

Constrictions Induced Metastability and Kinetic Stability for Advanced Solid-State Battery Design

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Background

Recently, it becomes a consensus in the field that solid-state batteries may offer paradigm shifting performances over conventional liquid-electrolyte based batteries. This is mainly because it can potentially enable the safe cycling of many higher-energy density electrode materials, while simultaneously providing improved temperature robustness. Obviously, solid-state batteries eliminate the most dangerous component in commercial batteries, the flammable liquid-electrolyte. Moreover, on the anode side, solid electrolytes can potentially enable the adoption of lithium metal by providing a mechanically robust physical barrier that prevents lithium dendrite penetration (Kasemchainan et al., 2019; Su et al., 2020). Regarding the cathode, solid electrolytes have demonstrated compatibility with a multitude of high-energy density cathodes (Li et al., 2015; Ye et al., 2020). Solid electrolytes also maintain superior performance at low temperatures, where viscosity increases can plague liquid-electrolytes, a key performance metric for many applications including electric-vehicles for low-temperature markets.

Solid electrolytes ideally should reach an ionic conductivity comparable to that of liquid electrolytes (approximately 10 mS/cm). Simultaneously, they must be stable in a wide range of alkali ion chemical potentials, known as the electrochemical or voltage stability window. The stability window constitutes the range of voltages versus lithium metal, in which the solid electrolyte will not electrochemically decompose. In addition, compatibility of the electrolytes with mass production procedures, including brittleness control and air stability, as well as the applicability of the low-cost cold press or rolling procedures, also remain as critical factors for solid-state battery development.

When the liquid electrolyte is replaced by the solid electrolyte in assembling solid-state batteries, the liquid-solid interface that was familiar to battery scientists now becomes the solid-solid interface between electrode and electrolyte particles, as well as the one between electrolyte particles themselves, which forms a new challenge to understand. During the solid-state battery development, high external pressures are often applied to press the solid sandwich formed by cathode, electrolyte and anode layers into a dense pellet at room temperature uniaxially (cold uniaxial press), and to even perform the battery test under a high stack pressure, especially for mechanically soft electrolytes like sulfides and halides (Kato et al., 2016; Asano et al., 2018; Li et al., 2019). Such operations were based on the wisdom to maintain a good contact on these solid-solid interfaces, as well as to prevent fractures, because significant degradation of battery performances will occur at voids or fractures, where Li ions cannot transport whereas Li dendrites can grow.

Pressure effects on solid state battery performances were later systematically investigated in experiments. In practice, the stack pressure was often limited to ~ 10 MPa for such a solid-solid interface with mechanically soft electrolytes (Doux et al., 2020b), beyond which Li can be squeezed through the electrolyte layer by the externally introduced stress to short the battery. Unfortunately, a 10 MPa stack pressure was shown to be insufficient in preventing the degradation of the interface at a current density beyond $1\text{--}2$ mA/cm², where porous Li was generated by the electrochemical cycling, recipient to a further growth of Li dendrites and the battery failure (Kasemchainan et al., 2019).

A stack pressure on the order of 100 MPa or beyond for such an interface was realized by applying a graphite protection layer between the Li metal and a sulfide solid electrolyte Li₁₀GeP₂S₁₂ (LGPS) (Su et al., 2020). Porous Li was prevented during battery cycling and a high current density up to 10 mA/cm² was achieved. In addition, high stack pressures in electrochemical tests were generally applied to solid state batteries based on sulfide and halide electrolytes (Asano et al., 2018; Doux et al., 2020a).

On the cathode side, the intrinsic thermodynamic voltage stability window of LGPS is correctly predicted to be 1.7–2.1 V by computational experts (Ong et al., 2013; Zhu et al., 2016). While in experiments, sulfide electrolyte-based solid state batteries were found to charge up to 5 V with minimal degradation (Kamaya et al., 2011; Wu et al., 2018). Recently, it was further shown, surprisingly, that LGPS electrolyte mixed with electronically conductive carbon can be held at up to 9.8 V for 10 h under ~ 200 MPa, without showing obvious phase decompositions (Ye et al., 2020). Different models were proposed to explain these seemingly contradictory results between computations and experiments. For example, it was believed that the application of cathode coatings that separate high voltage cathode from the direct contact with electrolytes can help stabilize the solid-state battery system

(Kato et al., 2016). It was also proposed that if the decomposition products beyond the intrinsic thermodynamic voltage window are electronically insulating, thus electrons cannot transport away from local decompositions, an electronic passivation layer will form, and further decompositions can be inhibited (Zhu et al., 2016; Wenzel et al., 2018). Others paid attention to the fact that sulfide electrolytes exhibit certain Li capacity upon lithiation and delithiation (Han et al., 2015), which can slightly widen the voltage stabilities of electrolytes (Du et al., 2014; Tan et al., 2019; Schwietert et al., 2020). These arguments captured different aspects of the problem, however, in practice they cannot function without considering the mechanical constriction effect that will be discussed in this chapter. That said, multiple levels of entangled mechanical constrictions induced metastability and kinetic stability, which will be the focus of this chapter, are considered to be the dominant effect in controlling multiple material and interface stabilities in operating solid-state batteries.

Practically, the stack pressure is less than 10 MPa for current commercial coin, pouch and prismatic cell designs, while the level of stack pressure at around 100 MPa or beyond must be applied through a bulky stainless-steel battery cells, which inhibits the application of high external pressure in the mass production of battery devices and the deployment in mobile devices and electric vehicles. Therefore, a further design of solid-solid interfaces is critical to obtain good battery performances at a much lowered and hence more practical stack pressure of around 10 MPa, ideally. Recently, it was demonstrated that when high isostatic pressure was applied to make the dense pellet using $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ as cathode and $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) as electrolyte at an elevated temperature, followed by applying a thin layer of Li and Ag alloy to the anode side of the pellet, such a solid state battery can show excellent cycling performances at high current densities and a low stack pressure below 10 MPa (Lee et al., 2020). The results emphasize the importance of engineering details in battery design and assembly to battery performances.

