WHERE ARE THOSE PROMISING SOLID-STATE BATTERIES?

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In recent years there have been regular reports about a new generation of batteries in which the liquid electrolyte is replaced by a solid material: the solid-state batteries. With a higher energy density and a better safety than current batteries, solid-state batteries potentially would boost electric mobility by enhancing the driving distance of e-cars and prevent extreme battery fires. Why are they not yet implemented in the latest generation of e-cars?

▲ E-cars will profit from solid-state batteries.

The focus of the development of a solid-state lithium-ion battery is to find solid electrolytes that not only have a good lithium conductivity but also show stable behaviour at the interfaces with the electrode materials in the battery. In addition, the resulting battery design must be fit for commercial mass production. Not an easy challenge. After a short introduction on the working principle of the current lithium-ion battery, we review the options. For details we refer to [1].

Lithium-ion battery with liquid electrolyte

Currently, lithium-ion batteries rely on the use of a liquid electrolyte for the transport of lithium ions between the electrodes (figure 1). The positive electrode is made of a material with strongly bound lithium such as for instance $LiCoO_2$; in the negative electrode, made of, *e.g.*, LiC_6 graphite, lithium is loosely bound. A separator prevents direct contact of the electrodes, but allows lithium-ions to pass. The battery cell is flooded by the liquid electrolyte. It is an organic solution containing lithium salts, which easily penetrates into the pores of the electrodes, thus providing optimal ionic contact. In the charged state, lithium in the negative electrode has a chemical potential energy with respect to the positive electrode. This drives the lithium-ion from the negative electrode material to the positive electrode. Externally, the chemical driving force manifests itself as the battery voltage. Since the electrolyte only allows lithium-ions to pass, the lithium-ions can only migrate from the negative to the positive electrode if the electrodes are electrically connected externally. Once this is the case, the internal chemical energy of the battery is converted into electrical energy during the discharge of the battery.

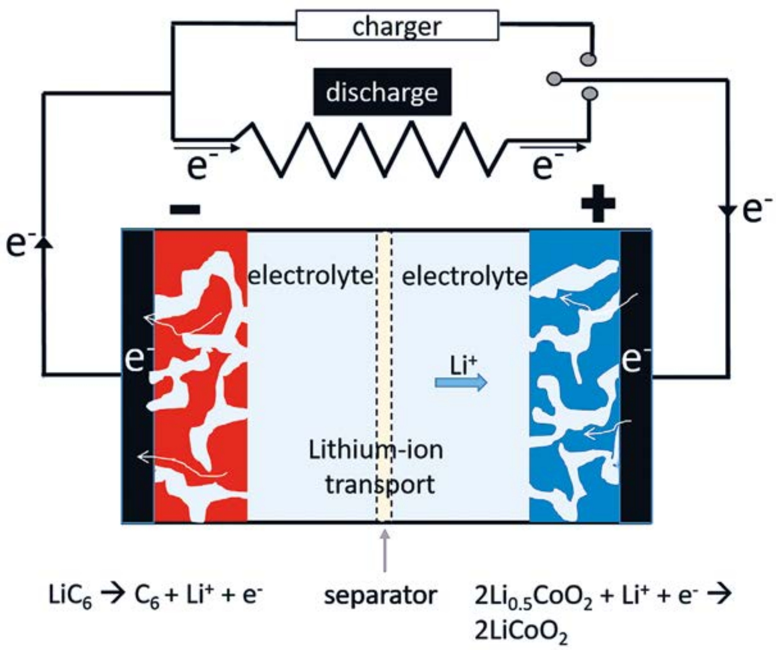
Replacing the liquid electrolyte by a solid electrolyte

Using liquid electrolyte in a battery has a few major drawbacks: Over time, the quality of the contact in the electrodes degrades due to unwanted chemical reactions and consequently the battery performance deteriorates. Additionally, the flammability of the liquid electrolyte and the possibility of leakage present a major safety risk. Replacing the liquid by a solid electrolyte could mitigate both problems. The promise of solid-state batteries is that they would charge quicker, last longer and have a larger energy density. That means that an e-car with a solid-state battery pack could go farther than it would go with an equal-weight conventional lithium-ion battery pack. The application of solid electrolyte materials for energy storage is being studied since more than fifty years. For a long time, the transport of ions such as lithium-ions through the material was not sufficient. However, in the past decade, several breakthroughs have led to solid-state electrolytes with an ionic conductivity that is sometimes even better than that of conventional liquid electrolytes.

