Solid-state Li-ion Battery Innovation & Patent Review

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  • Toyota
  • LG Chemical
  • Panasonic
  • Bosch/Seeo
  • Samsung
  • Hyundai Motor/Kia Motors
  • BYD
  • IBM
  • Hitachi Chemical
  • Toshiba
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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 1,600 citations.

Introduction

Focus of this Review

This review discusses different technical options chosen by key solid-state lithium-ion battery companies towards obtaining commercial products for different applications. The analysis is based on a proprietary machine learning-supported screening of global patent filings for commercial relevance.

Comprehension of the solid-state Li-ion battery decision tree allows for identification of promising future R&D directions that have not yet been explored, while an understanding of the technology readiness level of each effort allows for the generation of R&D roadmaps and assessments of necessary resources until a commercial product can be launched.

Patent portfolios by key commercial players have been classified into 6 categories and were assigned a patent portfolio readiness level (PPRL).

For tailored patent searches, the machine learning models used for preparation of this review are available to users on b-science.net (scoring based on commercial relevance).

Solid-State vs. Liquid Li-Ion Batteries

The different components of a Li-ion battery cell are shown in Figure 1. Each battery contains a positive electrode or cathode, a negative electrode or anode, and a Li-ion conducting, electrically isolating region that separates these two electrodes, which consists either of a separator soaked with liquid electrolytes or of a solid electrolyte. Frequently, no separator is employed in cells with solid electrolytes. Catholyte and anolyte regions have been annotated specifically because these regions are frequently adapted individually in solid-state batteries to achieve favorable Li-ion conductivity and electrochemical stability at the interface to each electrode.
Advantages of solid vs. liquid electrolytes:

- improved safety because no toxic, flammable or explosive liquid electrolyte can leak.
- improved energy density because a broader set of high energy materials can be used in the electrodes without chemical degradation.

Weaknesses of solid vs. liquid electrolytes:

- with few exceptions, solids are less Li-ion conductive than liquids, which limits power performance (fast charge/discharge).
- mechanical crack formation in solid electrolytes can contribute to aging.

The switch from liquid to solid electrolytes in Li-ion batteries holds the long range promise of energy density increases by a factor of 2-3.

Efforts to replace liquid electrolytes with solid electrolytes go back decades, yet the majority of batteries sold today contain liquid electrolytes.

The Solid-State Li-Ion Battery Market Today

Table 1 illustrates solid-state Li-ion batteries that are already mass-produced, for which initiation of mass production was announced, or that are available for sampling & homologation.

The number of identified suppliers has increased from 4 before December 2017 to currently 11.
Battery Technology Adoption Framework

Our approach to anticipating battery technology adoption is based on four pillars: 1) application requirements; 2) industrial logic; 3) machine learning-supported patent portfolio assessments; 4) public statements & news.

Application Requirements & Industrial Logic

Starting with application requirements, we plot the importance of different factors in Table 2. Based on industrial logic, the arrows indicate a ‘least resistance’ technology adoption pathway that goes along with a growing battery size for each newly accessed application, and with increasing cost sensitivity.
Industrial logic mandates that adoption will start in applications that are not very cost sensitive and require small scale batteries and small volumes. As production scales are increased, costs drop, performance improves across multiple dimensions and new technologies become viable in an increasing number of applications.

Micro-scale thin-film batteries rely on very thin (max. 2.5 µm) solid electrolyte layers to achieve sufficient Li-ion conductivity, which are frequently vacuum deposited with expensive processes. Large scale batteries require sufficiently thick (5-10 µm) electrolyte layers for safety reasons. The solid-state battery market is therefore affected by a non-linear technology switch at around 3 mWh cell size from thin to thick electrolytes with higher bulk Li-ion conductivity that can be deposited with scalable non-vacuum deposition techniques.

**Patent Portfolio Readiness Level (PPRL)**

*Figure 2: Patent Portfolio Readiness Level*

Figure 2 illustrates our approach to assessing the technological readiness of solid-state battery patent portfolios towards market introduction.

**Levels 1 and 2** reflect the typical scientific R&D steps of material research coupled with half cell electrochemical analysis (Level 1), followed by full cell (e.g. coin cell) manufacturing (Level 2).