The readers may have realized that large degrees of freedom in solid-state battery designs have emerged through the comparison of just a subset of previous works in the field. What is more challenging is that they often interplay strongly with each other. Sometimes a high stack pressure is necessary and critical to prevent detrimental interface electrochemical evolutions for good battery performances, while in some other experiments changing the initial cold press to a warm isostatic press, together with the anode chemistry, seems to bring down the required stack pressure to a lower level. It is of great interest to understand, going beyond the conventional wisdom of good interface contacts that are for sure important, whether there are other fundamentally critical roles the multiple pressure effects play to influence the interface electrochemistry and modulate the battery performance. For such an understanding, we expect that the theoretical picture should largely explain the complexities in experiments, based upon which the computational predictions can be quantitatively compared with experiments. More importantly, such predictions should be able to make practical impacts to the engineering design of solid-state batteries.

In this chapter, I will start with describing the picture of a critical factor, i.e., the reaction strain, that connects the pressure effect closely with electrochemical stabilities in solid state batteries. I will then talk about the unique property of solid state battery system compared with liquid electrolyte batteries, where mechanical constriction effect plays critical roles at multiple scales, effectively converting reaction strains in the chemical reaction space to metastability or kinetic stability states in the energy landscape. In the end, I will talk about how voltage stability window of solid electrolyte and multiple interfaces can thus be stabilized by these effects, giving a new degree of freedom for electrolyte, interface, and device designs of advanced solid-state batteries. Throughout the chapter, I will point readers to previous literatures relevant to my introduction here. The chapter aims to describe the general picture shared by multiple state-of-art research works, the underlying connection of these works, and the implication to practical battery designs, which the readers may not obtain by simply reading those articles separately. On the other hand, this chapter is not to repeat what has been elaborated in previous publications, and the readers are still encouraged to read those original research articles (Wu et al., 2018; Fitzhugh et al., 2019a, b, c; Su et al., 2020; Ye et al., 2020).

Interplay between reaction strain and constriction effect

The stability of solid-state interfaces in cathode or anode regions at different battery voltages can in principle be calculated by Density Functional Theory (DFT) simulations. Directly building such interfaces on the atomic scale requires substantial calculations. An alternative approach, the pseudo-phase method, enables only two calculations per interface (one for each of the two materials) to be needed (Fitzhugh et al., 2019b). An artificial interface is assumed to have energy and composition given by a linear combination of the energies and compositions of the two materials in question. Convex hull methods are used to calculate the stability of the artificial interface at different ratios of the two materials. The fraction of the two materials that yields the most strongly unstable artificial interface is taken to represent the instability of the interface as it will be the most kinetically drive fraction.

Explicitly considering in computations the interplay of these interface reactions with the abovementioned pressure effects is therefore critical to a more complete understanding of interface phenomena for the design of advanced solid-state batteries. One insight that led to the development along this direction is that these solid electrolytes and their interfaces show different reaction strains upon decomposition, and the reaction strain is particularly important in an all-solid-state system like solid-state batteries. In a chemical reaction, the decomposed products often show a different volume from the original reactants, which could be just the electrolyte if we only care about the voltage instability of the electrolyte itself, or both electrolyte and electrode or coating materials if we try to study the interface instability. The volume ratio between decomposition products and original reactants is defined as the reaction strain. Positive reaction strain means a volume expansion reaction, while negative means a volume shrink. A classic example that people are familiar with is when the reaction involves liquid and gas phase transformations. For example, when water is heated up to 100 °C, abrupt phase transformation to gas phase happens, associated with a significant volume expansion, or

positive reaction strain, due to the much larger distance between H_2O molecules in the gas phase. When ice melts to water at 0°C , the reaction strain is instead negative, as we know that the density of ice is lower than water, due to the special property of hydrogen bonding. However, it is not difficult to have the image that the absolute value of the reaction strain for the water boiling reaction is much larger than that for the melting reaction.

Here it comes to an interesting observation. If you boil the water in a pressure cooker, the boiling point is increased above 100°C , while on a high plateau where the atmospheric pressure is below 1 atm, the boiling point is decreased below 100°C . They correspond to the situations when the gas phase formation is inhibited or promoted, respectively. One critical statement in the language of reaction strain is that for boiling with a pressure cooker, the high pressure plays the role of applying a constriction to the reaction with positive reaction strains, which delays the transformation toward the gas phase, and increases the phase stability of the liquid phase. This shows the importance of the constriction concept, provided by the external pressure in this particular example, to widen the temperature stability range of the liquid phase.

For a liquid electrolyte battery, the multiple liquid and solid interfaces between electrode particles and the liquid electrolyte are, however, much less sensitive to such reaction strains. Because any interface reactions can change volume freely in the liquid electrolyte environment with either positive or negative strains, thus reactions can always happen at will. The battery device, instead of applying the influence on such reactions, can be influenced by them in certain extreme cases, through swelling of the pouch, for example, if the reaction involves a gas release, or gassing. That is why in the commercial prismatic cell, a gassing safety valve has to be designed. Other reactions that form the so-called solid electrolyte interface (SEI) layer on the cathode particle surface, usually will not show obviously observable influence on the battery device, nor to be influenced by the device.

Different from liquid electrolyte batteries, any volume change by reactions will immediately impact the surrounding solid environment, and simultaneously being impacted by the environment. This is the unique property of an all-solid-state system, especially when the aforementioned sandwich pellet is prepared into a dense form and the reaction of interest is associated with a positive reaction strain. You can imagine that any small local decompositions with a positive reaction strain will have to push the surrounding solid environment that is in a close contact with the decompositions. The decomposition reaction thus must take much higher energy to happen in such a solid battery environment than the liquid electrolyte one. Here, the dense solid pellet plays the role of local constriction to limit the reaction transformation toward decompositions, just like the pressure cooker in the previous example to delay the gas transformation. How well the constriction can be applied to limit the decomposition, however, depends on complicated details in mechanical properties of both the pellet and the battery device, which needs very careful discussions. But in general if the pellet is made by an electrolyte with high elastic modulus, pressed into a very dense form, tested under a constantly applied stack pressure, etc., the constriction will be strong. That is why in solid state batteries this constriction effect is called as a mechanical constriction effect. Analogous to the widened temperature stability of the liquid phase in the water boiling example, where the boiling point is pushed to a higher temperature by the pressure constriction, here it is the voltage stability that is widened for the solid electrolyte phase by the mechanical constriction, and the transformation toward the decomposition phases is delayed to happen at a higher voltage, if we talk about charging the battery to the high voltage direction. For battery discharge to low voltages, the mechanical constriction effect can play the same role, to push the low voltage decomposition to happen at a lower voltage.