Using solid-state electrolyte material would significantly reduce the weight and volume of batteries, because the separator between the electrodes of the battery and a rigid packaging to prevent leakage are both no longer needed. However, no-one has managed to mass produce one at a useful scale yet. It turns out that it is tricky to make them reliable. We go through a couple of options.

Metallic lithium anode

With a solid-state electrolyte it would also become possible to use pure metallic lithium as anode material, or at least, that is the hope. Metallic lithium has an energy density that is ten times higher than that of graphite, which is used in conventional lithium-ion batteries. Other advantages of using metallic lithium are its high electrochemical and thermal stability. However, imperfections at the interfaces between the electrodes and the electrolyte inside the battery can considerably reduce the lifetime and performance of the battery, and can pose safety risks. In addition, the metallic lithium is fragile and reactive, which are features that make mass production of the solid-state batteries challenging.



▲ **FIG. 1:** Schematic of a rechargeable lithium-ion battery during discharge. The electrolyte separating the two electrodes selectively let pass lithium ions. Electrons are therefore forced into the external circuit.

Solid polymer electrolytes

Solid polymer electrolytes offer the best mechanical flexibility. That is attractive for large-scale production of the batteries and to deal with the volumetric changes of the electrodes during battery cycling. Lithium salts are dissolved in the polymer solution to form positive (cations) and negative (anions) parts in the polymer material. The lithium-ion transport is mediated by the movements of the polymer chains. Higher conductivities of the material is achieved by making the polymer chains more flexible and by fixing the anions such that lithium-ions can move more freely. In this way, the goal is to achieve room-temperature operation of this type of batteries.

Ceramic sulfide electrolytes

Ceramic materials are characterised by a regular crystalline structure with sufficient space for small ions such as lithium to move through them. Lithium-conducting sulfides have an ionic conductivity close to that of conventional liquid electrolyte batteries. Extremely high lithium-conductivity can be achieved by replacing certain elements in the sulfides that make the Li-ion mobility higher. The current record holder is the complex $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ with a lithium conductivity of 25 mS · cm^{-1}, which is more than twice the conductivity of liquid electrolytes in current Lithium ion batteries, which is typically 10 mS · cm^{-1}. The mechanical softness of the sulfide-based solid electrolytes which are known as Lithium Super Ionic CONductors or LISICON, allow for good contact at the interface with the electrode. Unfortunately, the electrolytes also have major drawbacks. They are not stable when in contact with the electrodes: the solid electrolyte is oxidised by the positive electrode and/or reduced by the negative electrode, which lowers the conductivity. In addition, they can generate the harmful gas H_2S when they come in contact with water, making large-scale fabrication challenging.

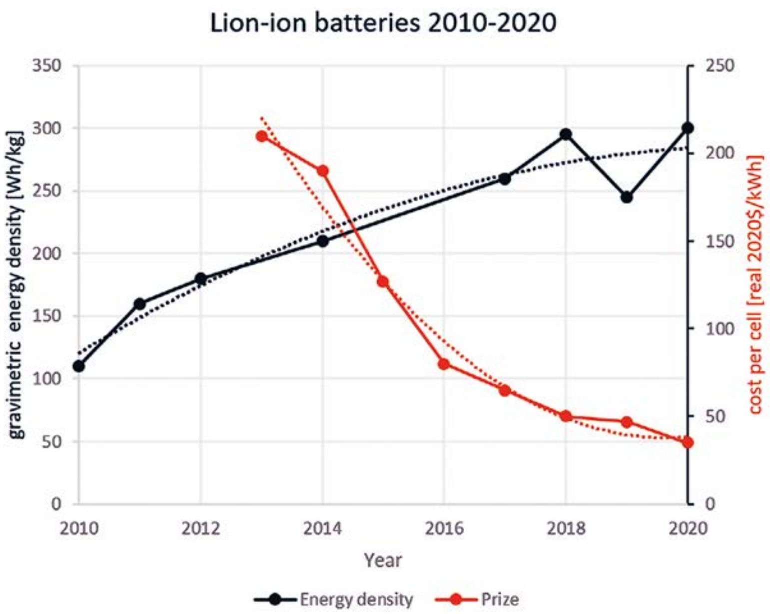
Crystalline oxide electrolytes

In the early 1990s, for the first time oxide materials were used as electrolyte. However, due to the amorphous interlayers of the material , which have no structural arrangement, the batteries had a poor mechanical stability and a low lithium conductivity. In the same period also the first crystalline oxide electrolytes were developed, which had a higher conductivity of lithium-ions because of the regular crystal structure. However, they still had a limited stability when the electrolyte came into contact with a negative electrode of pure metallic lithium. Fortunately, after 2000, it was shown that the crystalline $Li_7La_3Zr_2O_{12}$ was more stable and can work in combination with Li-metal negative electrodes, practically without undesired reactions. By partial replacement by other elements such as Aluminium, Tantalum, Niobium or Gallium, the structure is being further optimised. Currently, among oxide-based electrolytes $Li_{6.65}Ga_{0.05}La_{2.95}Ba_{0.05}Zr_{1.75}Ta_{0.25}O_{12}$ has the best lithium-conductivity of $7 \cdot 10^{-4}$ $S \cdot cm^{-1}$.

