Towards a mechanically stable solid electrolyte interphase (SEI)

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Summary

The correlation between solid electrolyte interphase (SEI) mechanical properties and battery electrochemical performances is complex and remains poorly understood. Gao *et al.* recently proposed a new mechanical parameter to predict the SEI stability, bringing new insights onto future battery design.

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High voltage batteries by their inherent nature are thermodynamically unstable, with kinetics playing a major role in deciding their stability, performance and life time.[1] During the cathodic reaction, the electrolyte is reduced at the anode, forming a thin decomposition layer (usually 1–10 nm thick), known as the solid electrolyte interphase (SEI), at the anode/electrolyte interface.[1] The success of intercalation-based Li-ion battery technology is largely due to the kinetic stability provided by the SEI at graphite anode/electrolyte interface. The physio-chemical nature of SEI determines the ability of the working cation (Li^+, Na^+ or K^+) to reversibly transport through the SEI layer with minimum resistance, which ultimately dictates the cycle-life and performance of batteries. However, the SEI properties (composition, morphology, thickness, *etc*.) are highly dependent on the specific electrode-electrolyte interaction and have been extensively studied but not yet fully understood.

Growing demand for high energy density has led the trend of pursuing high-capacity electrode materials such as metal alloy anodes (*e.g.*, Si, Sb, Sn, etc.), whose capacities are almost an order of magnitude higher than graphite (372 mAh/g). However, such high capacity comes at a cost:

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these materials experience > 300 % volume expansion upon working cation insertion. To be able to accommodate such high-volume changes, in addition to providing passivation and unhindered ion transport, the SEI should have a robust mechanical stability upon cycling. The conventional thinking so far has been that the SEI layer should have either high Young's modulus (E) to suppress the volume expansion or large elastic strain limit (ε_Y) to be flexible enough to accommodate the electrode volume change without breaking apart. However, measuring those mechanical properties of SEI layer using standard mechanical techniques, such as tensile test and indentation test, poses many challenges because of the very nature of the SEI layer. Variations of techniques based on atomic force microscope (AFM) can provide information on the mechanical properties via force-distance measurements.[2,3] Aside from the experimental challenges to measure the SEI mechanical properties, it is difficult to find a material that has both high Young's modulus and large elastic strain limit. Finding the proper trade-off between the two parameters without theoretical guideline is difficult. New techniques or parameters that can capture both hard and soft materials properties within the SEI layer at meso-scale are needed.

In a recent article published in *Joule*, Gao *et al*. proposed a new mechanical parameter – maximum elastic deformation energy (U), which takes both Young's modulus and elastic strain limit into account, to investigate the SEI stability.[4] The authors demonstrated a two-step approach to extract Young's modulus and elastic strain limit of the SEI layer individually by performing an ex-situ AFM nanoindentation on cycled anode electrodes (Fig. 1). In both steps, the AFM probe performed force-distance measurements, where the probe approached the electrode surface from above a certain distance, after it went in contact with the surface, the probe kept pressing onto the surface until the pre-registered force setpoint was reached and then withdrew from the surface (Fig. 1a). At the first step, the force setpoint was small (< 30 nN) to limit the SEI deformation within the elastic region. The Young's modulus was extracted from the slope of the tip-sample contact region (highlighted in yellow in Fig. 1b) by applying Hertz contact model. However, as the SEI layer is soft and thin, the underlying anode will affect the Young's moduli measured by nanoindentation and should be corrected. The authors conducted a finite element (FE) simulation to investigate the substrate effect on Young's moduli extracted from nanoindentation measurements. Their results indicate that the SEI Young's moduli were overestimated by 30 – 50 % if the substrate effect was not taken into account. At the second step, a large force setpoint was applied (> 900 nN) to the SEI to ensure it exceeds the elastic limit and reaches plastic deformation. The load to initiate the

yielding stress (F_Y, highlighted in yellow in Fig. 1c) can be extracted from the force-distance curve and the elastic strain limits of the SEI can then be calculated. The two-step AFM nanoindentation has been conducted on more than 100 positions on each electrode sample to obtain statistics. It should be noted that AFM force-distance curves vary a lot when measured in liquids or on soft materials. It is thus important and highly appreciated that the authors conducted a statistical analysis to capture meaningful data. Once Young's modulus and elastic strain limit are obtained, the maximum elastic deformation energy can be calculated by the following equation:

$$U = \frac{8}{15}\left(\frac{4}{5}\pi\right)^5 \cdot r^3 \cdot (1-\nu^2)^4 \cdot E \cdot (\varepsilon_Y)^5$$

where ν is SEI's Poisson's ratio and r is the radius of AFM indenter. Both are assumed the same for all the systems (ν = 0.3, r = 1 μm). The authors demonstrated this new concept in lithium and potassium batteries with different common carbonate and ether-based electrolytes using Li-Sn and K-Sb anodes, respectively. Unlike using the Young's modulus or elastic strain limit alone as a predictor, maximum elastic deformation energy, which combines both parameters, showed a clear trend that the systems with higher U values exhibit better Coulombic efficiency and cyclability (Fig. 1d). Moreover, higher U values were found for those cycled in ether-based electrolytes. X-ray photoelectron spectroscopy (XPS) results indicated that the SEI in carbonate electrolytes contains higher content of inorganic components, such as $ROCO_2Li(K)$ and Li_2CO_3, that that in ether-based electrolytes. Further FE simulations suggest that although the inorganic components have higher Young's moduli, the larger differences in Young's moduli between the organic and inorganic phases generates higher stress at their interfaces, resulting in low elastic strain limits. Therefore, the SEI with more inorganic components exhibits a lower U value.