Electrochemical metastability widens voltage stability

Although I used the analogy between the two cases of boiling the water and decomposing the electrolyte to help the readers understand the picture of the interplay between constriction effect and reaction strain, I have to emphasize that strictly speaking, they are not exactly the same. Based on Clapeyron equation, in the pressure (P) and temperature (T) phase diagram of H_2O , if at a given pressure P_1 the boiling point is T_1 , then at an increased pressure $P_2 > P_1$, the boiling point is also increased to T_2 , where $T_2 > T_1$. This is just to generalize the previous example. But the fact that with increasing pressure the phase transformation to the gas phase happens at higher temperatures reflects that the energy preference to the gas phase has been delayed to happen at higher temperatures. In the language of thermodynamics, the liquid and gas phases are thermodynamic ground states at low and high temperatures, respectively, with the transition temperature being the boiling point. With increasing pressure, the phase transform to gas phase as the ground state happens at higher temperatures and the ground state of liquid phase occupies larger space in the T - P phase diagram.

The interplay between mechanical constriction and electrolyte decomposition voltage is, however, much more complicated in this perspective. If beyond a voltage like 2.1 V, the solid electrolyte is not thermodynamically stable anymore, decomposition in principle should happen immediately, as the decomposed products now are at the ground state, just like below 2.1 V it is the solid electrolyte phase that is at the ground state. Now we apply a mechanical constriction to the electrolyte system, assuming that a dense electrolyte pellet is made without any voids, and the pellet is stacked by certain external pressure to maintain its integrity. If the electrolyte decomposition reaction is with a positive reaction strain, what will happen when we charge the cathode part of the electrolyte, i.e., electrolyte fully mixed with conductive carbon, above 2.1 V? Based on the previous discussion, mechanical constriction will suppress the decomposition, and the voltage stability of the electrolyte can be widened, e.g., to 4 V. Here is why I said that the analogy we made to the water boiling example is not strict, where the boiling point was shifted upward by external pressure. In that case, if not at superheating, a concept I will introduce later, the boiling point always represents the temperature beyond which the thermodynamic ground state of water vapor phase becomes lower than the liquid phase. In this all-solid-state

system, however, the thermodynamic ground state is still the decomposition phases in the range of 2–4 V, while what stabilizes the electrolyte to prevent its decomposition is a metastable state.

This can be understood from Fig. 1, where I use a specific type of sulfide electrolyte of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) to illustrate. Beyond the thermodynamic voltage stability window, the Gibbs free energy of the pristine electrolyte on the left side at $x_D = 0$ is higher than that of the full decompositions on the right side at $x_D = 1$, the thermodynamic ground state of this decomposition reaction thus will happen following the dashed orange line, with increasing decomposition ratio x_D . Whereas, in a mechanically constricted environment, any decomposition with positive reaction strain will experience an additional strain energy that can in principle create a local energy minimum. If this happens, any decomposition precipitations or nuclei will have to increase the free energy of the system following the solid green line, and thus will not grow in size. Since the thermodynamic ground state is still described by the dashed orange line at lower energies, the higher energy local minimum must be a metastable state.

However, one exception can make the decomposition propagate, that is when the fracture energy is comparable to the energy increase from fluctuation-induced decomposition nuclei. It takes certain energy to form fracture in a solid system. Once the fracture is formed, the void region created by fractures will be mechanically non-constricted, thus decomposition can happen following the same trend of the orange dashed line, as represented by the blue dashed line. The cross of this line and the green solid line defines a decomposition ratio x_f , which tells that if the nuclei decomposition by fluctuation can abruptly reach a local decomposition ratio beyond x_f , fracture will happen and the system will have to evolve toward a global decomposition. Otherwise, the system is stabilized by this metastate. More detailed discussions can be found in previous literatures (Fitzhugh et al., 2019a, c). In many solid electrolyte systems of interest, it is reasonable to assume that the decomposition nuclei induced local strain energy is much smaller than the fracture energy, as I will discuss more later. This assumption is also supported by recent simulations (Tu et al., 2020) that a relatively small external stack pressure in the range of a few MPa to 160 MPa can already prevent fracturing inside the electrolyte during electrochemical operations on the interface to Li anode, for those mechanically soft electrolytes like sulfides.

The above physical picture can be implemented in computations to evaluate quantitatively how much additional voltage stability can be created by such a metastable state, by using the effective local elastic modulus K_{eff} to represent the level of mechanical constriction. More details can be found in previous literatures (Wu et al., 2018; Fitzhugh et al., 2019a, c). For example, computations in Fig. 2 show that at zero mechanical constriction ($K_{\text{eff}} = 0$) the voltage stability window of LGPS is between 1.7 and 2.1 V, which means LGPS in the cathode region will decompose if the battery is charged beyond 2.1 V, and LGPS in the anode region will decompose if the battery is discharged below 1.7 V. This is a very narrow voltage window that almost inhibits any practical battery operations. When the constriction is increased to $K_{\text{eff}} = 20$ GPa, however, the voltage window is widened to be from around 1 to 4 V. So LGPS stays at metastable states between 2.1 and 4 V in charge, and between 1 and 1.7 V in discharge. You may have noticed that the mechanical constriction applied in the computation is on the order of 10–20 GPa, which is on the same order as the elastic modulus of these sulfide electrolytes. This can also be understood from the physical picture I described above. Any local decomposition nuclei will have to overcome the strain energy from the undecomposed electrolyte environment, which is in an