**Level 3** reflects engineering R&D steps that can be oriented in different directions depending on application requirements. **Level 3A** reflects module & packaging patents - assembly of multiple cells or coverage of a single cell with external sealing, temperature and/or pressure control layers. **Level 3B** covers system integration patents, such as the integration of a battery pack into an electric vehicle. **Level 3C** reflects reliability-focused patents, such as material purity control, sealing, mechanical stability, charge/discharge and heat management, which show that extensive development has occurred towards improving reliability and safety of a solid-state battery technology stack that go beyond an initial ‘proof-of-concept’. **Level 3D** reflects manufacturing patents that confirm solid-state battery production has been implemented already at pilot or industrial scale.

The PPRL correlates quite closely with commercial product availability & time-to-market projections because it measures engineering efforts that are necessary before a product can be launched successfully.
If a technology stack has not yet advanced to level 3, it is not necessarily inferior in terms of innovation potential, but the time-to-market is longer and the risk of unexpected roadblocks is higher.

**Machine Learning-Based Identification of Commercially Relevant Patents**

b-science.net has developed a supervised machine learning methodology to assess the commercial relevance of patents, combined with an automatic translation framework that makes sure Non-English patents are also identified. The methodology was validated as shown in the Appendix. With this unprecedented approach, we can comprehensively identify & classify organizations active in commercial solid-state Li-ion battery R&D. In this study, we have focused on commercial/private companies, while mentioning a few academic projects that have been licensed or were carried out in public/private collaborations.

In Table 4, the number of commercially relevant patents are listed for 67 organizations with at least 6 newly published patent families since 2018.

**Table 4: Number of Commercially Relevant Solid-State Li-Ion Battery Patent Families**

<table>
<thead>
<tr>
<th>Company</th>
<th>2018</th>
<th>2019</th>
<th>2020 (until Feb 14th)</th>
<th>Total</th>
<th>PPRL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toyota</td>
<td>92</td>
<td>170</td>
<td>28</td>
<td>290</td>
<td>3A/B/C/D</td>
</tr>
</tbody>
</table>

IP strategies between companies can vary considerably, as some companies file a patent for most inventions, while others file patents only for key breakthroughs and keep other inventions confidential as trade secrets. For that reason, the innovative strength of a company should not be judged purely based on the number of patent publications.

Some companies make patent filings across many territories, which results in large patent families. Other companies only file for patents in their home market, which results in small patent families that provide only for defensive protection outside of the home market (no one else can file for the same invention once it has been filed in one territory).

**Innovation Decision Tree**

The innovation decision tree reflects how various organizations have made substantially different decisions as to what materials, concepts and engineering targets to focus on in their patenting activity. This decision tree should not be regarded as comprehensive, but hopefully as a source of inspiration for novel inventions. With few exceptions, only recent patenting activity is covered, not patents filed in earlier years that might already have covered a topic listed in the decision tree.

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Figure 11 illustrates the very wide range of evaluated Li-ion conductive polymer alternatives. The versatility of polymer chemistry allows for tuning of electrolytes for favorable interface properties with respect to specific anodes, cathodes, along with performance optimization for specific application requirements (Blue Solutions, Bosch/Seeo, BrightVolt, BYD, Fujifilm, Hitachi Chemical, Hydro Québec individually and with Murata Manufacturing, Ionic Materials, LG Chemical, Lishen, Medtronic, Qingtao Kunshan, QuantumScape, Samsung, Seiko Epson, TDK, Toshiba). It has recently been understood that the electrochemical instability of PEO (and likely also of PEG) at >4 V vs. Li/Li$^+$ can cause insurmountable problems on the road towards commercialization (see study by Gasteiger et al., chapter on Bosch/Seeo). For this reason, in the majority of recently published patents, PEO is used only on the anode side (2-layer electrolytes) or with LFP cathodes operated at <4 V vs. Li/Li$^+$ (Blue Solutions, Hydro Québec, LG Chemical, Medtronic, Qingtao Kunshan, Samsung individually and with Stanford University).

Figure 11: solid electrolytes - organic polymers
Technology Gap Assessment - Liquid vs. Solid Electrolytes

A battery fails commercially if any performance & safety characteristic or costs do not match the requirements of the corresponding application (Table 2). Outperformance in one dimension usually does not compensate the biggest weakness.

In a comparison between liquid vs. solid electrolyte batteries, solid electrolyte batteries generally outperform in terms of safety, energy density, and underperform in terms of power density, manufacturing process efficiency (costs).

The tables below further illustrate how different R&D choices affect the expected performance in comparison to liquid electrolyte batteries.

