SOLID-STATE BATTERIES

The devil is in the electrons

The development of solid-state lithium batteries is largely hindered by the undesired lithium dendrite propagation during battery operations. High electronic conductivity of solid electrolytes is now revealed to be the main culprit.

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Current lithium (Li)-ion batteries face great challenges posed by the energy storage requirements of applications such as electric vehicles and grid-scale storage systems. Many types of next-generation batteries have been proposed to improve energy density and to mitigate safety hazards, among which solid-state batteries with metallic lithium anodes and nonflammable solid-state electrolytes (SSEs) are widely accepted as a promising approach[1]. However, metallic Li dendrites can be easily induced at the interface between the Li anode and most SSEs (for example, the garnet-structured $Li_7La_3Zr_2O_{12}$ (LLZO) and the sulfide-based glassy $Li_2S-P_2S_5$ (LPS)) due to their insufficient physical contact, and/or pristine defects on the surface of SSEs, such as voids, cracks and grain boundaries[2]. Great efforts have been made to improve the interfaces to suppress Li dendrite formation and propagation, but only limited success has been achieved[3]. For some other SSEs, such as amorphous lithium phosphorus oxynitride (LiPON), however, there is no sign of Li dendrite growth and propagation regardless of the abovementioned interfacial and surface defects[4]. The apparent SSE-dependent Li propagation behaviour therefore requires an in-depth understanding. Furthermore, despite many studies, the origin of Li propagation is still not well understood. Writing in *Nature Energy*[5], Chunsheng Wang, Howard Wang, Nancy Dudney and colleagues from University of Maryland and Oak Ridge National Laboratory now reconcile the SSE-dependent features and uncover high electronic conductivity of SSEs as the predominant factor for the Li propagation.

It is challenging to use conventional electronic or optical microscopies to monitor Li propagation inside SSEs with high time and spatial resolutions because Li is hard to detect and most SSEs are opaque. By contrast, the time-resolved operando neutron depth profiling technique works based on the nuclear reaction of $^6Li + neutrons \rightarrow {}^4He + {}^3H$, so that
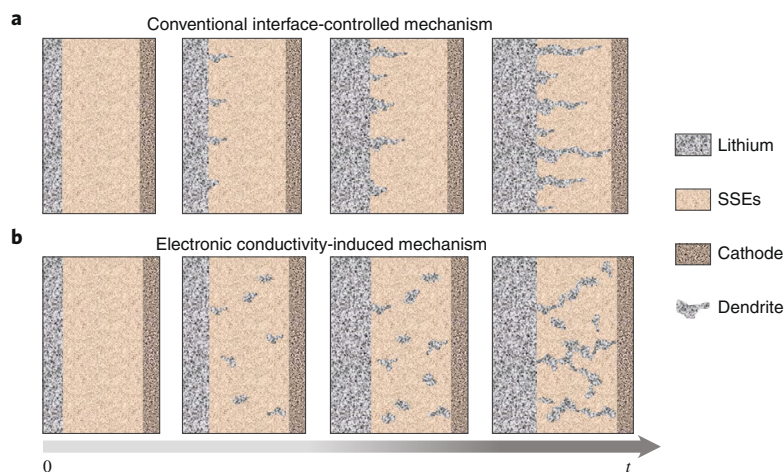

Fig. 1 | Mechanisms of Li propagation inside SSEs. a, In the conventional interface-controlled mechanism, lithium propagates from the anode to the cathode along the axis of the plating time t. The Li propagation is dependent on the SSE/anode interface defects and the Li content in SSEs is not uniformly distributed. Li eventually grows to contact the cathode resulting in shorting. **b**, In the electronic conductivity-induced mechanism, the high electronic conductivity of SSEs induces the formation of dispersed, instead of interconnected, metallic Li. Thus, Li is more uniformly distributed in this mechanism compared with the conventional scenario. On further Li plating, Li dendrites grow to connect with each other, shorting the cells.

the depth distribution of Li in specimens can be quantitatively deduced from the signals of the emitted ^4He and ^3H particles. In their study, the research team for the first time successfully applied this advanced technique to determine Li distribution inside the three abovementioned SSEs during Li plating processes in electrochemical cells.

The researchers find that the Li distribution inside LiPON is uniform and remains unchanged during the entire plating process, whereas the Li content inside LLZO and LPS increases with the plating time, suggesting that Li has propagated inside two SSEs. While these findings are consistent with literature results, the researchers observe that the amount of plated Li at different depths of LLZO and LPS at any given plating time is almost the same, which cannot be explained by the conventional interface-controlled

Li propagation mechanism[2]. As illustrated in Fig. 1a, in the conventional mechanism, the formed metallic Li is interconnected as it gradually propagates from the anode to the cathode through SSEs, which means that the plated Li content at different depths of SSEs cannot be the same. In their new explanation, which they call the electronic conductivity-induced propagation mechanism, the researchers consider that metallic Li can be directly formed inside the SSEs as long as an applied cell potential can allow Li ions to obtain electrons. In fact, a higher electronic conductivity of SSEs could facilitate electron transportation, making it easier for the formation of metallic Li inside SSEs. As a result, the resultant plated Li is isolated but rather uniformly distributed (Fig. 1b), in sharp contrast to the interconnected Li features in the conventional interface-controlled mechanism.

Given the high electronic conductivities of LLZO and LPS ($\sim10^{-8}$–10^{-7} S cm^{-1} and $\sim10^{-9}$–10^{-8} S cm^{-1}, respectively), the electronic conductivity-induced propagation mechanism well explains the nearly uniform Li distributions inside these two types of SSEs. In LiPON, however, Li dendrites cannot form because of the much lower electronic conductivity of the SSE ($\sim10^{-15}$–10^{-12} S cm^{-1}). Furthermore, the study from Wang, Wang, Dudney and team also indicates that minimizing interfacial and surface defects without significantly lowering electronic conductivity of SSEs cannot effectively suppress Li propagation, reconciling literature findings[3]. Importantly, we note that much has been emphasized in the literature on the importance of developing SSEs with high ionic conductivity (and rightly so for the

development of solid-state batteries with high power capability). In this respect, the electronic conductivity-induced propagation mechanism carries an important message to the current numerous efforts: the electronic conductivity of SSEs must not be high to alleviate Li propagation. While a stringent criterion is yet to be determined for the desired electronic conductivity of SSEs, Wang, Wang, Dudney and colleagues suggest an empirical value of an upper bound of 10^{-10} and 10^{-12} S cm^{-1} at a current density of 1 and 10 mA cm^{-2}, respectively. It would therefore be very interesting to see how future SSE design can meet this criterion to eventually eliminate the dendrite problems, while maintaining the requirement of high ionic conductivity (typically $>10^{-4}$ S cm^{-1}). ❑

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