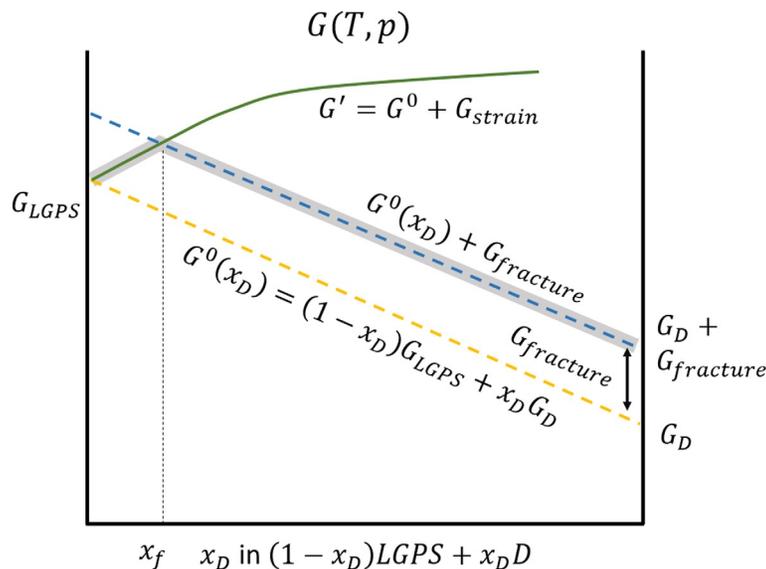


Fig. 1 Illustration of the impact of strain on LGPS decomposition, where x_D is the fraction of LGPS that has decomposed. The dashed-orange line represents the Gibbs energy, $G^0(x_D)$, of a binary combination of pristine LGPS and an arbitrary set of decay products, D, when negligible pressure is applied (isobaric decay with $p \approx 0$ GPa). The solid-green line shows the Gibbs when a mechanical constriction is applied to the LGPS. Since LGPS tends to expand upon decomposition, the strain Gibbs, G_{strain} , increases when such a mechanical constriction is applied. At some fracture point, denoted x_f , the Gibbs energy of the system exceeds the energy needed to fracture the mechanical constriction (the dashed-blue line). The highlighted grey path is the suggested ground state for a mechanically constrained LGPS system. The region $x_D < x_f$ is metastable if $\partial_{x_D} G' > 0$. Reproduced from Ref. Fitzhugh W, Wu F, Ye L, Su H, et al. (2019a) Strain-stabilized ceramic-sulfide electrolytes. *Small*, 1901470, 1–14, <https://doi.org/10.1002/sml.201901470> with permission of John Wiley and Sons.

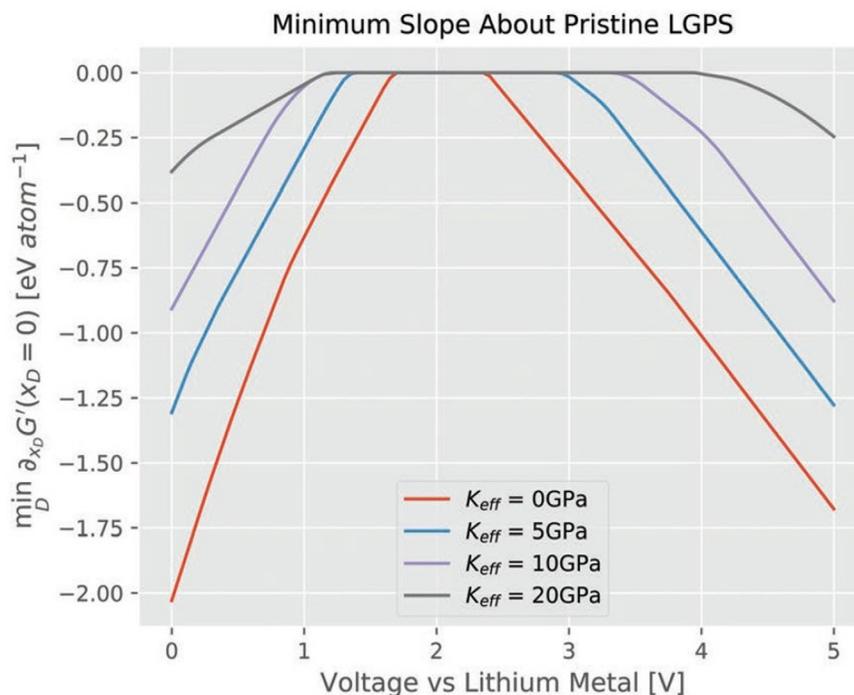


Fig. 2 Chemical potential window versus lithium metal for LGPS, in the hydrostatic limit, calculated via the minimization of the Gibbs slope about the pristine case. Reproduced from Ref. Fitzhugh W, Wu F, Ye L, Su H et al. (2019a) Strain-stabilized ceramic-sulfide electrolytes. *Small*, 1901470, 1–14, <https://doi.org/10.1002/sml.201901470> with permission of John Wiley and Sons.

immediate contact with the nuclei and thus constricts its further decomposition expansion at a strength that can be quantified by the elastic modulus of the electrolyte.

Now the readers can also understand one major difference between the temperature driven water boiling example and the voltage driven solid state decomposition here. The former is a switch of the ground state between the liquid and gas phases at the boiling point, while the latter is a switch from the ground state (e.g. 1.7–2.1 V) to the metastable state (2.1–4 V or 1.0–1.7 V) for the solid electrolyte relative to the decomposition phases. Thus, strictly speaking, a better analogy but less familiar to people is the “supercooling” of water. When water is cooled below 0 °C, in principle, the liquid phase should transform to the solid ice phase. However, if the water is treated to be very clean without any nucleation centers, it can stay at the “supercooling” liquid state down to a critical temperature range T^s from –30 to –48 °C. Liquid water between T^s and 0 °C is at a metastable state (Aliotta et al., 2014). Fluctuations can generate nucleation centers, which, once formed, will grow the ice phase, and bring the supercooled metastable water eventually to the ground state crystalline ice. One can imagine, if the supercooled water is sealed tightly in a tank that does not allow any volume expansion or under a high external pressure, the positive reaction strain of this solidification process in principle can widen the metastability of supercooled water to even lower temperatures below T^s . In reality, it did happen that this critical temperature can be brought down to –92 °C at 200 MPa external pressure (Prielmeier et al., 1987). However, the details are more complicated than the simple reaction strain model, as the liquid density and diffusivity etc. all can be changed by pressures (Marion and Jakubowski, 2004).

Kinetic stability and wider voltage stability

In experiments, people find that sulfide electrolyte like LGPS can be charged up to 9.8 V without seeing a decomposition current in the CV test (Ye et al., 2020), shown as the purple curve in Fig. 3. The measurement was performed on a solid-state battery with the sandwich pellet constructed by LGPS electrolyte mixed with conductive carbon as the cathode, surface protected Li metal as the anode, and pure LGPS layer between cathode and anode. The pellet was pressed densely at 467 MPa initially, and then tested in a pressurized cell at a constant external pressure of 250 MPa. The voltage sweeping was at a slow rate of 0.1 mV/s up to 9.8 V. If 1.7–2.1 V is the thermodynamic ground state of LGPS, and 2.1–4 V is a metastability, then what phenomenon stabilizes LGPS in the voltage range from 4 to 9.8 V?

