Solid-State Li-Ion Battery Innovation & Patent Review

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About the Authors

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 also was in charge of a collaboration with the Paul Scherrer Institute, evaluated outside technologies for the corporate strategy department, and made customer visits, including to major 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 1,400 citations.

Michael Schmidt studied economics at the University of Zurich (Switzerland). He started his career in the late 1980ies in the financial world by trading worldwide currencies, futures and options for a bank and a financial institute. He continued his career as a risk manager for a leading consumer goods manufacturer. At the beginning of this century, he worked successfully as a CFO supervising a factory, which belonged to a global holding company. From 2010 until 2015, he was Head of Purchasing and Sales Manager for a major battery materials manufacturer in Switzerland.

Introduction

The Race to Improve Battery Energy Density

Rising raw material prices (e.g. for cobalt, lithium) have an increasing impact on Li-ion battery costs and threaten to undermine historical cost improvements of >10%/year per kWh. These cost improvements have been achieved thus far through process upscaling/innovation, >5% per year, and energy density improvements (energy stored per weight or volume), 3-5% per year.

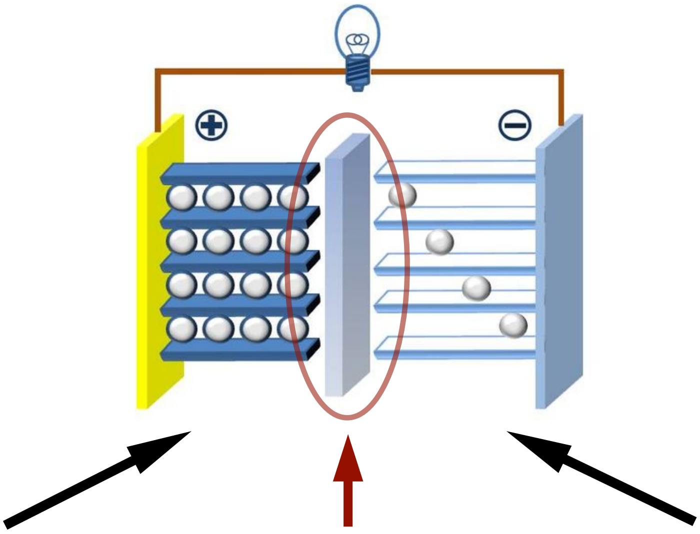
Panasonic/Tesla currently achieve the lowest EV battery pack costs of ca. 110 USD/kWh through minimization of cobalt content in the cathode (ca. 3 mass%), an industry-leading energy density, and highly efficient, large scale production that probably results in superior terms with suppliers.

Scaling up of lithium-ion battery production by a factor of ca. 100 (in kWh) is projected by 2040. This growth will only be feasible if energy density increases substantially, which will reduce the quantity of required raw materials and thus the scale of new mining, production and logistics infrastructure.

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

Solid-State vs. Liquid Li-Ion Batteries

Figure 1: Battery Cell



Positive Electrode / **Separator & Liquid Electrolyte vs. Solid Electrolyte** / Negative Electrode
Image credit: Wikimedia Commons

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**. Generally, no separator is needed for cells with solid electrolytes.

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, whereas liquid electrolytes naturally cannot form cracks.

Efforts to replace liquid electrolytes with solid electrolytes go back decades, yet almost every battery sold today contains liquid electrolytes.

Battery Technology Adoption Framework

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

Application Requirements & Industrial Logic

Table 1: Application Requirements & Battery Technology Adoption Pathway
Dark Blue: High Importance; Light Blue: Low Importance

	Electronics - Integrated Circuits	Medical Implants	Electronics - Mobile Computing	Automotive/ Rolling Stock	Stationary Applications
Safety					
Energy Density					
Power Density					
Longevity					
Variable Temperature Performance					
Cost Sensitivity					
Size	**0.2 mWh**	**0.1 Wh**	**100 Wh**	**200 kWh**	**>1 MWh**

Starting with application requirements, we plot the importance of different factors in Table 1. Based on industrial logic, we then plot a 'least resistance' technology adoption pathway. 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. Industrial logic to us also relates to the experience that technology stacks usually fail at interfaces and interdependencies.

