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

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- Contemporary Amperex Technology Ltd. (CATL)
- LG Energy Solution / LG Chemical
- Panasonic
- ProLogium Technology
- QuantumScape
- Samsung
- SES AI
- Solid Power
- Toyota
- WeLion
- Enpower Greentech / EGI Battery
- 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
- Maxell
- Mitsui Mining and Smelting / Mitsui Kinzoku
- Murata Manufacturing

- Ohara
- Piersica
- PolyPlus
- Qingtao Power
- Sakuú
- SVOLT Energy Technology
- Taiyo Yuden
- TDK
- TeraWatt Technology

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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
Ampcera	'sulfur-stuffed' argyrodite, $Li_8P_3S_{11+n}Cl$ or $Li_{8+2n}P_3S_{11+n}Cl$, n > 0	>1.2 × 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

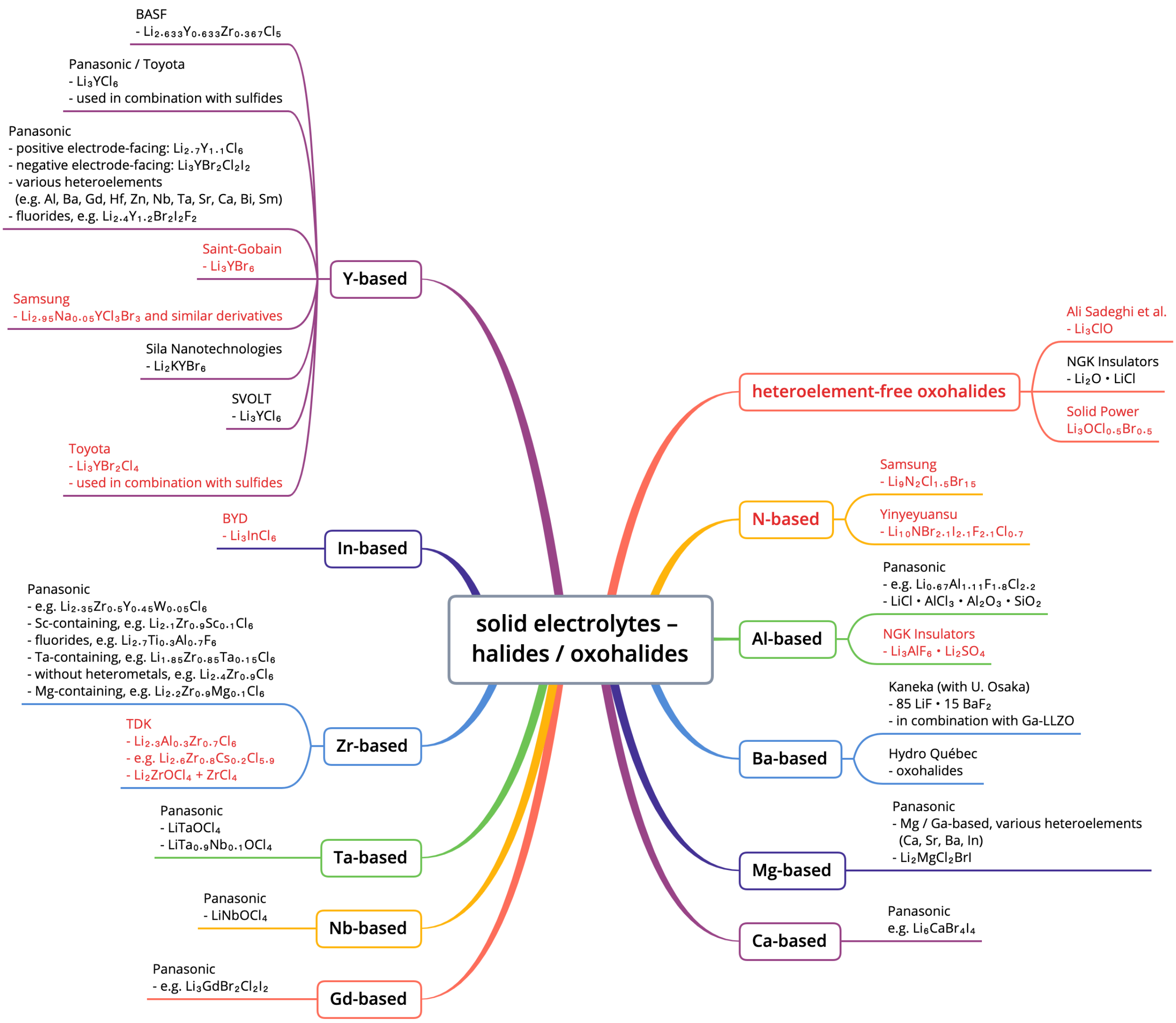
118 additional entries

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

Companies	Critical raw material or process aspects

19 entries

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



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. With BRUNP Recycling (subsidiary), CATL jointly develops positive electrode active materials.

