

# Review on Solid Electrolyte Interphase (SEI) Structure of Rechargeable Batteries

Changqing Lu.

University of Michigan – Shanghai Jiao Tong University Joint Institute (UMJI). Mechanical Engineering Department. 800 Dongchuan Road, Minhang District, Shanghai, 200240, China.

**KEYWORDS.** *Solid Electrolyte Interphase. SEI. Lithium-ion Batteries. Rechargeable Batteries. Sodium-ion Batteries.*

**ABSTRACT:** From the introduction of the solid-electrolyte interphase (SEI) by E. Peled, this model became one of the important foundation of the development of efficient rechargeable batteries. SEI acts as a barrier between the electrolyte and the negative electrode where cations are allowed to transfer but not electrons. In favor of the battery performance, good SEI structure and compositions are able to protect further erosion of negative electrode by the electrolytes. However, researchers are not able to fully understand the formation mechanism as well as the structure of the interphase. From the establishment of this model, improved techniques enable researchers to investigate the structure of SEI more clearly. In other words, it is important to know the limitations of the investigating techniques so as to correctly interpret the experimental data. In this review, some traditional sample investigation methods are introduced as well as two new innovative ones, which results in different SEI structure models. The SEI model can also be utilized into aqueous electrolyte-electrode interphase. However, the formation mechanism need further investigating as well. Based on the current understanding of the SEI structure and characteristics, artificial SEI might be a good way to improve the overall performance of the rechargeable batteries.

## Previous to the SEI Model

Solid-electrolyte interphase (SEI) is a widely-recognized scientific model in the rechargeable battery field nowadays. It is the layer that forms between the electrolyte and the negative electrode of the battery, which can explain the capacity loss of the battery as well as many other situations of poor battery performance. Before the introduction and establishment of this model in 1979 (13), researchers believed that the anode of the lithium-ion batteries was covered in a passivating layer that somehow suppressed the deposition/dissolution process, consequently resulting in a limited cycle life.

In a workshop about the “Lithium non-aqueous battery electrochemistry” in June 1980, S. B. Brummer reported his research about the “surface films” on lithium battery negative electrode and the influence of the films on the rechargeability of lithium (13). He presented a model (Figure 1) which explained the capacity loss due to the reaction between the deposited Li metal and the electrolyte, causing the consumption of the active lithium. He stated that there were two types of surface films. One type was not electronically conductive and with only low porosity that allowed lithium-ion to pass through. The other type was electronically conductive but very tight so that lithium-ions could not pass. Both of the established theories were based on the idea that the transfers of electrons and cations happened between the electrolyte and the electrode.

Based on his conclusions, Brummer presented several solutions to modify the surface films (13). By using “precursors”, Brummer hoped that they could compete lithium metal for the reaction with the solution so that there would be no reaction between the plated Li metal and the solution, hence, no formation of Li-solvent film (13).

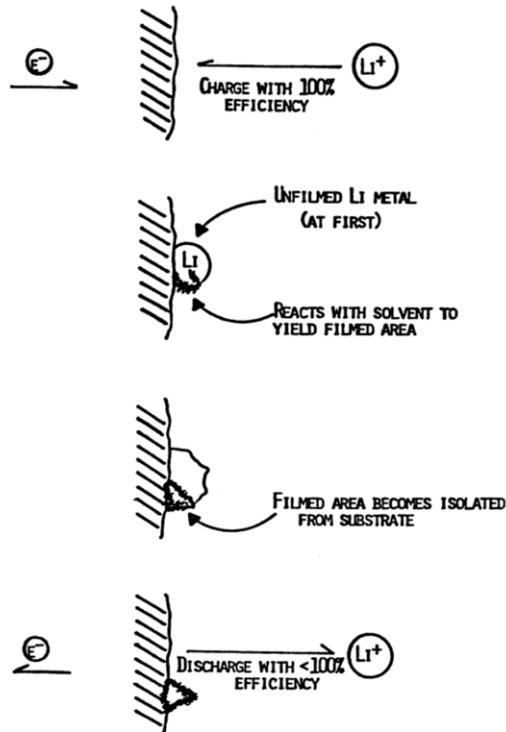


Figure 1. According to S.B. Brummer’s research (13), this is the model he made about the recharging of lithium on the negative electrode. The lithium is deposited with 100% faradic efficiency at first. Then some of the deposited Li metal reacts with the electrolyte, forming products that become isolated from the electrode. The stripping process of the lithium ion is

then not 100% complete due to the separation. Then cycle by cycle, Li is consumed by the reaction with the electrolyte, which results in the final zero-capacity of the battery.

