Solid-state / Semi-solid Li-ion Battery Innovation & Patent Review

Table of Contents

Page

Executive Summary 4
About the Author 5
Introduction 5
- Focus of this Review
- Solid-state / Semi-solid Li-ion Battery Components
- The Solid-state / Semi-solid Li-ion Battery Market Today
- (Projected) Market Launches – Solid-state / Semi-solid Li-ion Battery EVs

AI-based Identification of Commercially Relevant Patents 12
- Number of Commercially Relevant Patent Families / Utility Models Since 2019

Technology Decision Trees 30
- Solid Electrolytes – Types – Launched or Close to Market Launch
- Solid Electrolytes – Types – Based on Patent Filings
- Solid Electrolytes – Concepts
- Solid Electrolytes – Oxides That Do Not Contain Phosphorus – (Probably) Crystalline
- Solid Electrolytes – Phosphates / P-containing Oxides – (Probably) Crystalline
- Solid Electrolytes – Oxide / Phosphates – (Probably) Glasses
- Solid Electrolytes – Hydroxides
- Solid Electrolytes – Sulfides
- Solid Electrolytes – Mitigation of Hydrogen Sulfide Emissions
- Solid Electrolytes – Polymers
- Solid Electrolytes – Halides / Oxohalides
- Solid Electrolytes for Thin-film Batteries
- Solid Electrolytes – Boranes
- Lithium (Sodium) Salts
- Plasticizers
- Liquid Electrolyte Components / Liquid Additives
- Solid Electrolyte Additives / Support & Filler Materials That Do Not Contain Li
- Solid Electrolyte Binders
- Negative Electrode Active Materials
- Positive Electrode Active Materials
- Negative Electrode Additives
- Positive Electrode Additives
- Negative Electrode Binders

- Positive Electrode Binders
- Cell Design
- Cell Design – Concepts
- Pack Engineering
- Reliability
- Applications
- Electrolyte Film Deposition Processes

Benchmarking & Product Launch Risk Factors –
Cells with Liquid vs. Semi-Solid vs. Solid Electrolytes 54

- Inherent Safety – Key Risk Factors
- Energy Density – Positive & Negative Electrode Active Material Selections
- Power Density – Ion Conductivity of Solid / Semi-solid Electrolytes
- Longevity – Risk of Crack Formation & Chemical Instability
- Cell Size
- Raw Materials & Manufacturing Processes

Predictions (Until 2026) 68

Assessment of Companies 70

- Ampcera
- BASF
- Blue Current
- Blue Solutions
- BrightVolt
- BYD
- Contemporary Amperex Technology Ltd. (CATL)
- Corning
- Enpower Greentech
- Factorial Energy
- FDK / Fujitsu
- Foxconn (Hon Hai Precision Industry) / SolidEdge Solution
- Ganfeng Lithium / Zhejiang Fengli / Zhejiang Funlithium
- GM
- Hydro Québec
- Idemitsu Kosan
- Ilika Technologies
- ION Storage Systems
- JX Nippon Mining and Metals / Eneos
- LG Energy Solution / LG Chemical
- Maxell
- Mitsui Mining and Smelting / Mitsui Kinzoku
- Murata Manufacturing
- NGK Insulators
- Ohara
- Panasonic
- Piersica

- PolyPlus
- ProLogium Technology
- Qingtao Kunshan New Energy Materials / Suzhou Qingtao New Energy Technology / Yichung Qingtao Energy Technology
- QuantumScape
- Sakuú
- Samsung
- SES Holdings
- Soelect
- Solid Power
- SVOLT Energy Technology / Fengchao Energy Technology / Honeycomb Technology
- Taiyo Yuden
- TDK
- TeraWatt Technology
- Toshiba
- Toyota
- WeLion