Unique capability: 1) supramolecular ionic liquid / polymer / lithium salt electrolyte membranes with very favorable ionic conductivity (up to 2.4×10^{-3} S/cm) and high boiling point (>438 °C), along with corresponding cells with lithium metal negative electrodes; 2) sulfide electrolyte-based lithium metal cells based on ≥5 complementary concepts to mitigate various failure modes.
Leap of faith: 1) the toxicity of triphenylene-containing electrolytes will be acceptable; 2) the risk of toxic hydrogen sulfide gas emissions when sulfide electrolytes are in contact with water or moisture will not be a showstopper during production, operation and / or recycling.
Comment: approaches 1) and 2) 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).

News reports & press releases

This information is included in the full version.

General patent portfolio characteristics

68 new patent families by CATL related to semi-solid or solid-state Li-ion batteries have been published since 2022 (level 1: 42, level 2: 46, level 3A: 9, level 3B: 1, level 3C: 32, level 3D: 11, see adjacent Excel file). Polymer / oligomer and sulfide electrolytes constitute key patenting focus areas (Figure CA-1).

Figure CA-1: AI-based classification of patent families by CATL published since 2022 related to solid electrolytes categories 1-6. Patents without direct relation to one category (e.g. because of solid-state cell packaging focus) were excluded.

CATEGORY	PATENT COUNT	PERCENTAGE	VISUAL
Category 4: sulfides	23	43.4%	
Category 5: polymers / oligomers	22	41.5%	
Category 6: halides / oxyhalides	4	7.5%	
Category 2 & 3: oxide / polymer composites	3	5.7%	
Category 1: oxides	1	1.9%	

Key Polymer Electrolyte Product Development Concepts

Figure CA-2: AI-based polymer electrolyte product development concept identification (CATL)

Figure CA-2 illustrates how CATL pursues a range of polymer / oligomer-related product development approaches, among which 2 concepts appear complementary, even though no patent has been identified yet that confirms their simultaneous use.

Concept 1: Supramolecular Ionic Liquids, WO 2022021231 A1 (EPO / Google)

KEY FINDINGS

2.4 × 10^{-3} S/cm ionic conductivity in membranes based on supramolecular assembly of ion-channels, comparably low density, based on abundant precursors.

TECHNICAL DESCRIPTION

Benzophenanthrene-based supramolecular ionic liquids with π-π stacking creating ordered ion transport pathways. Ether side chains (1-16 carbons, see Figure CA-3) balance molecular assembly with ion mobility. Synthesis via Williamson reaction and $FeCl_3$ cyclization, resulting in 6.5×10^{-3} S/cm bulk conductivity at 25°C.