Before answering this question, let us again look at the abundant phase transformations of water. Now we boil the clean water in a clean container at the ambient pressure. The boiling point can be shifted to a few degrees Celsius higher than 100 °C, with the water staying at a “superheating” metastable state. The reason is the following. Boiling needs the vapor bubble to form and grow in water as an initial step, which has to overcome both the ambient pressure and the surface tension of the vapor bubble. This initial

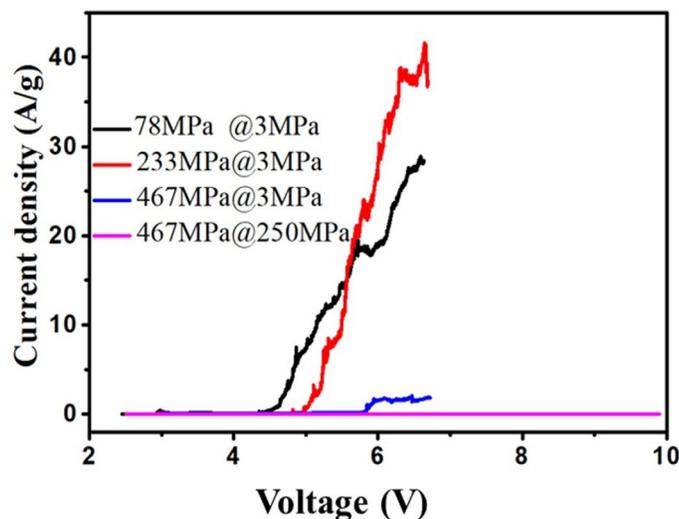


Fig. 3 CV tests at 0.1 mV/s in Swagelok battery cells at negligible external pressure after they were initially pressed with 78 MPa (black), 233 MPa (red), 467 MPa (blue), then released in the Swagelok battery tests with the external pressure calibrated as 3 MPa, compared with the test under pressurized cell initially pressed at 467 MPa and tested at around 250 MPa (purple). 10 wt% carbon is added in the cathode. The voltage range is set from open circuit to 9.8 V versus lithium metal. Reproduced from Ref. Ye L. et al. (2020) Toward higher voltage solid-state batteries by metastability and kinetic stability design. *Advanced Energy Materials*, 2001569, 1–13, <https://doi.org/10.1002/aenm.202001569>.) with permission of John Wiley and Sons.

step could be difficult if the water and the container both are very clean without nucleation centers, or without rough walls in the container for large bubbles to preexist, because a small micrometer-sized bubble exhibits much larger surface tension than a large bubble. The added a few degrees Celsius to the boiling point is due to this nonnegligible surface tension in such clean water. Disturbing a superheated water at ambient pressure away from this metastability is easy, sometimes inevitable. For example, using a microwave oven to heat the water, which lacks the convection disturbance in heating of using a kettle, is easier to reach the superheating status. When bringing it out of the oven, any small shaking of the cup is likely to introduce large bubbles with negligible surface tension to grow in size, which explosively boil the water and push it away from the metastability.

Now let us imagine an interesting change of details. If the vapor bubble is “magic,” in the sense that its surface tension increases with the bubble size, rather than decreases as in reality. Then the vapor pressure inside the bubble will have to overcome increasingly larger pressure from the surface tension plus the constant atmospheric pressure. The process will eventually reach an equilibrium and the bubble will stay at a fixed radius without growing larger at a given temperature. When temperature further increases, due to the increased internal vapor pressure inside the bubble, the bubble will grow accordingly to the next equilibrium point, balanced with the further increased surface tension plus the constant ambient pressure. Assuming these bubbles do not break inside the water, they will have to come up to the water surface and then leave the water as vapor, together with the direct vaporization at the water surface. The entire process of gas transformation will still happen quickly because of the high temperature, but the vibrant boiling phenomenon of the entire water that you are familiar with will not happen. As you can also easily appreciate, the few degrees Celsius temperature range of the superheated water can be largely expanded in such magic water. This hypothetical example emphasizes the importance of the property at the interface between the nuclei and the original phase when a phase transformation happens.

Coming back to the question about the stabilization mechanism for LGPS voltage stability in the range of 4–9.8 V, it can be considered as an analogy in reality to the magic water in the above imaginary example, but of course with some difference in the exact thermodynamic and kinetic languages. Above 4 V, as we mentioned, the solid electrolyte phase is not metastable anymore, but rather thermodynamically unstable, thus decomposition is inevitable. Instead of taking a homogeneous decay, following the mean field type, there is enough reasons to argue that decompositions of solid electrolyte tend to follow the type of nucleation decay (Fitzhugh et al., 2019a; Ye et al., 2020).

To understand the difference between the two decay mechanisms, we can go back to the supercooled water. The supercooled water below 0 °C can stay in the liquid phase due to the lack of nucleation centers, down to T^* . Fluctuations, however, can disturb the metastable phase to create nuclei, from which crystalline ice can grow. Below T^* the liquid phase is not at metastability anymore, crystal ice will more homogeneously freeze the supercooled water, without relying on nucleation centers. Decay of LGPS solid electrolyte between 4 and 9.8 V in Fig. 3, however, prefers nucleation decay, because compared with liquid, solid electrolyte is much less homogeneous in microstructures, with abundant point defects, stacking faults, dislocations, and chemical inhomogeneities, which all can serve as nucleation centers.

Furthermore, although once the supercooled water starts to nucleate in the metastable state, the transformation to the crystalline ice phase will propagate with time to solidify the entire water, the decomposition phases in solid electrolyte may not. This is, again, due to the mechanical constriction effect. But instead of creating a metastability as in the lower voltage range, e.g. 2.1–4 V for LGPS,

here a local constriction on the interface between the decomposed phases and pristine LGPS kinetically stabilizes the electrolyte through the interaction with global constrictions.