Deep Dive – Lithium Metal Negative Electrodes for Solid-state and Semi-solid Li-ion Batteries 276
- Introduction
- Properties of Lithium Metal
- Why Solid Electrolytes Are Key to Achieving Favorable Cycling Stability with Lithium Metal Negative Electrodes
- Estimate of Current State of the Art
- Does Metallic Lithium Need to Be Handled During Production?
- Avoidance of Cell Failure at Electrode Edges
- Two Pressure Regimes in Cells with Lithium Metal Electrodes
- Under-explored Product Development Approaches

Deep Dive – Halide Electrolyte Options & Selection Trade-offs (added on 2024-02-03) 288
- Introduction
- Halides with Ion Conductivities Identified in the Patent Literature (Table with 70 Entries)
- Halides in Prospective Next-generation Solid-state Li-ion Battery Cells for Microscale Electronics Applications
- Halide Catholytes in Prospective Next-generation Sulfide Solid-state Li-ion Battery EV Cells
- Further Examples of Conceptually Unique Halides
- Trade-offs When Selecting Halides (Incl. Decision Sequence)
- Conclusion

Deep Dive – Interfaces: Li Metal Electrodes – Polymer-based Electrolytes (added on 2024-05-06) 303
- Introduction

- Ion-conductive Polymers – Estimate of the Current State of the Art
- Reducing the Need for Electrochemical Stability of Polymer Electrolytes
- Incorporation of Non-conducting Porous Polymer Films
- A Four-track Product Development Approach
- Cell Failure Root Causes That Cannot Easily Be Identified at Lab Scale
- Conclusion

Deep Dive – Catholyte Options & Selection 314
(added on 2024-06-17)
- Introduction
- All-solid vs. Semi-solid vs. Liquid Catholytes & Anolytes – General Considerations
- Summary – Catholyte Component Options & Trade-offs
- Estimate of Current State of the Art
- Under-explored Materials & Chemicals

Deep Dive – Interfaces: Si-based Electrodes – Sulfide Electrolytes 326
(added on 2024-12-10)
- Introduction
- 'Decision Maze' Towards Product Launch
- Academic Findings on Si-sulfide Interface Reactions
- Parasitic Reactions of Carbon Additives in Si-based Negative Electrodes
- Electronic Conductivity of Si and Si-Li Alloys in Carbon-free Negative Electrodes
- Role of Porosity and Tortuosity in Si-based Negative Electrodes
- Active Material Optimization for Dry Processing
- Reconsidering the 'Decision Maze' – Under-explored Approaches
- Conclusion

Deep Dive – Interfaces: Si-based Electrodes – Polymer & Oxide Electrolytes 342
(added on 2025-02-03)
- Introduction
- 'Semi-solid' Electrolytes & Si-based Active Materials – A Pair of 'Imperfect' Materials That Enabled Above-average Progress to Market Launches
- Estimate of Current State of the Art
- 'Decision Maze' Towards Product Launch
- Hypothesis- and Data-driven Interface Design
- Impact of the Negative Electrode / Electrolyte Interface on Cell Performance
- Feasibility of Data-driven Screening Approaches
- Which Si-based Active Materials Have Been 'Under-explored' in Combination with Oxide and / or Polymer-based Electrolytes?
- The Lowest-Cost Solution Wins if Performance & Safety Are Almost Equal

AI Patent Analysis Methodology 352
List of Abbreviations 353
Disclaimer 355

About the Author

Pirmin Ulmann obtained a diploma in chemistry from ETH Zurich (Switzerland) in 2004 and a PhD from Northwestern University (USA) in 2009. Thereafter, he was a JSPS Foreign Fellow in an ERATO academic-industrial project at the University of Tokyo (Japan). From 2010 to 2016, while working at a major battery materials manufacturer in Switzerland, he was a co-inventor of 7 patent families related to lithium-ion batteries. He was also in charge of a collaboration with the Paul Scherrer Institute, evaluated outside technologies for corporate strategy, and made customer visits to battery manufacturers in East Asia, North America & Europe. He holds the credential Stanford Certified Project Manager (SCPM) and has co-authored scientific articles with more than 2,000 citations.