While Brummer's research was just an example of the previous understanding of the electrochemical reaction mechanism at the negative electrode, we could see that most of the conclusions drawn at that time was based on the belief that both electrons and cations were transferred between electrolyte and electrode. During that workshop, A. N. Dey also presented his conclusions on the two-stage passivating Li-solvent film growth (Figure 2) (1).

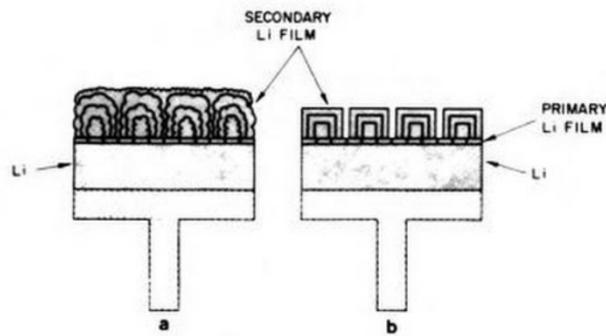


Figure 2 (1). The primary Li-solvent film growth was a thin and compact layer. While the following secondary stage of Li-solvent film was a crystalline film. The growth happened in the holes and cracks of the first layer where Li metal and the solvent were still in contact. And the structure of the thicker second film was also more dependent on the characteristics of the solvent such as the concentration, additive and impurities.

We can see from the researches before the introduction of solid-electrolyte interphase that there were no clear theoretical models brought up explaining the detailed mechanism of the reaction on negative electrode by strict experimental methods. All of the explanations were based on analysis of electrochemical reaction equations.

### Introduction of SEI Model

In 1979, E. Peled introduced the solid-electrolyte interphase model to explain the electrochemical reactions that happen at the negative electrode of the batteries (3). The solid-electrolyte interphase is an unavoidable electrochemical reaction product at the negative electrode that can result in poor battery performance such as capacity loss.

Compared to the previous understanding, Peled stated that the solid-electrolyte interphase is highly electronically resistive and only lithium cations can pass through (3). As we can see from the schematic in Figure 3, the electrons are conducted through the negative electrode instead of the layer between the electrolyte and the electrode according to the previous explanations. This fundamental change of understanding and establishment of the model proved to be a step stone for the research in rechargeable batteries.

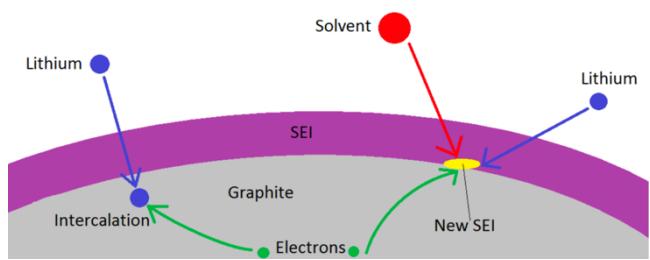


Figure 3 (10). This is a schematic for the solid-electrolyte interphase (SEI) model. The interphase is formed due to the reaction of the solvent and the lithium, which is the reaction competing with the lithium intercalation reaction, causing lithium loss during battery operation.

For the lithium cations to travel through SEI, three processes are involved. Firstly, the lithium cations move through electrolyte solution and enter the vacancies in the solid-electrolyte interphase. Then due to the electric potential difference, the cations pass through the interphase. Finally, the cations and the negative electrode material react with the transferred electrons, which completes the intercalation process.

The reaction rate of the intercalation process is vital to the discharge/charge process of the battery. The macropolarization curves showed that when the SEI thickness was over 400 Å, the Tafel slope was greater than 3V (3), which indicated that the rate-determining step is cations traveling through the SEI.

### Past Research on SEI Structure

After the introduction of the SEI model, more efforts were made into the investigation of the detailed ion transport mechanism through the SEI, how SEI is formed based on different types of negative electrode and electrolytes as well as whether we can change the characteristics of the SEI such that the presence of SEI can improve the battery performance.