The picture is described in Fig. 4. Above 4 V, LGPS is thermodynamically unstable, for any nucleation decay region (red region 2), its interface with the pristine LGPS (grey region 1) is called the decomposition front and is of interest here. To grow in size, the decomposition front must propagate, which relies on the interdiffusion of ions from LGPS crystal lattice to that of decomposed compounds. The process highly relies on sufficient ionic conductivities on the decomposition front. However, under a global mechanical constriction, the pellet was densely packed, and could also be held at certain external pressure during the battery test, as in the particular example of Fig. 3, where the required external pressure is at most on the order of several hundred MPa. Any local decompositions with positive reaction strain will have to overcome the local constriction effect enforced by the immediate LGPS environment, which is on the order of the elastic modulus of the electrolyte, e.g., around 15–20 GPa for sulfide electrolytes. Such local mechanical constriction induced negative strain in the thin layer of LGPS surrounding the decomposition front largely reduces the ionic diffusivity, by orders of magnitude, which effectively inhibits the propagation of the decomposition front. This picture describes how the global mechanical constriction on the order of MPa is transferred to the local constriction on the order of GPa to inhibit the growth of small local decompositions, creating a kinetic stability to electrolytes in the thermodynamically unstable voltage range, i.e., 4–9.8 V for LGPS. The local strain effect induced by the constricted small local decomposition was also observed from X-ray diffraction (XRD) analysis through the strain broadening effect of XRD peaks, as well as from some other spectroscopy measurements and simulations (Ye et al., 2020). Therefore, allowing a local stress field to distribute in the solid-state battery system, where the environmental pressure is not a valid state variable for the thermodynamic ensemble anymore, becomes one main difference from the liquid electrolyte battery system.

Lithium metal anode enabled by interface mechanical constriction

In addition to the mechanical constriction induced metastability and kinetic stability at high voltages up to 9.8 V in LGPS, anode side is also governed by this effect. One motivation to go solid is that it may enable the usage of Li metal anode with much higher energy density than the commercial graphite anode. Li metal anode shows the notorious lithium dendrite problem in liquid electrolyte environment, to cause the short of batteries with serious safety concerns. The mechanical strength of ceramic solid electrolyte in principle can suppress the Li dendrite penetration. However, previous research finds that the critical current density in solid electrolyte battery is often lower than the liquid one, beyond which dendrite grows. This limit was found to be at around

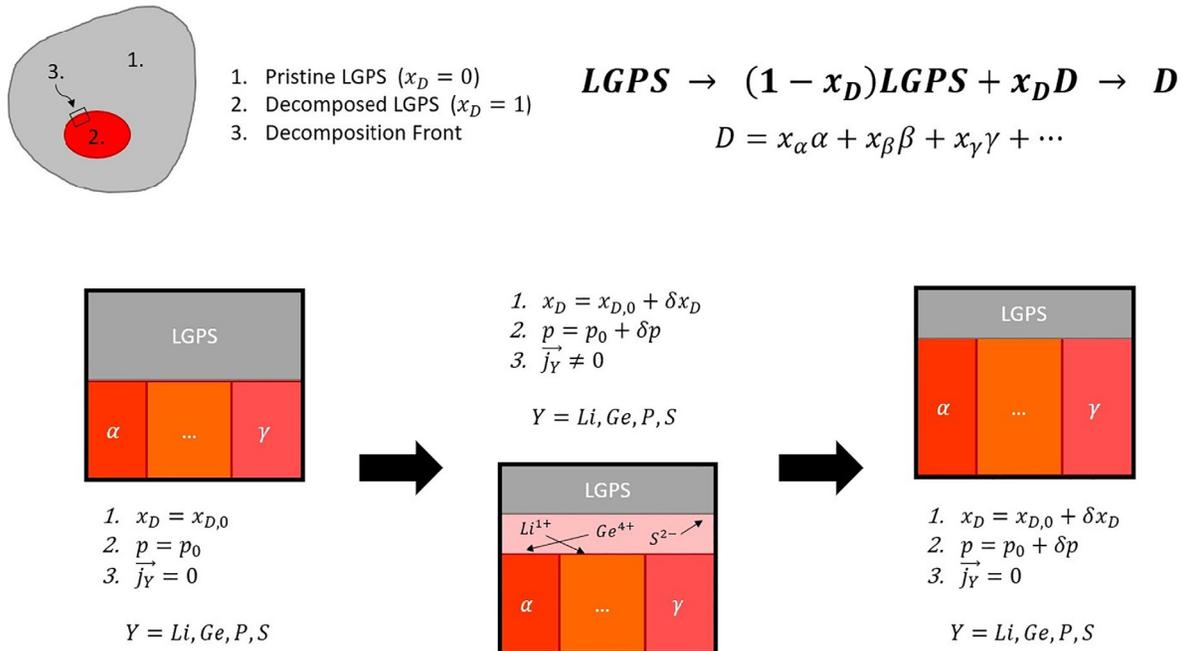


Fig. 4 Illustration of restricted decomposition front propagation limited by kinetics. Pristine (grey, region 1) and decomposed (reddish, region 2) LGPS are indicated by the mole fraction of decomposed LGPS ($x_D = 1$ for purely decomposed, $x_D = 0$ for pristine). On their interface or the decomposition front (rectangular region 3 in the top-left particle, with the magnified decomposition evolution shown in the bottom three illustrations), the mole fraction transitions from 0 to 1. Decomposed phases are marked with $\alpha, \beta, \gamma, \dots$ with the corresponding fractions of $x_\alpha, x_\beta, x_\gamma, \dots$. Such propagation is seen to require tangential ionic conduction with an ionic current \vec{j}_i for each elemental species in the decomposition front (pink region in the bottom-middle illustration). Reproduced from Ref. Ye, L. et al. (2020) Toward higher voltage solid-state batteries by metastability and kinetic stability design. *Advanced Energy Materials*, 2001569, 1–13, <https://doi.org/10.1002/aenm.202001569> with permission of John Wiley and Sons.

1 mA/cm² at an external pressure of less than 10 MPa with sulfide electrolytes (Kasemchainan et al., 2019). Detailed characterization unveiled that the lithium plating and stripping process can cause porous lithium deposition on the interface between Li metal and solid electrolyte, thus local high electric field around certain sharp geometry in the porous Li can promote the dendrite growth.