Introduction

Focus of this Review

In this review, technical options are discussed that are being evaluated by key solid-state / semi-solid lithium-ion battery companies towards the launch of commercial products for various applications, in particular electronics and EVs. The analysis is based on a unique AI-supported screening approach for the identification of patent filings with high prospective commercial relevance, which are compared with public statements (incl. at conferences).

Comprehension of solid-state / semi-solid Li-ion battery technology decision trees allows for the identification of promising product development directions that have not yet been explored.

Patent portfolios by key commercial players have been classified into 6 categories:

- Level 1) **Electrolyte & electrode patents**
- Level 2) **Cell patents (chemistry & architecture)**
- Level 3A) **Pack / form factor / packaging patents**
- Level 3B) **Application patents**
- Level 3C) **Reliability patents (e.g. mitigation of short circuits / heat & gas formation)**
- Level 3D) **Manufacturing patents (electrolytes, electrodes, cells)**

A patent portfolio that covers all of these categories generally reflects a substantial product development effort that addresses all aspects necessary for a successful launch.

For tailored patent searches, the AI model used for preparation of this review is available to users on b-science.net.

Table 2: (projected) market launches for solid-state / semi-solid battery EVs; color labels: midnight blue: oxide / phosphate-based electrolytes (may contain polymers); mocha: sulfide-based electrolytes (may contain halides, polymers); teal: halide-based electrolytes (without sulfur); plum: polymer-based electrolytes (predominant component)

Company	Country	Year	Possible Electrolyte / Negative Electrode Type / Other Info

20 entries

Benchmarking & Product Launch Risk Factors – Cells with Liquid vs. Semi-Solid vs. Solid Electrolytes

A battery fails commercially if any performance & safety characteristic or costs do not match the requirements of the corresponding application. Outperformance in one dimension usually does not compensate for the biggest weakness.

Table 6: targeted energy density

Companies (approximate cell capacity)	Approximate volumetric / gravimetric energy density (for >1 Ah cells unless if mentioned otherwise)	Positive electrode	Negative electrode

20 entries

Technology Decision Trees

Table 7: ion conductivity of solid electrolytes (as identified in patent applications, in public statements, or by reference to an academic publication); color labels: midnight blue: oxide / phosphate-based electrolytes (may contain polymers, may contain minor amount of halide); mocha: sulfide-based electrolytes (may contain halides, polymers); teal: halide-based electrolytes (without sulfur, may contain oxygen); plum: polymer-based electrolytes (predominant component)

Companies	Possible electrolyte	Approximate ion conductivity at 25 °C unless if otherwise mentioned
Škoda (VW)	'Li-glasses' based on complex mixture, e.g. P_2O_5 / LiCl / Li_2O / Al_2O_3 / B_2O_3 / LiI	5.5×10^{-2} S/cm
Hydro Québec (licensed from Texas University / Porto University / Laboratório Nacional de Energia e Geologia)	'Li-glasses' based on dried LiOH, LiCl, $Ba(OH)_2$	4×10^{-2} S/cm
Toyota	$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$	2.5×10^{-2} S/cm
SVOLT	$Li_{5.85}P_{0.8}Bi_{0.1}Sn_{0.1}S_{4.4}O_{0.15}Cl_{1.45}$	1.5×10^{-2} S/cm

Companies	Possible electrolyte	Approximate ion conductivity at 25 °C unless if otherwise mentioned
Ampcera	‘sulfur-stuffed’ argyrodite, $Li_8P_3S_{11+n}Cl$ or $Li_{8+2n}P_3S_{11+n}Cl$, $n > 0$	$>1.2 \times 10^{-2}$ S/cm (public statement that presumably corresponds to the electrolyte on the left)
Dynanonic	Supramolecular siloxane-PEO, coupled with click chemistry	1.2×10^{-2} S/cm