Initially, the structure of SEI was believed to have two layers with different properties. The first layer is thin and compact. The second layer is porous, which inhibits the ion transport from the electrolyte to the anode (Figure 4) (6).

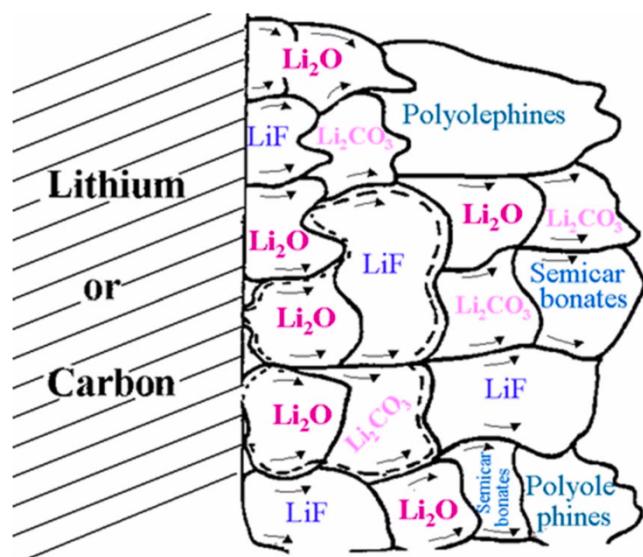


Figure 4 (6). Schematic showing a model of SEI structure with two layers, the first thin and compact and the second more porous.

However, modifications are constantly proposed on the structure of the SEI. In 1987, Thevenin and Muller suggested two possible types of models against SEI (7). They studied the impedance behaviors of the “metal/surface-layer/solution system” and concluded that for propylene carbonate (PC) electrolyte, the polymer-electrolyte-interphase (PEI) model consists of a mixture of  $\text{Li}_2\text{CO}_3$ ,  $\text{P}(\text{PO})_x$ , and  $\text{LiClO}_4$  (7). Or the surface layer can be modeled by a “solid-polymer layer (SPL)” model consisting of a mixture of solid and polymer electrolytes (7). The approach they used was to establish some models first, predict the equivalent impedance behavior and compare the experimental results with the theoretical predictions. The impedance behavior reproduction results were their proof of the possible models. In 2000, according to E. Peled et al. (4), TOF-SIMS and XPS depth profile shows a microphase distribution of organic and inorganic materials due to the anion and electrolyte reduction. TOF SIMS is time-of-flight secondary ion mass spectrometry, which utilizes a pulsed ion beam to remove molecules from the outer surface of the sample. These removed particles are accelerated to a tube where their time-of-flight through the tube is measured by a detector as well as their mass.

#### Innovative Methods of SEI Structure Investigation

For 30 years, many other techniques are used for the structure and composition analysis of the SEI as well. Through the improvements of the techniques, researchers are able to investigate the detailed structures of SEI in some new light.

Two traditional ways are X-ray photoelectron spectroscopy (XPS) and the Fourier transform infrared spectroscopy (FTIR). However, these methods are limited in their capability of fully revealing the formation mechanism. For FTIR, for example, it is a method based on the different vibrational energy between the bonds. To investigate the compositions of the SEI, the vibration signals may not be strong enough due to the small thickness of the SEI (13). What's more, the structure of SEI is not usually homogeneous. Therefore, FTIR cannot reveal the distribution of certain compositions within the interphase (13).. For XPS, it is a method utilizing high-energy X-ray photons to excite the sample. The sample would eject the photons as photoelectrons and the kinetic energy of the ejected photoelectrons are proportional to the energy level from which they are ejected from. However, for SEI, it is possible that the compositions of the SEI are degraded due to the high energy level of the electrons (13). Since the structure of SEI is quite vulnerable for such destructive method as XPS.

However, new methods are introduced recently to investigate the SEI on lithium ion batteries with graphite electrode. The first method is transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDX), while the second method is the multi-nuclear magnetic resonance (NMR) spectroscopy of  $\text{D}_2\text{O}$  extracts from the cycled anodes (lithium ion battery graphite solid electrolyte interphase revealed by microscopy and spectroscopy). The implementation of these two methods are based on the manufacture of binder-free (BF) graphite electrode (Figure 5). The implementation of BF electrode can simplify the data interpretation for the SEI (16).