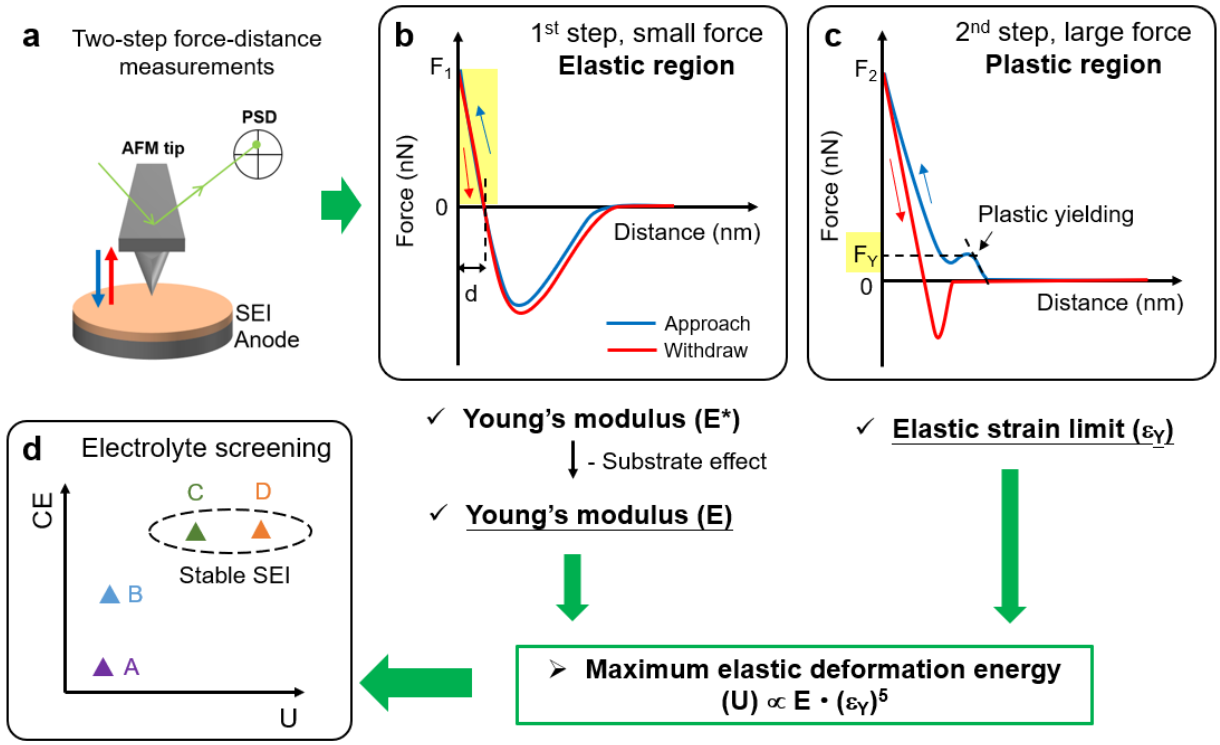

Figure 1. Two-step AFM nanoindentation to extract maximum elastic deformation energy of SEI to predict SEI stability for better cycling performance. (a) AFM nanoindentation via force-distance measurement; (b) 1st step: apply a small force setpoint to limit the sample deformation within its elastic region. When in the elastic region, the withdrawal curve will be linear and overlap the approach curve in the tip-sample contact zone (F > 0, highlighted in yellow); (c) 2nd step: apply a large force setpoint to exceed the sample's elastic limit. the approach curve shows discontinuity once it reaches the plastic yielding point (indicated by arrow); (d) the maximum elastic deformation energy (*U*) obtained via Young's modulus and elastic strain limit can be used to predict SEI stability and screen the suitable solvent/electrolyte for a selected anode to improve Coulombic efficiency (CE) and cyclability.

Overall, this work brought an inspiring new angle to investigate the mechanical aspects of SEI. The proposed approach, which allows correlating SEI microstructure (organic vs inorganic phases) and mechanical properties, can be also be applied to ceramic-polymer composite solid electrolyte for all-solid-state batteries. However, for the proposed approach to extend beyond the reported material systems, a more complex model incorporating realistic values of the physical properties (SEI Poisson's ratio, tip radius, *etc.*) should be used. It should be noted that AFM force-distance based measurement is highly sensitive to sample morphology as the tip-sample contact area (which is a key parameter in calculating both E and ε_Y) varies across the sample. The battery electrode surfaces are generally rough before cycling, and their roughness evolves/increases with cycles.

This should be taken into account when further implementing the reported approach to other materials. Moreover, the techniques to characterize mechanical properties are usually force-based techniques, which cannot provide chemical information. More effort towards advanced characterizations combining more complex AFM techniques (*e.g.*, microcantilever electrode[5] or band-excitation[6]) and other light-based or electron-based techniques (*e.g.*, tip-enhanced Raman spectroscopy[7,8]), are necessary to understand the electro-chemo-mechanical properties of the complex SEI layer and achieve next generation batteries.

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