118 additional entries

Figure 12: technology decision tree – solid electrolytes – halides / oxohalides
(in red: newly added branches as compared to prior review)

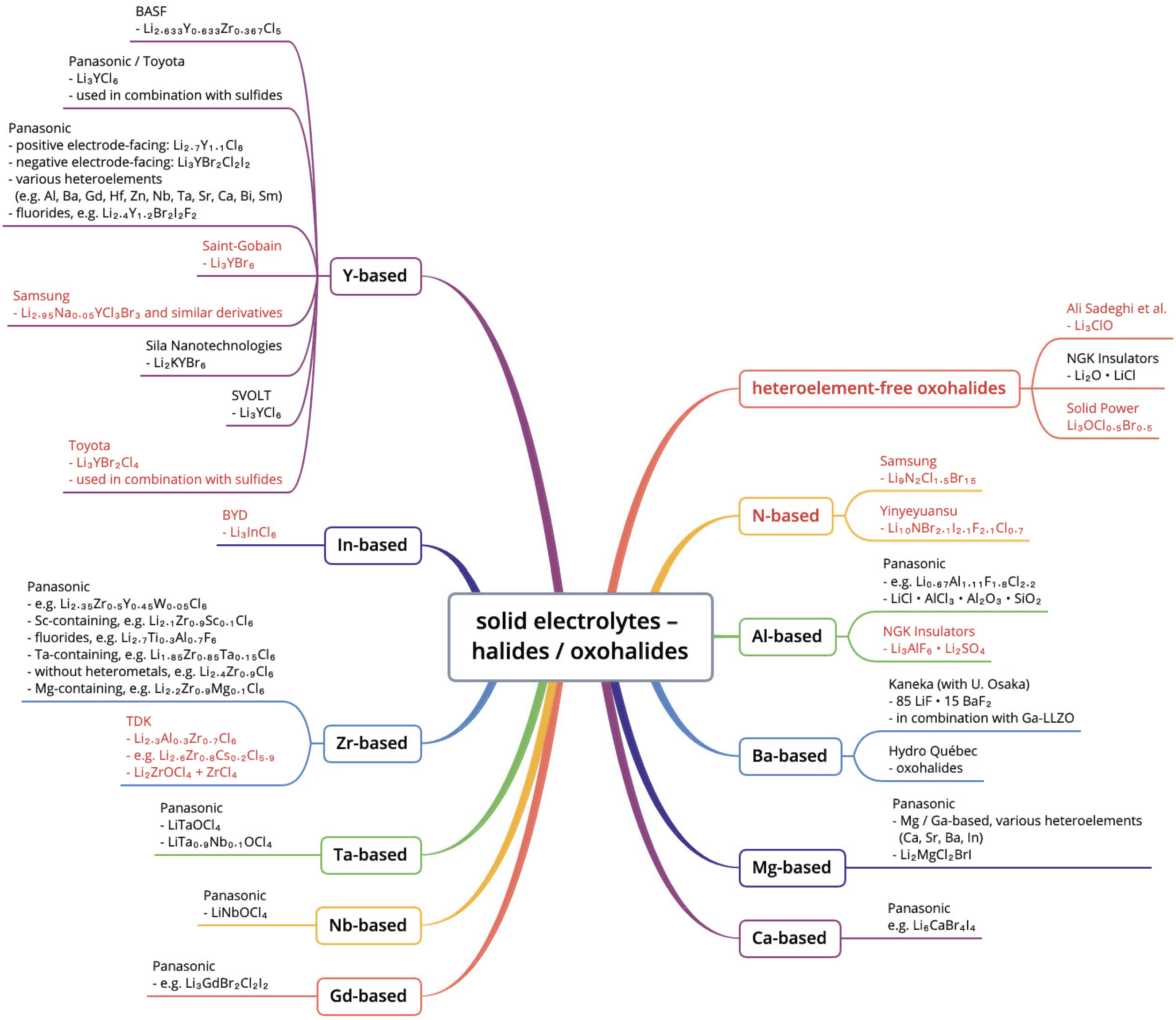


Table 10: raw material / process aspects that could impact costs

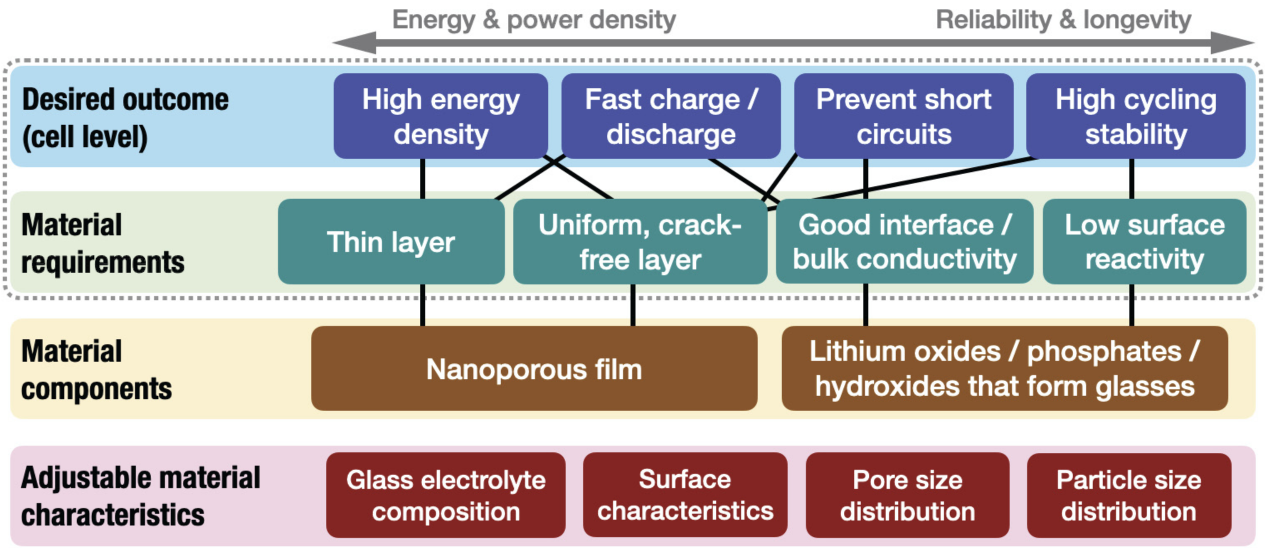
Companies	Critical raw material or process aspects
19 entries	

Under-explored Product Development Approaches

Method 1 – Under-explored Connections Between Decision Trees

Under-explored product development approaches below were identified by contemplating on the decision trees in Figures 3-31 and trying to find connections between them. Surely, many other examples can be identified by our readers that will lead to improved lithium-ion semi-solid and solid-state batteries.

Figure 132: potential synergies between two material classes



Assessment of Companies

Author comments are displayed in maroon.

Contemporary Amperex Technology (CATL) – China

Organization profile

Contemporary Amperex Technology Limited (CATL, https://www.catl.com/en/) is the world's largest Li-ion battery producer. CATL was founded in 2011 in Ningde, China. In 2017, CATL has completed a split from its parent company ATL/TDK. A commercial sodium-ion battery was launched in 2021. With BRUNP Recycling (subsidiary), and Dynanonic (publicly traded, >60% floating stock), CATL jointly develops positive electrode active materials. CATL recently launched LMFP-based M3P liquid electrolyte Li-ion batteries along with Qiling packs ('cell-to-pack' architecture).