Energy Density - Cathode & Anode Material Selections

Table 6: Targeted Energy Density

<table>
<thead>
<tr>
<th>Companies</th>
<th>Cathode</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO, NMC, NCA, Ni-Mn spinel, silver vanadium oxide/carbon fluoride</td>
<td>Lithium metal</td>
<td></td>
</tr>
<tr>
<td>LCO, NMC, NCA, Ni-Mn spinel</td>
<td>Si-based</td>
<td></td>
</tr>
<tr>
<td>Li₂CoP₂O₇</td>
<td>LTO or LVP</td>
<td></td>
</tr>
<tr>
<td>LCO, NMC or NCA</td>
<td>Graphite</td>
<td></td>
</tr>
<tr>
<td>LFP</td>
<td>Lithium metal</td>
<td></td>
</tr>
<tr>
<td>LCO or NMC</td>
<td>LTO</td>
<td></td>
</tr>
<tr>
<td>LVP</td>
<td>LVP</td>
<td></td>
</tr>
</tbody>
</table>

Table 6 illustrates how high energy densities are a clear potential medium term advantage of solid-state batteries, while products with comparably low energy density have found market acceptance through superior safety, longevity and suitable form factors.

Power Density - Li-Ion Conductivity of Solid Electrolytes

Table 7: Li-Ion Conductivity of Solid Electrolytes

<table>
<thead>
<tr>
<th>Organization</th>
<th>Possible electrolyte</th>
<th>Approximate Li-ion conductivity at 25 °C unless if otherwise mentioned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Texas University/Porto University &amp; Laboratório Nacional de Energia e Geologia (licensed by Hydro Québec)</td>
<td>‘Li-glasses’ based on dried LiOH, LiCl, Ba(OH)₂</td>
<td>4 * 10⁻² S/cm</td>
</tr>
</tbody>
</table>

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Table 7 illustrates how the bulk Li-ion conductivity of most solid-state electrolytes is lower than for current liquid electrolytes, while professors Goodenough, Braga & coworkers demonstrated exceptional Li-ion conductivity with ‘Li-glasses’. Products have been launched successfully based on solid electrolytes with comparatively low Li-ion conductivities by implementing a short solid electrolyte layer thickness and by targeting applications that do not demand high power performance.

Assessment of Companies

Patent families listed below with initial publication dates after 2018-10-30 (cut-off date prior edition of this review) are labeled orange. Patent families with initial publication dates between 2018-01-01 and 2018-10-30 are displayed in black. Patents families that were published before 2018-01-01 are listed with the publication year in parentheses.

If not mentioned otherwise, Li-ion conductivities have been measured at 25 °C or room temperature.

Suppliers of Solid-State Li-Ion Batteries
(Mass Production or Wide Sampling for Homologation Purposes)

Qingtao Kunshan New Energy Materials - China - PPRL: 3A/B/C/D

Organization profile

Qingtao Kunshan New Energy Materials/Suzhou Qingtao New Energy Technology (http://www.jsqingtao.com/) was founded by Prof. Nan Cewen from Tsinghua University together with PhD graduates in 2014. In 2018, Qingtao Kunshan received investments of 144 Mio. USD.

What's New?

In April 2019, it was reported that solid-state battery production was started, and that Qingtao Kunshan has “successfully realized the industrialization of research and development achievements such as oxide solid electrolyte materials and functional ion conductor ceramic composite diaphragms”.

Recently Published Patent Filings

Recent patent filings focus on two-layer solid electrolytes in which PEO is used at the interface to the anode and electrochemically stable PVDF or PVDF-HFP in combination with a lithium salt is used at the interface to the cathode. Multiple novel manufacturing equipment & process engineering inventions are consistent with statements that batteries are already being manufactured at significant scale.
Innovation profile

In November 2018, Qingtao Kunshan announced the establishment of a 100 MWh/year production capacity for 400 Wh/kg solid-state batteries in Kunshan near Shanghai, to be increased to 700 MWh/year by 2020. The application focus is initially on high-end electronics products and special equipment, to be followed by EVs.

Some patents were filed jointly with SAIC Motor and China Aviation (CALB).

PPRL of solid-state batteries

21 new patent families were published by Qingtao Kunshan since 2018, which correspond to a maximal PPRL of 3A/B/C/D.

