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

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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

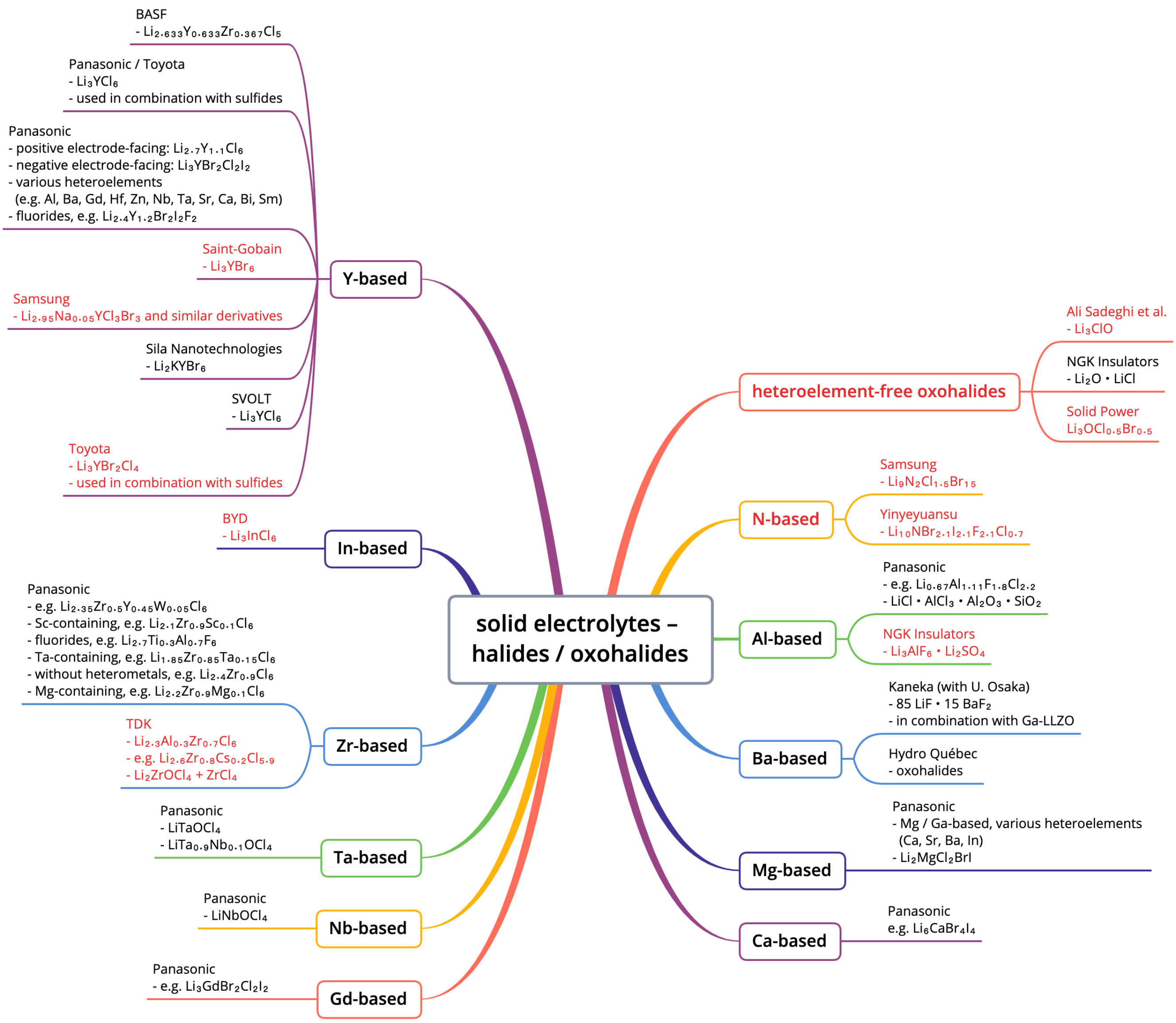
Table 7: ion conductivity of solid electrolytes (as identified in patent applications, in public statements, or by reference to an academic publication); color labels: midnight blue: oxide / phosphate-based electrolytes (may contain polymers, may contain minor amount of halide); mocha: sulfide-based 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.

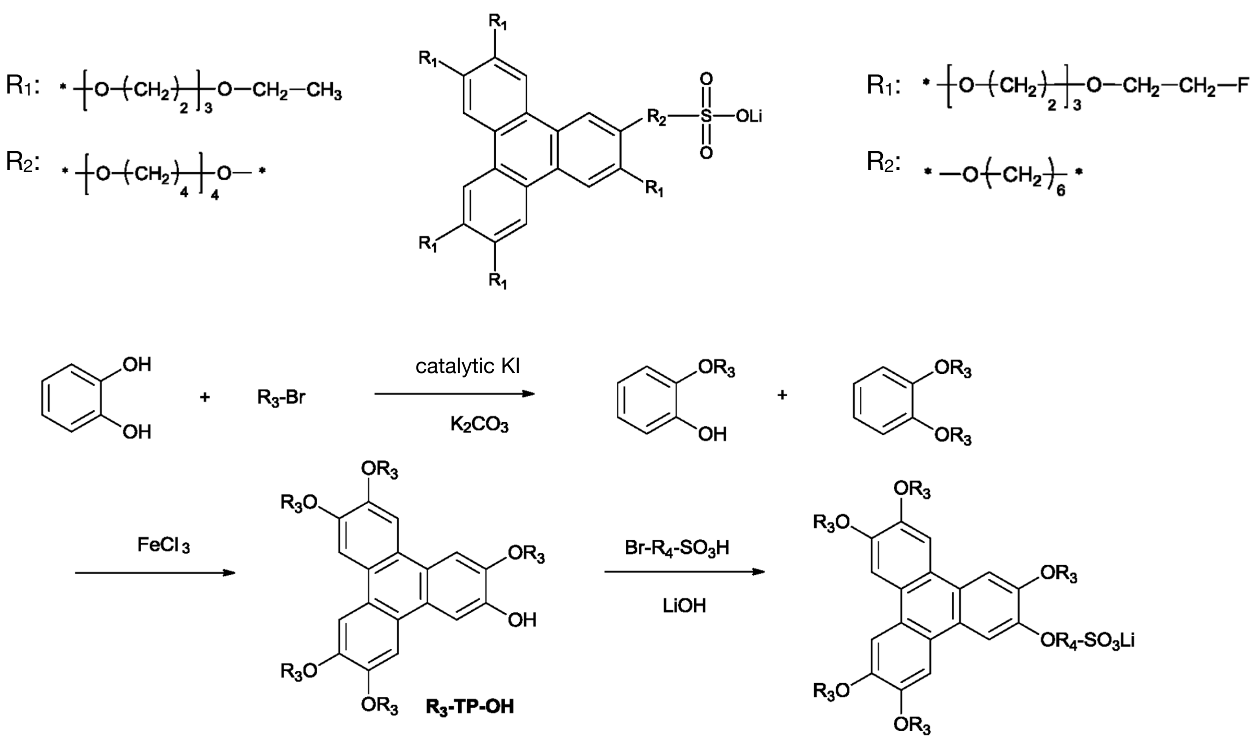
BACKGROUND INFORMATION

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).

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. >3M 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.

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