Unique capability: supramolecular ionic liquid / polymer / lithium salt electrolytes with very favorable ion conductivity (up to 2.4×10^{-3} S/cm) and high boiling point (>438 °C), along with corresponding cells with lithium metal negative electrodes.
Leap of faith: the toxicity of triphenylene-containing electrolytes will be acceptable.
Comment: this work could finally enable the operation of lithium metal negative electrodes at room temperature and below with favorable fast charge / discharge characteristics (along with favorable energy density), without employing scarce elements in the electrolyte (aside from lithium). The use of triphenylene-containing ionic liquids requires sufficiently strict protocols during manufacturing, operation and recycling to avoid PAH (polycyclic aromatic hydrocarbon) contamination.

Possible material / cell / process characteristics (estimate based on public information)

- **Electrolyte:** supramolecular ionic liquids with triphenylene cores and (optionally fluorinated) ethylene oxide oligomers / lithium sulfonate groups (Figure 71, top) exhibit an ion conductivity of up to **6.5×10^{-3} S/cm** (R_1 / R_2 groups on the left). This ionic liquid was combined with (PEO / PVDF) and LiTFSI (10-80 : 100 : 5-40 by mass, 100 corresponds to combined mass PEO / PVDF) to form electrolyte films (25 µm thickness) with an ion conductivity of **2.4×10^{-3} S/cm**. Boiling point: >438 °C.
- **Negative electrode:** lithium metal. Although Li metal processing patents have been filed by CATL, employment of an ‘anode-free’ cell design is also a possibility.
- **Positive electrode:** NMC9½½ or NMC811 / conductive carbon / PVDF (96 : 2 : 2 by mass), see ‘Lithium-ion Battery High Energy Positive Electrode Innovation & Patent Review’.
- **Design:** stacked multilayer, prismatic cells.
- **Process:**
  1) Mix electrolyte components.
  2) Hot pressing (1-20 MPa, 50-100 °C) to produce electrolyte film.
  3) Vacuum annealing (60-80 °C, 1-8 h).
  4) Electrode and electrolyte layers were laminated through cold-pressing (250 MPa, 25 °C, 2 min) to obtain 10-layer cells.
  5) Encapsulation inside prismatic or pouch cell housing.

News reports and press releases

In April 2023, CATL unveiled its 500 Wh/kg ‘condensed battery’ for electric aircrafts and EVs (additional article). The limited technical details that were disclosed are consistent with the description of supramolecular ionic liquid-based Li metal batteries described in this chapter.

In December 2022, it was reported that companies CATL and CALB have filed lawsuits with respect to each other related to Li-ion battery intellectual property (not related to solid-state batteries).

In August 2022, it was reported that CATL plans to introduce ‘condensed batteries’ in 2023, which according to some experts provides favorable safety, reliability and cycle life by achieving a ‘superfluid state, superconducting state, stability, and superior conduction’.