The technology stack of Qingtao Kunshan consists of multiple complementary innovations: 1) two layer polymer-ceramic solid electrolytes that simultaneously exhibit high Li-ion conductivity and low resistance at the cathode & anode interfaces; 2) cathode engineering that allows for favorable Li-ion and electric conductivity; 3) flexible aluminum plastic film packaging that allows for flexible batteries; 4) numerous manufacturing equipment & process innovations, e.g. doctor blade coating machine with controlled heating, hot pressing equipment, processing of lithium metal, washing procedure to remove impurities from solid electrolytes.

The potential weakness mentioned in the prior edition of this review (PEO in contact with high voltage cathode materials that cause electrochemical decomposition) has been addressed by employing fluorinated polymers (PVDF, PVDF-HFP) mixed with lithium salts (Table 15) at the interface to the cathode. Presumably, evaluations are ongoing regarding the robustness of these lithium salt/fluorinated polymer layers in terms of maintaining Li-ion conductivity.

Unique capability: comparably large production scale for high energy density medium sized solid-state cells.

Potential roadblock: insufficient power performance for some applications.

Possible cell characteristics

**Negative electrode:** lithium metal (400 Wh/kg cells).

**Electrolyte:** 2-layer solid electrolyte (see Table 15), polyimide polymers might be employed as alternative to PEO in the anode. **Li-ion conductivities at 25 °C for LLTO:** $6 \times 10^{-4}$ S/cm, for **LATP:** $7 \times 10^{-4}$ S/cm, for **LLZTO:** $1.6 \times 10^{-3}$ S/cm.

**Positive electrode:** NMC with 20-60 nm LLZTO or LLZNO coating. Formulation: coated NMC, graphene, PVDF or PVDF-HFP, possibly polypropylene acrylate, perfluoropolyether, lithium salt (80 : 2 : 3 : 10 : 5 by weight).
**Design:** laminate.

**Deposition process:** liquid coating, hot pressing of electrode/electrolyte laminate at 80 °C.

**Examples from the patent portfolio**

**Level 1) Battery materials & electrode patents**

- **Composite solid electrolyte, preparation method thereof and all-solid-state lithium ion battery containing same** ([Google](#)) (Suzhou Qingtao New Energy Technology): 2-layer solid electrolyte with minimized contact resistance to cathode and anode. PEO is used only at the interface to the anode because it is not stable at >4 V vs. Li/Li⁺. PVDF, PVDF-HFP and PAN exhibit favorable performance at the interface to the NMC cathode in combination with multiple oxide or phosphate solid electrolytes (Table 15, Figure 37).

**Table 15: two-layer electrolyte compositions, application examples 1-5 employ two-layer electrolytes described in examples 1-5 in corresponding order (Qingtao Kunshan)**

<table>
<thead>
<tr>
<th>Electrolyte layer composition</th>
<th>First solid electrolyte layer</th>
<th>Second solid electrolyte layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First polymer electrolyte</td>
<td>Oxide solid electrolyte</td>
</tr>
<tr>
<td>Li salt</td>
<td>LiClO₄ 10 weight%</td>
<td>PVDF-HFP 10 weight% LLTO</td>
</tr>
<tr>
<td>Example 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 2</td>
<td>LiTFSI 25 weight%</td>
<td>PVDF none</td>
</tr>
<tr>
<td>Example 3</td>
<td>LiPF₆ 50 weight%</td>
<td>PAN LATP 15 weight%</td>
</tr>
<tr>
<td>Example 4</td>
<td>LiTFSI 20 weight%</td>
<td>PVDF none</td>
</tr>
<tr>
<td>Example 5</td>
<td>LiSO₂CF₃/LiFSI (3:1) 30 weight%</td>
<td>PVDF LLZTO 20 weight%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test cell</th>
<th>Lithium metal anode</th>
<th>Graphite anode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Energy density (Wh/kg)</td>
<td>Specific capacity (mAh/g)</td>
</tr>
<tr>
<td>Application example 1</td>
<td>376</td>
<td>196</td>
</tr>
<tr>
<td>Application example 2</td>
<td>382</td>
<td>200</td>
</tr>
<tr>
<td>Application example 3</td>
<td>364</td>
<td>185</td>
</tr>
<tr>
<td>Application example 4</td>
<td>371</td>
<td>192</td>
</tr>
<tr>
<td>Application example 5</td>
<td>392</td>
<td>203</td>
</tr>
</tbody>
</table>
• **Novel solid electrolyte and preparation method thereof** (Google) (Suzhou Qingtao New Energy Technology): solid electrolyte that exhibits reduced interface resistance with respect to lithium metal anodes, based on polyimide, lithium salt (e.g. LiClO₄), ceramic powder (e.g. LLZO), polyurethane (10 : 10 : 5 : 0.2).