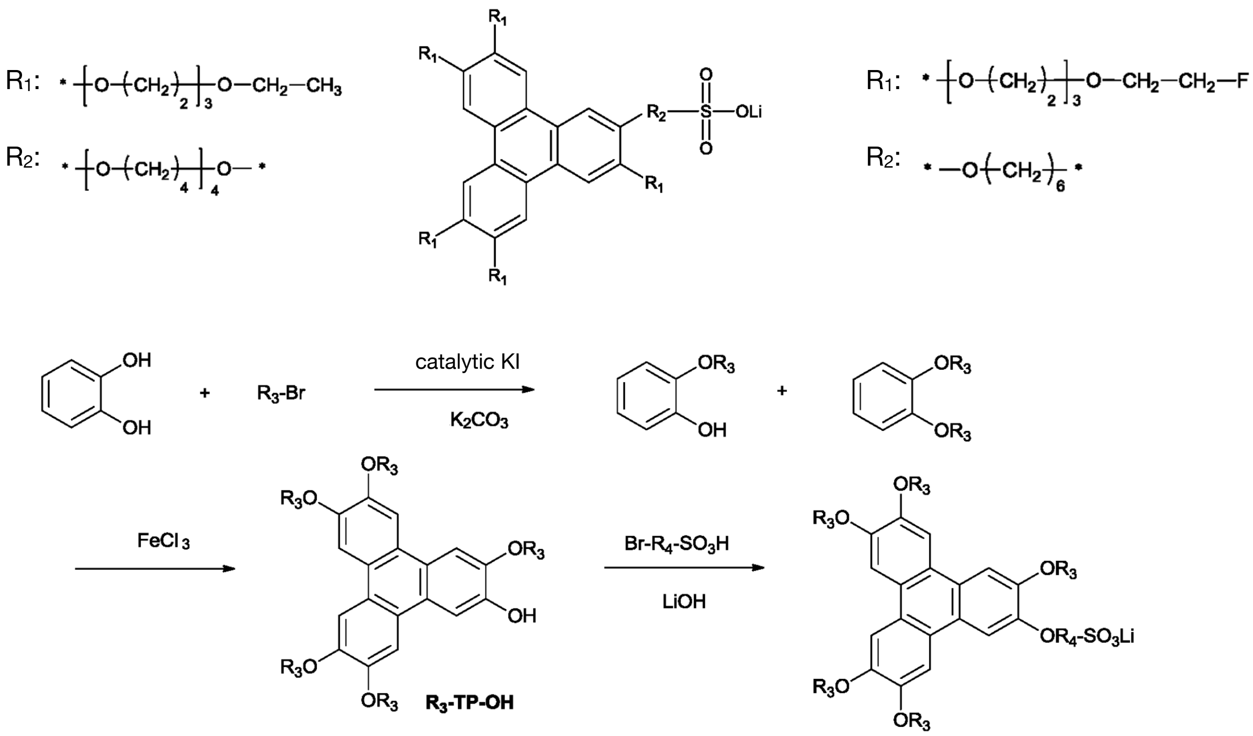
BACKGROUND INFORMATION

Patent WO 2022021231 A1 addresses the polymer ionic conductivity bottleneck. A self-assembly approach results in near-liquid conductivity (2.4×10^{-3} S/cm in membrane), while offering safety advantages for which solid-state Li-ion batteries are known (triphenylene shown in Figure CA-3 exhibits a boiling point of 438°C). Manufacturing is based on organic chemistry and comparably abundant precursors.

ELECTRODE CONFIGURATION

Negative electrode: lithium metal | Positive electrode: NMC811.

Figure CA-3: 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)



<u>The full version includes a discussion of polymer electrolyte product development concepts 2-5.</u>

Potential Synergies Between Concepts

R&D concepts 1 (supramolecular ionic liquids) and 3 (gradient crosslinking systems) offer synergies in terms of overcoming the fundamental trade-offs in solid-state battery development. Concept 1 addresses the critical ionic conductivity bottleneck that has limited solid-state batteries, achieving near-liquid ionic transport through self-assembled molecular architectures. Concept 3 solves mechanical integrity and safety challenges by providing spatially optimized structural reinforcement. The combination could enable solid-state batteries that achieve both liquid-like ionic conductivity and superior structural integrity – previously mutually exclusive characteristics.

Possible Material / Cell / Process Characteristics (Projection Based on Public Information)

- **Electrolyte:** benzophenanthrene-based supramolecular ionic liquids with π-π stacking architecture and ether side chains (1-16 carbons) that exhibit an ionic conductivity of 6.5×10^{-3} S/cm at 25°C (WO 2022021231 A1, Example 22). When integrated with a polymer matrix (PEO/PVDF/LiTFSI at 10-80 : 100 : 5-40 by mass), the composite electrolyte exhibits 2.4×10^{-3} S/cm conductivity. Gradient acrylate crosslinking systems (WO 2024243875 A1) might be incorporated into side chains to tune mechanical characteristics.
- **Negative electrode:** lithium metal on copper foil (WO 2022021231 A1).
- **Positive electrode:** NMC811 with conductive carbon (2 mass%) and PVDF binder (2 mass%) on aluminum current collector (WO 2022021231 A1).
- **Design:** prismatic stacked multilayer cells with favorable deformation resistance (WO 2024243875 A1).
- **Process:**
  1) Supramolecular ionic liquid synthesis via Williamson reaction and $FeCl_3$ cyclization (WO 2022021231 A1).
  2) Sequential or parallel (such as with multi-slurry feeder) injection gradient crosslinking film formation (WO 2024243875 A1).
  3) Hot pressing (1-20 MPa, 50-100°C) with spatially controlled crosslinking density.
  4) Vacuum annealing (60-80°C, 1-8 h).
  5) Electrode and electrolyte layer lamination through cold-pressing (250 MPa, 25 °C, 2 min) to obtain multi-layer cells.
  6) Prismatic cell encapsulation.

Supporting inventions listed in Figure CA-2 (bottom) might additionally be employed in this context.

Key Sulfide Electrolyte Product Development Concepts

The full version includes a discussion of sulfide electrolyte product development concepts 1-5, synergies and possible material / cell / process characteristics.

Highly Relevant Inventions Covered in Recent Triweekly Patent Updates

The full version includes a summary and discussion of 3 additional highly relevant all-solid / semi-solid Li-ion battery electrolyte patents that have been identified during our triweekly patent screening process.

AI-based Patent Summaries

The adjacent Excel file contains AI-based patent summaries for all patents mentioned in this chapter, classified in terms of electrolyte type (Figure CA-1) and level 1 (electrode / electrolyte patents) to level 3D (manufacturing patents).

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