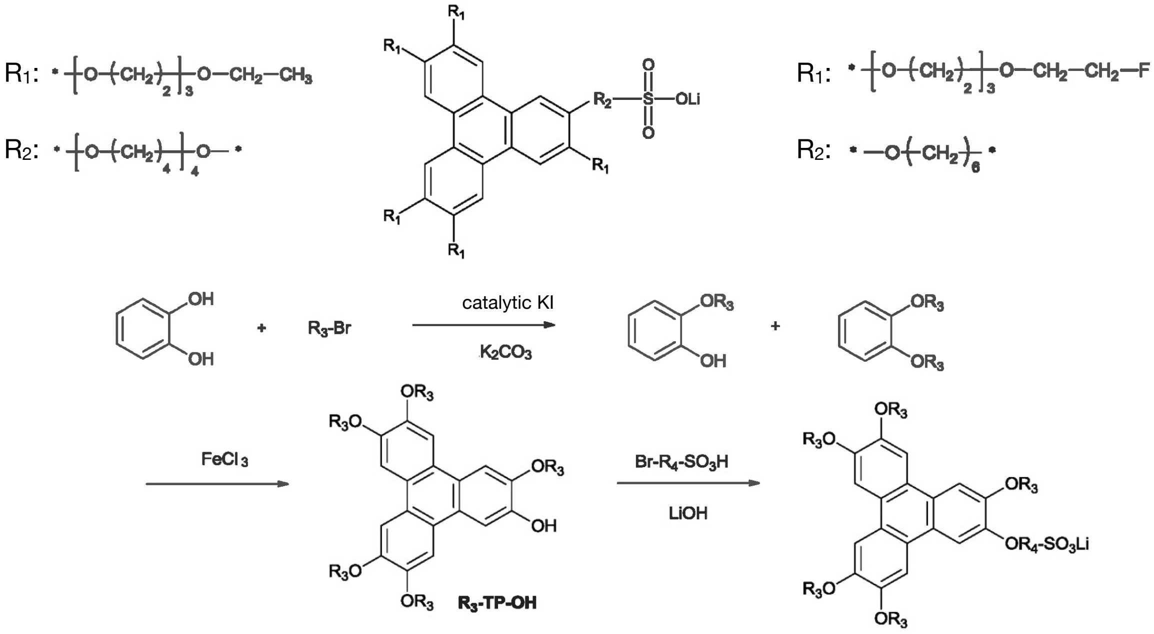
In January 2022, it was reported that CATL expects that 1st generation solid-state batteries with roughly the same energy density as current Li-ion batteries will capture about 1% market share by 2030, while 2nd generation solid-state Li-ion batteries with new positive / negative electrode active materials are expected to emerge after 2030 (additional report).

Examples from the patent portfolio

Level 1) Electrolyte & electrode patents, level 2) cell patents

- SUPRAMOLECULAR IONIC LIQUIDS, SOLID STATE ELECTROLYTE MEMBRANE, SOLID STATE LITHIUM METAL BATTERY, AND DEVICE (Google, published in 2022): **semi-solid electrolyte layer (25 µm):** supramolecular ionic liquids with triphenylene cores and (optionally fluorinated) ethylene oxide oligomers and lithium sulfonate groups (Figure 71) exhibit an ion conductivity of **6.5×10^{-3} S/cm** (R_1 / R_2 groups on the left). This ionic liquid was combined with (PEO / PVDF) and LiTFSI (10-80 : 100 : 5-40 by mass, 100 corresponds to combined mass PEO / PVDF) to form electrolyte films (25 µm thickness) with an ion conductivity of **2.4×10^{-3} S/cm**.
  Negative electrode: lithium metal.
  Positive electrode: NMC811 / conductive carbon / PVDF (96 : 2 : 2 by mass).
  Small-angle X-ray scattering (SAXS) measurements exhibit a channel size of about 17 nm between π-stacked triphenylene units through which Li-ions can diffuse.
  Electrolyte layers were produced through hot pressing (1-20 MPa, 50-100 °C), followed by vacuum annealing (60-80 °C, 1-8 h). Electrode and electrolyte layers were laminated through cold-pressing (250 MPa, 25 °C, 2 min) to obtain 10-layer cells.
  In cycling tests (0.5 C charge / discharge), cells that contain triphenylene molecules with R_1 / R_2 groups shown on the top left of Figure 71 exhibit 409 cycles (prior to reaching 80% remaining capacity cutoff), while cells that contain triphenylene molecules with R_1 / R_2 groups shown on the top right of Figure 71 exhibit 1,002 cycles (ion conductivity of molecule: **4.4×10^{-3} S/cm**, ion conductivity of PEO / PVDF / LiTFSI-containing film: **1.8×10^{-3} S/cm**).

Figure 71: top – two triphenylene derivatives with (optionally fluorinated) ethylene oxide / lithium sulfonate groups. The derivative on the left exhibits particularly favorable ion conductivity (6.5 × 10^{-3} S/cm), while the derivative on the right exhibits particularly favorable cycling stability, bottom – synthesis procedure, OR_3 = R_1, OR_4 = R_2 (CATL)



This work illustrates how very favorable ion conductivity and cycling characteristics can be achieved upon incorporating a polycyclic aromatic hydrocarbon (triphenylene) that undergoes π-stacking interactions to form nano-columns. Supramolecular aggregates presumably are substantially immobile in the electrolyte layer, while providing functional PEG and lithium sulfonate edge groups that promote Li-ion diffusion.