• **A composite conductive coating aluminum foil for solid-state battery and a preparation process thereof** (Google) (Suzhou Qingtao New Energy Technology): current collector coating to reduce contact resistance between current collector and cathode, based on acetylene black, PVDF binder, LiTFSI, LLZO (80 : 5 : 10 : 5 by weight).

• **Preparation method and application of high-voltage cathode material suitable for core-shell structure of polymer-based solid electrolyte** (Google) (Qingtao Kunshan New Energy Material Research Institute): mechanochemical coating of high voltage NMC with LLZTO or LLZNO (20-60 nm). **Cathode formulation**: coated NMC, graphene, polypropylene acrylate, perfluoropolyether, LiBF₄ (80 : 2 : 3 : 10 : 5 by weight).

• **Preparation method of polymer-added composite cathode and application of composite cathode in solid-state battery** (Google) (Qingtao Kunshan Energy Development, with China Aviation): polymers based on long chain polyurethane/polyethylene oxide, reacted with a lithium salt & solid inorganic electrolytes: Li₇La₃M₂O₁₂ (M = Zr, Ta). Ionic liquids are added to the electrolyte in some cases.

• **Organic silicon-based buffer layer used for solid state batteries, preparation method and application thereof** (Google) (Qingtao Kunshan Energy Development): electrolyte based on PC/polydimethylsiloxane/LiTFSI/lithium niobium titanium oxide (70 : 5 : 10 : 15) with low impedance in NMC/graphite cells.

• **Electrolyte membrane and preparation method thereof** (Google) (Qingtao Kunshan Energy Development): polymer (e.g. PEO)-ceramic (lithium niobium titanium oxide or lanthanum...
zirconium oxide with 500 nm diameter) hybrid solid electrolyte that also contains a lithium salt (e.g. LiTFSI).

- **PMMA-based buffer layer for solid-state battery, preparation method thereof and application thereof (Google) (Qingtao Kunshan Energy Development):** PMMA-based buffer material that is mixed with the solid electrolyte to increase cycling stability.

- **Silicon-carbon composite negative electrode for solid-state batteries and preparation method of silicon-carbon composite negative electrode (Google) (Qingtao Kunshan Energy Development):** silicon-carbon anode for solid-state batteries.

- **Composite silane coupling agent ternary composite positive electrode material for solid-state battery, and preparation method and application thereof (Google) (Qingtao Kunshan Energy Development with China Aviation):** use of a silane coupling agent on the cathode surface for improved adhesion to the solid electrolyte layer.

### Level 2) Cell patents

- **Polyacrylate solid polymer electrolyte and preparation method thereof and application thereof in solid lithium battery (Google) (Qingtao Kunshan Energy Development):** polyacrylate-based solid polymer electrolyte mixed with lithium perchlorate, lithium trifluoromethanesulfonate or a similar lithium salt and an azo or peroxide initiator. For example, lithium-rich LMO cathodes and lithium metal anodes are used.

- **Synthesis of solid-state lithium battery as well as preparation methods of graphite composite negative plate and LiFePO4 composite positive plate (Google) (Qingtao Kunshan Energy Development):** cells based on PEO polymer electrolytes, LFP cathodes and graphite anodes.

### Level 3A) Module & packaging patents

- **Integrated flexible solid-state lithium ion battery and preparation method thereof (Google) (Qingtao Kunshan Energy Development):** flexible solid-state battery based on oxygen- and water-blocking polymers, e.g. polyimides.

### Level 3B) Application patents

- **Flexible all-solid lithium ion battery and preparation method thereof (Google) (Qingtao Kunshan Energy Development):** flexible battery for wearable and portable electronics applications.

- **Composite negative electrode sheet for flexible solid state lithium ion battery and preparation method thereof and application thereof in solid lithium ion battery (Google) (Qingtao Kunshan New Energy Material Research Institute):** anode with optimized bending properties for flexible applications.

### Level 3C) Reliability patents

- **The invention discloses a device applied to solid-state battery assembly (Google) (Suzhou Qingtao New Energy Technology):** solid-state cell assembly equipment in which vacuum is employed to prevent bubble formation, which leads to decreased contact resistance.