Recently, it was found that higher external pressure on the order of 100 to 200 MPa can effectively suppress the formation of porous Li in the Li stripping and plating cycling process (Su et al., 2020). To enable the pressure on this order, a graphite protection layer was covered on the Li metal anode to separate it from LGPS electrolyte, which prevents the external pressure induced Li penetration through the solid electrolyte layer. It was demonstrated that high current density up to 10 mA/cm² can be achieved in such a battery system without Li dendrite formation during the symmetric battery cycling tests. The dense pellet pressed by high initial pressure and the constantly applied external pressure during battery tests serve as a global mechanical constriction condition. The local constriction on the order of 15–20 GPa moves the low voltage window of LGPS from 1.7 V to around 1.0 V, giving a metastable state between 1.0 and 1.7 V. Similar to the high voltage side, in the voltage range from 0 V of Li metal anode to the 1.0 V metastability boundary of LGPS, it is a kinetic stability.

Solid electrolyte in the kinetic stability voltage range on the interface to Li metal anode will experience small local decompositions, which can be predicted by computations. Fig. 5 shows that at different levels of local mechanical constriction from 0 GPa up to 15 GPa, LGPS decomposition products near 0 V are different. At the 0 GPa constriction, Ge and P in LGPS are highly reduced in decompositions to form Li_xGe_y alloy and Li₃P, while at high local constrictions, these reductions are suppressed.

This prediction is observed in X-ray photoelectron spectroscopy (XPS) shown in Fig. 6. When Li metal is in a direct contact with LGPS, the interface is at 0 V and reactions happen immediately to decompose the LGPS without an effective mechanical constriction. Both predicted Li_xGe_y alloy and Li₃P are observed in XPS. However, when the global constriction of 100 MPa is applied with a graphite layer separating LGPS and Li metal, the local constriction at the interface effectively suppresses the reduction of both Ge and P for batteries after electrochemical cycling. This shows that not only the voltage metastability window can be calculated, the decompositions beyond the metastability window can also be correctly predicted with local mechanical constrictions applied explicitly in the computational platform.

More details on theoretical derivations, computations and experimental designs can be found in the literature (Su et al., 2020; Ye et al., 2020), where high voltage interface stabilities on the cathode side are also emphasized (Ye et al., 2020). The readers are encouraged to read through these original papers to obtain a more quantitative understanding after digesting the physical picture described in this chapter.

The central role of constrictions induced stabilities in solid-state batteries

Before I finish this chapter, I want to reemphasize the central role of the multiple levels of entangled constrictions in solid-state batteries to create metastability and kinetic stability in a wide operational voltage range. Other details such as cathode or electrolyte coatings (Kato et al., 2016), electronic passivation layers (Zhu et al., 2016; Wenzel et al., 2018), and Li composition changes of electrolytes (Du et al., 2014; Tan et al., 2019; Schwietert et al., 2020), all have to function assuming a proper design and implementation of the constriction effect. First, the widely used LiNbO₃ coating (Ohta et al., 2007; Kato et al., 2016) is actually shown to be just thermodynamically less unstable compared with the direct interface between LGPS and various high voltage cathodes (Ye et al., 2020). The stabilization of the LiNbO₃ coating, as well as many other coatings, will have to rely on the constriction effect. In addition, coatings will not change the voltage stability of the electrolyte in the electrode region, unless the coating functions as the electrolyte while the original electrolyte is completely isolated from the electrochemical system. Second, electronic insulation or passivation cannot work individually without a proper mechanical constriction. This has been

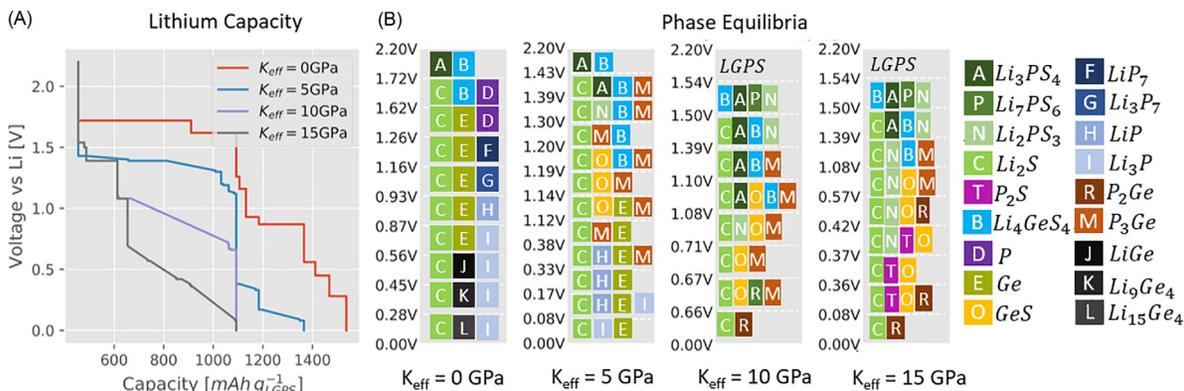


Fig. 5 (A) Voltage profiles of LGPS decomposition at different effective modules (K_{eff}). (B) Reduction reaction pathways corresponding to different K_{eff} and the products in different phase equilibria within each voltage range. All decomposition products here are the ground state phases within each voltage range. Reproduced from Ref. Su Y. et al. (2020) A more stable lithium anode by mechanical constriction for solid state batteries. *Energy & Environmental Science*, 13(3): 908–916, <https://doi.org/10.1039/c9ee04007b> with permission of The Royal Society of Chemistry.

