ Wh/l
cost at pack level < 75 €/kWh

| 1–6 TWh | | 2–8 TWh |

5–10 GWh		10–20 GWh
5–15 GWh		20–50 GWh
5–30 GWh		10–50 GWh

Industrial heavy duty & harsh environment equipment

Passenger cars

Autonomous aircrafts (drones)

Passenger aviation

Passenger cars

Trucks

torage

Passenger cars and trucks

rmation for sulfides in case of accident have to be considered

pressure required (oxides, sulfides) / small external pressure required (polymers)

| Energy density:
310–350 Wh/kg, 750–950 Wh/l | | Energy density:
320–360 Wh/kg, 800–960 Wh/l |
| Price: 45–105 €/kWh | | Price: 45–90 €/kWh |

tal] / [Oxide SE] / [Gel catholyte, NMC]
st. values: 315 Wh/kg, 1020 Wh/l

[Li metal] / [Oxide SE] /
[Sulfide SC, NMC]

350 Wh/kg, 1140 Wh/l

Sulfide SE] / [Sulfide SC, NMC]
alues: 275 Wh/kg, 650 Wh/l

325 Wh/kg, 835 Wh/l

[Li metal] / [Sulfide SE] / [Sulfide SC, NMC]
est. values: 340 Wh/kg, 770 Wh/l

410 Wh/kg, 1150 Wh/l

[Li metal] / [Polymer SE] / [Polymer SC, NMC]
est. values: 440 Wh/kg, 900 Wh/l

500 Wh/kg, 1150 Wh/l

6. Conclusions & Outlook

Conclusions and implications

Driven by the increasing market diffusion of electric vehicles, the market for liquid electrolyte-based lithium-ion batteries (LIB) will expand drastically in the next decades. Of all the emerging battery technologies that are potential competitors for state-of-the-art liquid electrolyte-based LIB, solid-state batteries (SSB) are considered to have the highest maturity. However, their current market share is well below 1 % (based mainly on polymer electrolyte SSB), and it is assumed that this will only increase slightly in the coming decade. SSB are still in the R&D phase and face a number of challenges.

SSB need to outperform conventional LIB in terms of parameters such as energy density, safety, lifetime, fast charging and cost. Additionally, in the current phase of a massive market ramp-up of lithium-ion batteries, SSB or any other battery technology will have to show the potential to be scaled up in a similar way, in order to secure a relevant share of this expanding market. This includes the processability, raw material availability and economic feasability of the technology. Any SSB technology entering the market is expected to start at higher costs compared to the LIB benchmark at that time, mainly due to new manufacturing technologies and smaller-scale production.

Liquid electrolyte LIB are expected to improve significantly in terms of both performance and cost in the next few years, with an anticipated slowdown of improvements by the end of this decade, when they approach their theoretical performance limits. In this context, the expected market entry of oxide- and sulfide-based SSB between 2025–2030 might mark the beginning of a new technology, which will not be disruptive, but instead represents the continued evolution of the Li-based battery technology.

There is a strategic interest to invest in future technologies in order to surpass the limits of existing technologies, and to expand the portfolio of alternatives, especially if there are risks concerning access to a given technology for economic, ecological or political reasons. Similar to liquid electrolyte LIB, which came onto the scene ten years ago as a niche technology alongside Ni-metal-hydride and lead-acid batteries, SSB (as potential future successor of LIB) might evolve from a niche to a mass market. Even if SSB are not expected to supersede liquid electrolyte LIB in the near future, their technological potentials and the strategic need for alternative battery technologies are the current motivations for investing in R&D on SSB.

Opportunities and Challenges for the EU and Germany

Japan, South Korea, China and the USA are the leading players in SSB as indicated by publication and patent data. It seems that they cannot be matched at national, but only at EU level, even though Germany is one of the strongest countries worldwide in terms of R&D on SSB.

Germany is assessed as among the leading countries internationally with respect to R&D on solid electrolyte materials. However, with respect to cell concepts, production processes and production equipment, Germany's R&D on SSB is rated as average among those countries active in this field. For pilot production, the German activities are regarded as clearly below average. While Japan is seen as the global leader in the R&D on solid electrolyte materials, South Korea, the US and China are assessed as its equals with respect to cell concepts, production processes and production equipment. For pilot production of solid-state batteries, the USA is seen as leading ahead of Japan, South Korea and China.

For SSB, the survey results, patent data, and market analyses all indicate that Japan, South Korea and the USA are currently investing the most in R&D on SSB. In contrast, in state-of-the-art LIB developments, China is now the market leader in terms of production. Germany and the EU are lagging behind the Asian leaders, even when considering the planned expansion of liquid electrolyte LIB production capacity in Europe, which is based strongly on Asian cell manufacturers. Solid-state batteries, on the other hand, are in a relatively early development stage, so that there is still a chance for Germany and the EU to become an early player and achieve a leading market position in this field. This strategic potential, however, still has to be exploited. Joint European projects (e.g., IPCEI – Important Project of Common European Interest) and EU strategies (e.g., intellectual property strategies) and further actions to set the relevant frame conditions could provide the support needed to create a strong European counterpart to Asian and American competitors in SSB technologies.

An R&D base already exists due to intensive funding in recent years, but the industry base is currently very limited, with relevant players only in the field of polymer SSB. Materials production and availability are also restricted, especially with regard to sulfide electrolytes. Similar to the development of a European liquid electrolyte LIB value chain, an SSB value chain would require a supply chain for the respective materials, pilot production with promising cell concepts, and finally the scale-up of production. The main focus of the R&D and scaling-up activities for SSB must be on the development of the production, processing and interface engineering of solid electrolyte materials, as well as the other components required for SSB, such as the lithium anode, in order to be able to establish large-scale cell production.

Outlook

Besides SSB, other next-generation battery technologies might evolve for some applications in the future as alternatives to LIB, and be ready for market, e.g., beyond 2030. Recently, there has been a new diversification of battery technologies in contrast to the years before, when the focus of research and development seemed to be almost exclusively on high-energy LIB for automotive applications.

This recent trend might be due to the wider range of battery applications, which often start at growth rates similar to electric vehicle batteries, but still have a smaller demand in terms of GWh. There is therefore still huge scope for R&D and advances in new materials and cell concepts for future battery applications. Furthermore, there are potential spillover effects from LIB research and production to other next-generation battery concepts.

It is therefore essential to monitor and roadmap not only the progress of high-energy LIB, but also SSB and other next-generation batteries. In this sense, this SSB roadmap can be considered an update and successor of the Battery Roadmap 2017: High-energy batteries 2030+ and prospects for future battery technologies [19]. In addition, in 2022 and 2023, the Fraunhofer ISI will compile a roadmap on next-generation batteries and update the roadmap on high-energy LIB.

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