- **A method for preventing PVDF slurry discoloring gel of lithium lanthanum zirconium tantalum oxide (Google):** washing procedure for LLZO with isopropanol to prepare solid electrolyte slurries with higher reproducibility.

- **Novel high-safety lithium ion battery and preparation method thereof (Google):** solid-state battery with favorable high temperature and safety performance.

- **Novel high-security lithium ion battery and process of manufacturing same (Google):** solid-state battery that contains a diaphragm (separator).
Level 3D) Manufacturing patents

- **Organic-inorganic composite electrolyte, preparation method thereof, and application in solid lithium ion secondary battery** (Google) (Suzhou Qingtao New Energy Technology): hybrid electrolyte film: 1) medium-temperature viscoelastic-transformable polymer based on methyl methacrylate and methoxy polyethylene glycol acrylate monomers; 2) LLZO; 3) LiTFSI. Advantages are favorable Li-ion conductivity along with convenient processing of the electrolyte film at elevated temperature in combination with favorable adhesion to the electrodes at room temperature.

- **Preparation technology of solid-state lithium ion battery** (Google) (Qingtao Kunshan New Energy Material Research Institute): fabrication of aluminum plastic film pouch cells based on 2-layer electrolyte: 1) LLZO, PTFE; 2) LiTFSI, polyether silane plus a minor amount of EC, manufacturing steps: deposition of NMP slurries and hot pressing (0.12 MPa/85 °C).

- **Lithium negative electrode device for simplifying battery assembly and preparation method thereof** (Google) (Qingtao Kunshan Energy Development, with SAIC Motor): manufacturing process for optimal lithium electrode/solid electrolyte (e.g. LLZO) interface.

- **Preparation technology of solid-state lithium ion battery** (Google) (Qingtao Kunshan New Energy Material Research Institute): doctor blade coating machine with controlled heating.

- **All-solid-state lithium ion battery interface improved hot pressing process** (Google) (Qingtao Kunshan New Energy Material Research Institute): hot pressing process for optimal interface between electrodes and solid electrolyte, suitable for mass production.

- **Composite anode for all-solid lithium ion battery and preparation method thereof** (Google) (Qingtao Kunshan New Energy Material Research Institute): electrode manufacturing process.

Patent Analysis Methodology & Validation

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. >1.8 Mio. patent documents are included in the b-science.net database that were published between 1980 and February 14th, 2020 (cutoff date for this review), 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). Patent families that were not available in English in the EPO database were Google machine translated (titles, abstracts, applicants). Some Google translations of applicants were manually corrected. An analysis of all patent families published since 2018 was carried out with a proprietary supervised machine learning (ML) approach based on titles, abstracts, applicants and IPC classifications. An ML model was defined for commercially relevant Li-ion battery solid/gel electrolytes that consists of several thousand patent relevancy data points. Patent documents were grouped into patent families and were scored with the ML model. An ML relevancy score cutoff value of 40 was applied (100: very relevant, 0: not relevant). Scores between 40-70 were checked manually and false-positives were eliminated if necessary. Aside from a few exceptions, only private/commercial companies are included in this review.
The methodology was validated with patent families published by BYD (2018 - February 14th, 2020). 35 patent families by BYD were manually classified as commercially relevant with respect to solid-state Li-ion batteries and 675 patent families were manually classified as not relevant. Of these 35 commercially relevant patent families, 34 exhibit an ML relevancy score of ≥40, and 1 patent family exhibits an ML relevancy score of <40 (3% false negatives, 0% false positives).