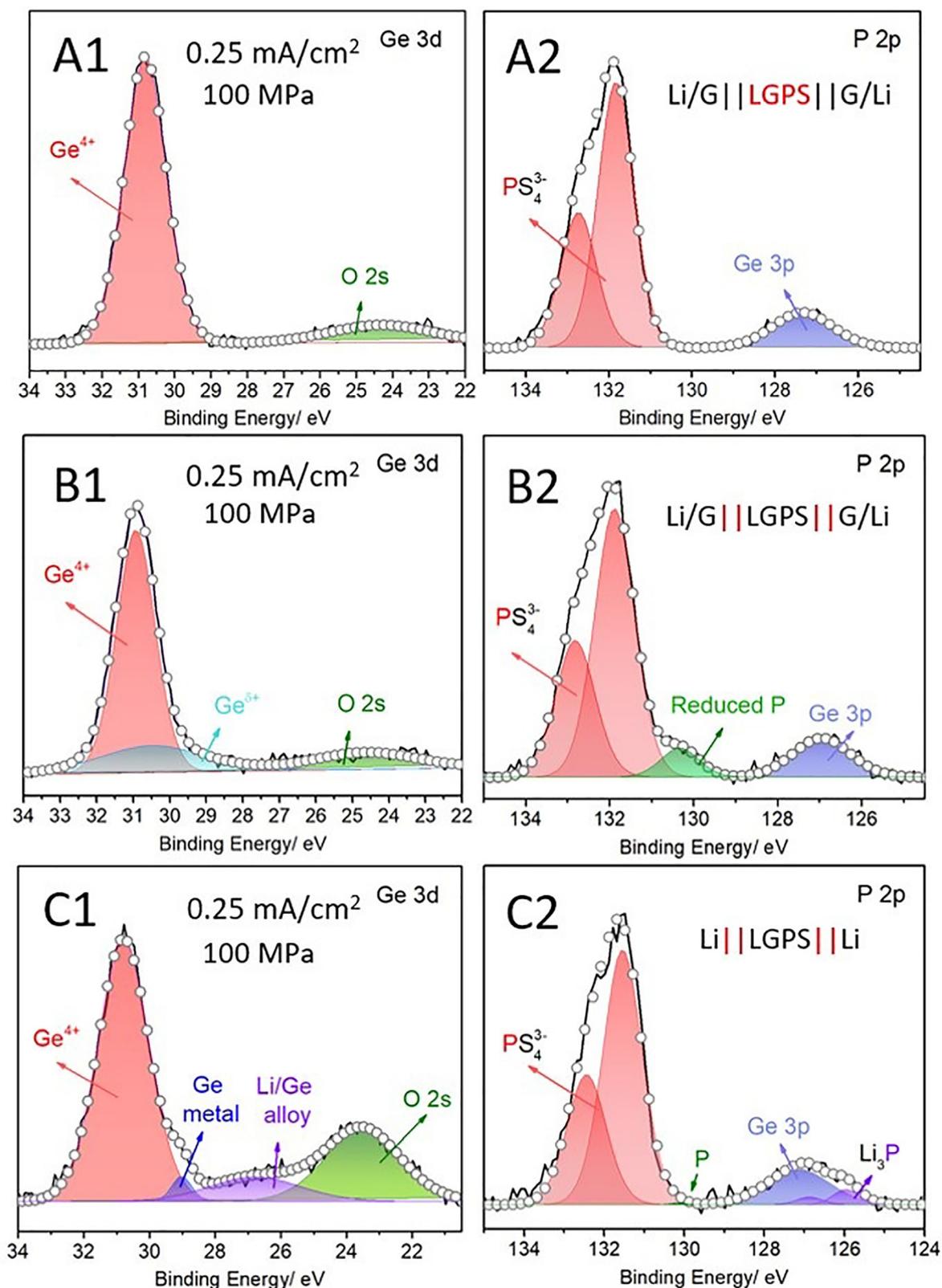


Fig. 6 XPS measurement of Ge and P for anode-LGPS-anode symmetric batteries with the X-ray beam focused on (A) the center part LGPS away from the interface to Li/G and (B) the interface between Li/G and LGPS in Li/G-LGPS-G/Li cell under 100 MPa after 12 h cycle at 0.25 mA cm⁻²; (C) the interface between Li and LGPS in Li-LGPS-Li symmetric battery under 100 MPa after 10 h cycles at 0.25 mA cm⁻² (failed). Reproduced from Ref. Su Y. et al. (2020) A more stable lithium anode by mechanical constriction for solid state batteries. *Energy & Environmental Science*, 13(3): 908–916, <https://doi.org/10.1039/c9ee04007b> with permission of The Royal Society of Chemistry.

demonstrated from two aspects. LGPS cathode thoroughly mixed with electron conductive carbon in a solid-state environment can be held at 3.2, 7.5 and 9.8 V for 10 h, without showing any decomposition current under the mechanical constriction design (Ye et al., 2020). Conductive carbon in this experiment already breaks the electronic insulation, thus LGPS should decay with detectable decomposition current if the constriction condition is removed, as what was also demonstrated using a non-constricted liquid electrolyte environment, where LGPS completely decomposes (Ye et al., 2020). Third, Li capacity change in solid electrolytes can only adjust the voltage window in a relatively narrow range, e.g., up to 3 V in charge (Schwieter et al., 2020). This effect thus cannot account for the wide voltage stability of LGPS mixed with conductive carbon held at 3.2, 7.5 and 9.8 V mentioned above (Ye et al., 2020). That said, all these secondary effects may exist to help the stability if combined with the primary effect of mechanical constrictions. Therefore, constrictions induced metastability and kinetic stability, as discussed in detail in this chapter, is the central effect that dominates the electrolyte and interface voltage stabilities, as well as modulates all other secondary effects, in solid-state batteries.

Perspective on interface design and battery device design

The principles and pictures introduced in this chapter describe the main differences between the solid and the liquid electrolyte battery systems. The mechanical constriction effect in an all-solid-state battery can interact much more strongly with the electrochemical properties than the liquid electrolyte battery, to open the voltage metastability window, modulate decompositions, and create the kinetic stability. In the last example, we have already demonstrated that the interface between Li metal and solid electrolyte can be influenced by the mechanical constriction effect, and a special constriction design of using graphite protection layer can largely improve the battery performance. The mechanical constriction principle also applies to all kinds of interfaces in a solid-state battery system, especially those between the cathode and the electrolyte particles, operated at high voltages. This effect has been partly considered in the previous literature (Ye et al., 2020), studying of which represents one fast growing direction in the field.

In the future, there needs a systematic way to design such interfaces with the best coatings for cathode, anode and electrolyte particles, with the electrochemical response of interfaces to multiple levels of mechanical constrictions explicitly considered. What makes it more interesting and challenging is that these multiple levels of constrictions are also entangled, with the local mechanical constriction being modulated through global mechanical constrictions. The latter is actually controlled by the engineering approaches and procedures of making and assembling the batteries, as well as the design of the entire battery device. Therefore, applying mechanical constriction principles to the solid-state battery design includes the designs on multiscale at the material, interface, and device levels. I thus consider that understanding and controlling the complicated interactions of electrochemistry, materials, and devices through the mechanical constriction modulation forms one of the most important and challenging topics in advanced solid-state battery designs.

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