We argue (consistent with TDK/ATL and other early market players) that safety & longevity initially drives adoption of solid-state batteries, e.g. in integrated circuits (ICs) with surface mounted batteries for Internet of Things (IoT) and similar applications. Safety is more important in medical implants and battery sizes are typically larger than in ICs. Therefore, we expect adoption takes a bit longer in this application (see Time-to-Market - Medical Implants).

Upon adoption in medical devices and applications of similar scale, solid-state batteries will likely become economical enough and energy density will have increased sufficiently for adoption in consumer electronics, where solid-state batteries will provide improved safety and the convenience of not having to recharge notebooks every few hours (see Time-to-Market - Electronics Applications).

Adoption in the automotive sector will require sufficient power performance, longevity, robustness at variable temperature and safety at acceptable costs, which will probably be achieved with the help of supercapacitors that protect solid-state batteries from high current peaks (see Time-to-Market - Automotive Applications).

'Violation' of industrial logic by directly targeting the automotive sector is only affordable for very large corporations who can support major investments and pilot trials without short-term payoff. Late stage risk of failure and issues along the supply chain are nonetheless higher than if a new technology is introduced into the market at gradually increasing scale.

Adoption of solid-state batteries will likely occur last in stationary applications, once they are superior in costs and longevity at large volume production.

Patent Portfolio Readiness Level (PPRL)

Figure 2: Patent Portfolio Readiness Level

Level 4C) Upscaling patents
Level 4B) Reliability patents
Level 4A) Application patents
Level 3) Module patents
Level 2) Cell patents
Level 1) Materials patents

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

Levels 1 to 3 reflect the typical 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**). Module manufacturing (**level 3**) typically involves several cells or relates to sophisticated encapsulation.

Level 4A reflects system integration patents, such as the integration of a battery pack into an electric vehicle. **Level 4B** reflects reliability-focused patents for modules, such as 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 module that go beyond an initial module patent. Finally, **level 4C** reflects upscaling patents that confirm solid-state battery manufacturing occurs already at pilot or industrial scale.

If a technology stack has not yet advanced to level 4, it is not necessarily inferior in terms of innovation potential, but the time-to-market is longer and the risk of roadblocks is higher.

Machine Learning-Based Identification of Commercially Relevant Patents

b-science.net has developed a proprietary 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 Table 2, the number of commercially relevant patents are listed for 29 organizations & alliances with at least 10 newly published patent families since 2017.

Table 2: Number of Commercially Relevant Solid-State Li-ion Battery Patent Families

Company/Alliance	2016	2017	2018 (until Oct)	Total (2017/2018)	PPRL
Available in full version.	78	99	93	**192**	**4A/B/C**
	29	36	41	**77**	**3**
	19	20	28	**48**	**3**
	27	25	23	**48**	**materials supplier**
	9	22	25	**47**	**3**
	40	28	18	**46**	**3**
	14	17	23	**40**	**4A/B/C**
	20	25	13	**38**	**4A/B/C**
	35	18	18	**36**	**4A/B/C**
	13	14	20	**34**	**4A**
	6	8	23	**31**	**4A/B**
	17	6	24	**30**	**4A/B/C**
	0	4	23	**27**	**4A/B/C**
	0	0	23	**23**	**3**
	1	7	16	**23**	**3**
	4	5	17	**22**	**2**
	4	1	20	**21**	**3**
	18	11	10	**21**	**materials supplier**
	4	9	10	**19**	**4A/B/C**

Company/Alliance	2016	2017	2018 (until Oct)	Total (2017/2018)	PPRL
Available in full version.	10	9	8	**17**	**2**
	6	9	5	**14**	**materials supplier**
	2	1	12	**13**	**materials supplier**
	4	5	8	**13**	**4A/B/C**
	0	7	6	**13**	**technology supplier**
	1	3	9	**12**	**2**
	9	6	6	**12**	**4A/B/C**
	4	7	3	**10**	**materials supplier**
	1	7	3	**10**	**2**
	11	10	7	**17**	**4B/C**
	1	8	2	**10**	**2**

Discussion available in full version.