List of Abbreviations

ASR  Area Specific Resistance
BET  Brunauer–Emmett–Teller (theory used to determine surface area through gas adsorption measurement)
BMS  Battery Management System
BOB  Bis(oxalato)borate (non-coordinating anion)
CMOS  Complementary Metal-Oxide-Semiconductor
CVD  Chemical Vapor Deposition
DBP  Dibutyl Phthalate (plasticizer)
DMC  Dimethyl Carbonate (liquid electrolyte component)
EBSD  Electron Backscatter Diffraction
EC  Ethylene Carbonate (liquid electrolyte component)
EMIM or EMI  1-Ethyl-3-methylimidazolium (ionic liquid cation)
EPMA  Electron Probe Microanalyzer
FIB  Focused Ion-Beam
FSI  Bis(fluorosulfonyl)imide (non-coordinating anion)
Ga-LLZO  e.g. Li_{6.55}Ga_{0.15}La_{2}Zr_{2}O_{12} (solid electrolyte)
HTPP  Trimethylolpropane Ethoxylate Triacrylate (UV-curable monomer)
IoT  Internet of Things
ITO  Indium Tin Oxide
LAGP  e.g. Li_{1.5}Al_{0.5}Ge_{1.5}(PO_{4})_{3} (solid electrolyte)
LATP  e.g. Li_{1.3}Al_{3}Ti_{1.7}(PO_{4})_{3} (solid electrolyte)
LCO  Lithium Cobalt Oxide, LiCoO_{2} (Li-ion battery cathode material)
LFP  Lithium Iron Phosphate, LiFePO_{4} (Li-ion battery cathode material)
LiBON  Lithium Boron Oxynitride (solid electrolyte)
LiPON  Lithium Phosphorus Oxynitride (solid electrolyte)
LiSICON  Lithium Super Ionic Conductor, e.g. Li_{3.5}Ge_{0.5}V_{0.5}O_{4} (solid electrolyte)
LLTO or LLT  e.g. La_{0.57}Li_{0.23}TiO_{3} (solid electrolyte)
LLZ or LLZO  e.g. Li_{7}La_{3}Zr_{2}O_{12} (solid electrolyte)
LLZ-MgSr  e.g. Li_{6.95}Mg_{0.15}La_{2.75}Sn_{0.25}Zr_{2.0}O_{12} (solid electrolyte)
LLZNb or LLZNO  e.g. Li_{6.8}La_{2}Zr_{1.8}Nb_{0.2}O_{12}, Li_{6.5}La_{2}Zr_{1.8}Nb_{0.5}O_{12} (solid electrolyte)
LLZTO  e.g. Li_{6.5}La_{2}Zr_{1.5}Ta_{0.5}O_{12} (solid electrolyte)
LMO  LiMn_{2}O_{4} (positive electrode material)
LSTPS  e.g. Li_{10}Si_{0.5}Sn_{0.5}P_{2}S_{12} (solid electrolyte)
LTO  Li_{4}Ti_{5}O_{12} (negative electrode material)
LVP  Li_{3}V_{2}(PO_{4})_{3} (positive electrode material)
MEEP  Poly[bis((methoxyethoxy)ethoxy)-phosphazene] (polymer)
MLCC  Multilayer Ceramic Chip Capacitor
MOF  Metal-Organic Framework
NBR  Nitrile Rubber (binder)
NCA  Lithium Nickel Cobalt Aluminum Oxide, LiNiCoAlO$_2$  
     (Li-ion battery cathode material)
NMC  Lithium Nickel Cobalt Manganese Oxide, LiNiCoMnO$_2$  
     (Li-ion battery cathode material)
PAN  Polyacrylonitrile (Li-ion conducting polymer/binder)
PC  Propylene Carbonate (liquid electrolyte component)
PDMS  Polydimethylsiloxane (polymer)
PEEK  Polyether Ether Ketone (polymer)
PEGDME  Polyethylene Glycol Dimethyl Ether (Li-ion conducting oligomer)
PEO  Polyethylene Oxide (Li-ion conducting polymer)
PMMA  Poly(methyl Methacrylate) (polymer)
PPC  Polypropylene Carbonate (Li-ion conducting polymer)
PPO  Polyphenylene Ether (polymer)
PPS  Polyphenylene Sulfide (polymer)
PVA  Polyvinyl Alcohol (polymer)
PVB  Polyvinyl Butyral (polymer)
PVD  Physical Vapor Deposition
PVDC  Polyvinylidene Chloride (sealant)
PVDF  Polyvinylidene Difluoride (binder)
PVDF-HFP  Poly(vinylidene Difluoride-co-hexafluoropropylene) (binder)
PTC Resistor  Positive Temperature Coefficient Resistor
PTFE  Polytetrafluoroethylene (binder)
SBR  Styrene-Butadiene Rubber (binder)
SEI  Solid Electrolyte Interphase  
     (intermediate layer between electrode and electrolyte)
SMD  Surface-Mount Device
SSA  Specific Surface Area (usually determined using a BET measurement)
VGCF  Vapor Grown Carbon Fibers (conductive additive)
TFSI  Bis(trifluoromethane)sulfonimide (non-coordinating anion)
TRL  Technology Readiness Level
WDS  Wavelength Dispersive X-ray Spectroscopy