The resulting electrolyte layer apparently prevents short circuits due to lithium dendrite formation by exhibiting sufficient mechanical resistance in the absence of cracks through which lithium dendrites could grow (self-healing character of supramolecular interactions).

The SEI layer that likely forms between the electrolyte and the lithium metal layer presumably is sufficiently supported by the electrolyte layer as not to crack during cycling (avoidance of excess SEI formation).

As triphenylene (without further functional groups) exhibits a boiling point of 438 °C, the safety characteristics of this electrolyte system could be more favorable as compared to plasticizers that exhibit a lower boiling point.

A potential disadvantage relates to the toxicity of polycyclic aromatic hydrocarbons (PAH).

Presumably, a coating on NMC811 is deployed that prevents decomposition of ethylene oxide groups at high voltages.

The synthesis procedure shown in Figure 71 (bottom) suggests that large scale chemical synthesis should be possible without overly expensive reactants or process conditions.

- Solid-state electrolyte membrane, solid-state battery and device (Google, published in 2022): **solid electrolyte layer** (20-30 μm): **Li_6PS_5** / binder (80 : 20 by mass, binder type: probably SBR, screened with specific mesh number, 99 mass% of particles exhibit a particle size of 5-20 μm). Ion conductivity: **1.2 × 10^{-3} S/cm**.

Positive electrode: NMC / Li_6PS_5 / carbon black (Super P, IMERYS Graphite & Carbon) / SBR binder (70 : 24 : 3 : 3 mass ratio), on aluminum foil.
Negative electrode: lithium foil, on copper foil.
Cells with an electrolyte layer thickness of 30 µm (303 Wh/kg energy density) exhibit 165 cycles until 50% capacity is reached (0.1 C charge / discharge). Cells with an electrolyte layer thickness of 20 µm (310 Wh/kg energy density) exhibit 116 cycles under the same conditions. Cells without SBR binder with an electrolyte layer thickness of 30 µm exhibit 9 cycles under the same conditions.
Electrolyte and electrodes were prepared, in case of the electrolyte layer through ball milling (in toluene), in case of the positive electrode through slurry mixing (in NMP). These layers were laminated with the negative electrode (pressing at 300 MPa).
It is argued that a solid electrolyte layer breaking strength of >50 MPa supports favorable electrochemical performance.
This work illustrates the importance of using a mechanically flexible binder in combination with sulfide.

Level 3A) Module / form factor / packaging patents; level 3B) application patents; level 3C) reliability patents

Included in full version

AI Patent Analysis Methodology

The patent information source for this review is the European Patent Office (EPO), which covers patent filings from more than 100 patent offices around the world. >2.4M patent documents are included in the b-science.net database that were published since 1980, which either contain the words 'battery' or 'batteries' in the title or abstract, or were assigned to one of the energy storage-related CPC (cooperative patent classification) or IPC (international patent classification) codes: H01M (batteries & fuel cells) or H01G (capacitors). An AI model was defined for commercially relevant Li-ion battery solid / semi-solid / gel electrolytes. Patent documents were grouped into patent families and scored with the AI model. An AI relevancy score cutoff value of 40 was applied (100: very relevant, 0: not relevant). For companies covered with a chapter, AI scores between 35 and 45 were checked manually and false-positives / false-negatives were corrected if necessary.

Disclaimer

All warranties and liabilities on the part of b-science.net GmbH (LLC) and its affiliates are excluded, including, without limitation, guarantees as to fitness for a specific purpose, non-infringement, accuracy or completeness. Please check our Terms & Conditions and Privacy Policy, which apply to this document.