The Solid-State Li-Ion Battery Market Today

Table 3: Existing Solid-State Li-Ion Battery Suppliers

Company/Alliance	Country	Year of Market Entry	Application

Time-to-Market Projections by Prospective Solid-State Li-Ion Battery Producers

In Table 4, public statements are listed by prospective solid-state battery producers with a PPRL of at least 3.

Table 4: Time-to-Market Projections by Prospective Suppliers

Company/Alliance	Country	Year	PPRL	Application

11 market entry projections range between 2018 and 2030.

Assessment of Companies & Alliances

Current Suppliers of Solid-State Li-Ion Batteries

TDK/ATL - Japan/China - PPRL: 4A/B/C

Organisation profile

TDK (http://www.global.tdk.com/) produces batteries mainly for electronics applications. In 2005, TDK took over Hong Kong-based Amperex Technology Limited (ATL). TDK/ATL have long been a supplier of lithium polymer batteries to the consumer electronics sector, such as to Apple. CATL has completed its split from ATL/TDK in 2017. The exact IP position of TDK/ATL/CATL is hard to identify because some IP contracts might exist between CATL & ATL/TDK. Nonetheless, we tried to separate these IP portfolios and have included the following patent applicants in this section:
- TDK
- Dongguan Amperex Technology Limited

Innovation profile

At the end of 2017, TDK launched its CeraCharge solid-state battery measuring 4.5 mm * 3.2 mm * 1.1 mm with 100 µAh capacity at a rated voltage of 1.4 V for SMD (surface mount devices) applications, which in 2018 has been commercially available at a scale of 30,000/month. We calculated the volumetric energy density at 9 Wh/L, which is about a third of Cymbet batteries. The unique selling proposition for these devices is not yet energy density, but the absence of potential leaks, risks of fire or explosion, extremely small size, wide temperature range (-20 to 80 °C), mechanical robustness and (as claimed) lower production costs compared to thin-film batteries provided for example by Cymbet.

IOT (Internet of Things), wearable and related devices are targeted, which can function autonomously for years when the solid-state battery is combined with an energy harvesting capability.

PPRL of solid-state batteries

Since 2016, TDK/ATL have filed 47 patent families related to Li-ion solid state batteries. Consistent with having already a product on the market, the TDK/ATL patent portfolio exhibits a PPRL of 4A/B/C.

Purportedly, a ceramic oxide solid electrolyte is used with a multilayer cell design, which is consistent with patent filings shown below. Although we could not find a solid-state battery process patent filing related to a multilayer cell design, TDK has extensive manufacturing capabilities in this area related to its product line of MLCC (multilayer ceramic chip capacitors), as well as extensive SMD application know-how.

The symmetric cell design in a patent filing (LITHIUM ION SECONDARY BATTERY) is consistent with the battery specifications and is described in this related system from an academic standpoint (contact resistance minimization through common NASICON structure).

The fact that multiple solid-state battery module patents were already filed indicates ambitions to expand into further markets, which will require switching to higher energy active materials for which patents have already been filed.

Unique capability: High safety.
Potential roadblock: increase of energy density.

Possible cell characteristics

Negative electrode: $LiVOPO_4/Li_3V_2(PO_4)_3$.
Electrolyte: $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0 \leqq x \leqq 0.6$) (LATP, Li-ion conductivity: ca. 10^{-3} S/cm, reference), polyvinylbutyral binder.
Positive electrode: $LiVOPO_4/Li_3V_2(PO_4)_3$.
Design: multilayer cell design.
Deposition process: similar to MLCC (multilayer ceramic chip capacitors) fabrication processes, liquid film coating.