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Iodoboro-oxysulfides with favorable ionic conductivity of up to 1.96 mS/cm (see Table below) and with favorable stability with respect to moisture, air (minimal formation of toxic hydrogen sulfide gas, see Figure below) and lithium metal were synthesized from Li₂S, boron, sulfur, SiO₂ and LiI.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂ content</th>
<th>I content</th>
<th>Ionic Conductivity (mS/cm) with standard deviation of 5 measurements per sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiB₀.₅S₁₀.₅</td>
<td>0</td>
<td>0.5</td>
<td>0.64 ± 0.03</td>
</tr>
<tr>
<td>Li₀.₉₁B₀.₄₆S₁₀.₀₉O₀.₅₉S₁₀.₀₉I₀.₄₆</td>
<td>0.09</td>
<td>0.46</td>
<td>0.55 ± 0.01</td>
</tr>
<tr>
<td>Li₀.₈₃B₀.₄₂S₁₀.₁₇O₀.₃₄S₁₀.₃₄I₀.₄₂</td>
<td>0.17</td>
<td>0.42</td>
<td>0.43 ± 0.01</td>
</tr>
<tr>
<td>Li₀.₈B₀.₆S₁₀.₂O₀.₄S₀.₈I₀.₄</td>
<td>0.2</td>
<td>0.4</td>
<td>1.96 ± 0.04</td>
</tr>
<tr>
<td>Li₀.₇₇B₀.₃₉S₁₀.₂₃O₀.₄₆S₀.₇₇I₀.₃₉</td>
<td>0.23</td>
<td>0.39</td>
<td>1.59 ± 0.04</td>
</tr>
<tr>
<td>Li₀.₇₁B₀.₃₆S₁₀.₂₉O₀.₃₆S₀.₇₁I₀.₃₆</td>
<td>0.29</td>
<td>0.36</td>
<td>1.60 ± 0.02</td>
</tr>
<tr>
<td>Li₀.₆₇B₀.₃₃S₁₀.₃₃O₀.₆₇S₀.₆₇I₀.₃₃</td>
<td>0.33</td>
<td>0.33</td>
<td>1.07 ± 0.02</td>
</tr>
<tr>
<td>Li₀.₅B₀.₅S₁₀.₅O₁₀.₂₅</td>
<td>0.5</td>
<td>0.25</td>
<td>0.093 ± 0.002</td>
</tr>
</tbody>
</table>

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This key invention could allow for solid electrolyte materials that combine high Li-ion conductivity (similar to sulfides) with high stability (similar to oxides). Reduced emissions of hydrogen sulfide upon contact with air is a key advantage during battery cell production (avoidance of super-dry conditions with very low dew point) and during battery operation (improved inherent safety profile that requires less engineering measures to assure no emission of hydrogen sulfide is possible in case of an accident).

Related academic papers:

- **CN 112242555 A (Google)**, Applicant: Contemporary Amperex Technology Co., Ltd. (CATL), Title: Sulfide solid electrolyte sheet and preparation method thereof

Boron-doped sulfide electrolytes that allow for improved Li-ion conductivity, cycling stability along with low surface roughness of the electrolyte film. Borate ester I-1 and pyridine were mixed with sulfide electrolyte, and treated with a variable temperature drying, pressing and sintering program.

![image](image)

Together with the patent filing reported in the patent update from 2020-01-26, this invention could allow for favorable Li-ion conductivity (important for fast charge/discharge) while suppressing Li dendrite formation.

- **CN 112242564 A (Google)**, Applicant: GM Global Technology Operations, Title: Solid state battery with capacitor auxiliary interlayer

To improve interfacial contacts between the negative electrode (102, graphite or Si-containing high energy active material), the positive electrode (104, e.g. based on LiNbO3-coated LiMn2O4) and the solid electrolyte layer (106, sulfide-based), capacitor auxiliary interlayer 118 (example: activated carbon/metal sulfide, such as Li2S) was employed along with separator layer 302 (example: Al2O3, poly(ethylene glycol), methyl ether acrylate, LiTFSI, no capacitive function).

LiTFSI: Lithium bis(trifluoromethanesulfonyl)imide
This invention illustrates how a high surface carbon layer with capacitive properties between the negative electrode and the solid electrolyte could allow for improved fast charge pulse performance.