Stability of solid-state batteries

The electrochemical stability of a solid-state electrolyte when in contact with the electrodes determines the choice of electrode material and thus the voltage range of the battery. If the electrochemical contact is not stable, the electrolyte will oxidise or reduce, leading to a decomposition at the electrode interface and to unwanted, low-conducting reaction products. Contrary to initial reports of high stability for various solid-state electrolytes, today most materials which are optimal for high energy density unfortunately appear to be unstable in contact with electrodes. Theoretical models of the stability range of promising electrolytes which are in good agreement with the experimental data show that currently there is no solid-state material that has the extremely high lithium-conductivity that meets the desired voltage range for electrode combinations that are necessary to achieve a high energy density. A possible solution is to prevent the electrolyte from decomposing by placing protective thin layers between the electrodes and the electrolyte. The challenge is to develop the structure of such protective layers for controlled and large-scale production.

▾ **FIG. 2:** Trends in the gravimetric energy density and price of Lithium-ion battery in the period 2010-2020. Data source: BloombergNEF.



Hybrid electrolytes

In addition to single-phase solid electrolytes, hybrid systems such as solid-liquid or polymer-ceramic electrolytes are also being considered. In a composite of a polymer with a ceramic electrolyte, the ceramic would offer high mechanical stiffness and high ionic conductivity while the polymer provides flexibility, simplified fabrication and scale-up and improved electrode adhesion. Again, as in the case of single-phase solid electrolytes, the challenge is to find materials which provide a stable interface between the composite electrolyte and the electrodes in combination with a high Li-ion conductivity.

Modelling

The trial-and-error search for promising new solid electrolyte materials that meet the high standards of ionic conductivity and stability is time consuming and expensive. Therefore, data-driven classification models for ionic conductivity using advanced machine learning algorithms are used to distinguish between potential solid electrolytes with highly conductive and low conductive ionic structures. Density functional theory (DFT) and molecular dynamics (MD) simulations are performed to study the structural properties of the most promising materials, taking into account the basic quantum mechanical interactions of atoms. Also in current working batteries the degradation processes using innovative characterisation techniques is extensively studied. For example, both the ion and the electron dynamics as well as the chemical and structural transformations at the interfaces between electrodes and electrolyte are being studied. With the acquired fundamental understanding, strategies are now being developed to prevent undesirable decomposition at the interfaces between the electrodes and the solid electrolyte with advanced coatings.

Where are the promising solid-state batteries?

Worldwide, researchers are using advanced computational battery models and experimental setups to study the behaviour at the interfaces in solid-state batteries (see, *e.g.*, [1-4]). Many companies such as Toyota, Solid Energy, Infinite Power Solution, Seeo, Sakti3, Front Edge Technology Inc., QuantumScape, Bolloré, BrightVolt, Prologium, SolidPower and Ionic Materials are working at commercialising the new generation of batteries in their products. This, however, turns out to be a great challenge. Of course, most companies do not disclose which technology they plan to use in their future generation batteries. The QuantumScape company claims to be ahead of the competition in solid-state battery development and has been successful in bringing in investors, including Volkswagen. According to their website, during testing their batteries could be charged to 80% in fifteen minutes and would contain 80% more energy than comparable conventional lithium-ion batteries. However, the question remains whether they will be able to mass-produce their batteries in the short term. The Solid Power company recently received a major investment from Ford and BMW, while Taiwanese Prologium is working closely with a number of Chinese car builders. Toyota has been working on their own technology for many years and owns more than a thousand patents in the field of solid-state batteries. The company announced that it would present the first electric car with solid-state batteries at this year's Olympic Games. That has not happened.

In conclusion, many battery experts worldwide remain skeptical about a large-scale use of solid-state batteries within a short time frame, because it is not easy to mass-produce a battery that is shown to work in the lab. Nevertheless, the potential of solid-state batteries is enormous and well worth keeping a close eye on. ■

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