Examples from the patent portfolio

Level 1) Battery materials patents
- SOLID ELECTROLYTE AND ALL-SOLID LITHIUM-ION SECONDARY BATTERY (TDK): $LiMn_{0.1}Zr_{1.9}(PO_4)_3$ and related phosphates, advantages lie in the avoidance of self discharge, Li-ion conductivity: **$9 * 10^{-6}$ S/cm**.
- SOLID ELECTROLYTE AND ALL-SOLID SECONDARY BATTERY (TDK): $Li_{1.12}Ca_{0.1}Zr_2P_{2.84}B_{0.16}O_{12}$ and related oxides, Li-ion conductivity: **$5 * 10^{-6}$ S/cm**.
- LITHIUM ION CONDUCTIVE OXIDE CERAMIC MATERIAL INCLUDING GARNET-TYPE OR

SIMILAR CRYSTAL STRUCTURE: improvement of Li-ion conductivity based on rare earth element addition: **1.2 * 10^{-3} S/cm**.

Level 2) Cell patents

- Inorganic solid electrolyte film and preparation method thereof and inorganic all-solid-state battery (Dongguan ATL): $Li_7P_3S_{11}$-NBR (nitrile rubber) solid electrolyte membrane, Li-ion conductivity of $Li_7P_3S_{11}$: **2 * 10^{-3} S/cm**. A cell was made based on a lithium metal anode and a LCO cathode coated with lithium niobate, leading to favorable energy density and cycling stability.
- Solid electrolyte, preparation method thereof and all-solid-state lithium secondary battery (Dongguan ATL): solid electrolyte based on Li_2S-P_2S_5-M, M represents a lithium sulfonimide salt, which leads to high ion conductivity (**2 * 10^{-3} S/cm**) and interfacial stability.
- LITHIUM ION SECONDARY BATTERY (TDK): cell with low interface resistance between electrodes and solid-state electrolyte, based on favorable interaction between $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ ($0 \leqq x \leqq 0.6$) electrolyte and $LiVOPO_4$/$Li_3V_2(PO_4)_3$ cathode materials. The solid electrolyte was mixed with a polyvinylbutyral binder.
- LITHIUM ION SECONDARY BATTERY (TDK): all-solid cell architecture with high rate discharge performance and stable cycling due to direct bonding between electrodes and electrolyte.
- All-solid-state polymer lithium battery: based on lithium alloy anodes.

Level 3) Module patents

- SOLID BATTERY AND BATTERY PACK USING THE SAME (TDK): prevention of current leakage between terminals of different batteries.

Level 4A) Application patents

- LAYERED CAPACITOR AND PACKAGING STRUCTURE OF THE LAYERED CAPACITOR; Double sided multi-layer metal substrate PCB with SMD components mounted to top traces and lead wire components mounted to opposite side for heat dissipation (TDK): capacitor SMD patents that can be adapted to solid-state battery SMD applications.

Level 4B) Reliability patents

- ALL-SOLID LITHIUM ION SECONDARY BATTERY (TDK): elastic, moisture-proof cell packaging that leads to high reliability.
- SOLID BATTERY AND BATTERY PACK USING THE SAME: prevention of damage by external forces.
- ALL-SOLID-STATE LITHIUM ION SECONDARY BATTERY (TDK): use of glass layers to protect laminate cells from moisture.
- STATE DETECTING DEVICE (TDK): monitoring of solid-state batteries with sensors, especially during charging.

Level 4C) Manufacturing patents

- Method of manufacturing multilayer electronic component; Method of manufacturing multilayer electronic component (TDK): generic manufacturing processes for multilayer electronic components that can be adapted to solid-state batteries.

Appendix: 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. >1.6 Mio. patent documents are included in the b-science.net database that were published between 1980 and October 30th, 2018 (cutoff date for this module), 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 2016 was carried out with a **proprietary supervised machine learning (ML) framework** based on titles, abstracts, applicants and IPC classifications. An ML model was defined for commercially relevant Li-ion battery solid 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).

The methodology was validated with patent families published by Toyota in 2018. 90 patent families by Toyota were manually classified as relevant. Of these 90 patent families, 4 exhibit an ML score of <40 **(4% false negatives)**. For 7 patent families, the ML score was ≥40 even though they are not relevant **(8% false positives)**.

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