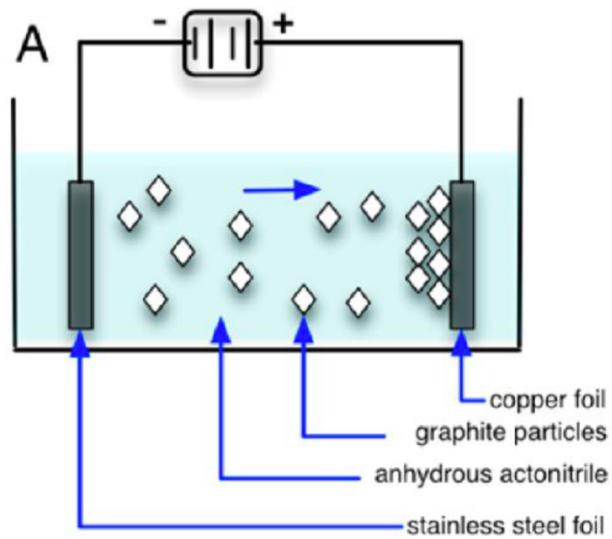


Figure 5 (11). This is a schematic of manufacturing binder-free (BF) graphite electrode. It is manufactured by electrophoretic deposition (EPD) method.

For the TEM method proposed by Mengyun Nie (11), the innovative technique involves the integration of the TEM grid into the electrode (Figure 6). In this way, no great amount of graphite SEI sample is needed, neither is the electrode dispersion, which can potentially alter the SEI structure. Instead, graphite electrode particles prepared *in situ* can be directly analyzed (11). The NMR method involves rinsing the cycled electrode with  $\text{D}_2\text{O}$  in an Ar glovebox, which limits SEI's exposure to air, thus limiting the possibility of structure alteration of the SEI (11).

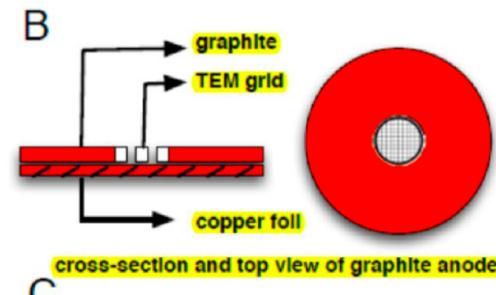


Figure 6 (11). The schematic of the TEM grid integration into the graphite electrode.

The effectiveness of the  $\text{D}_2\text{O}$  rinse can be shown in Figure 7. The IR spectra on the fresh graphite electrode and the cycled graphite electrode after rinse basically showed the same pattern, while applying different voltage potentials, the IR spectra of the cycled graphite with SEI reflect different wavelengths, which means the  $\text{D}_2\text{O}$  rinse removes the SEI from the electrode. The XPS inspection also shows the same results.

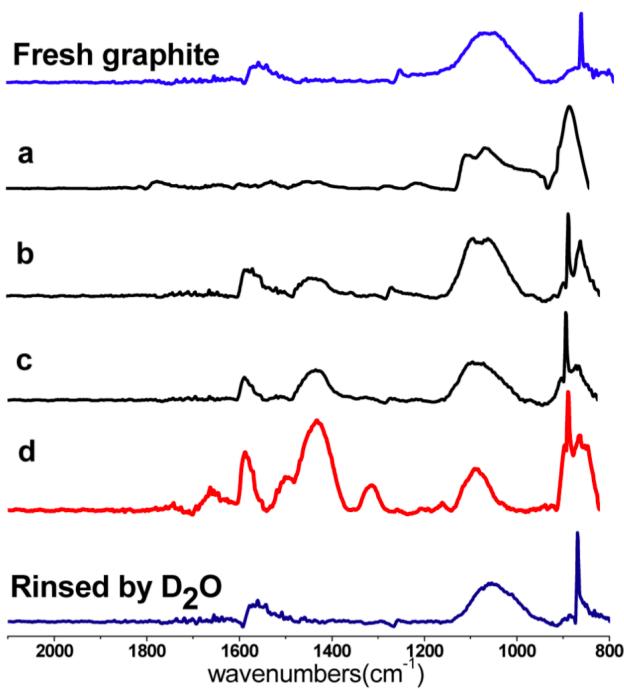


Figure 7 (11). IR spectra of 1.2 M LiPF<sub>6</sub>/EC electrolyte with binder-free cycled graphite electrode. (a) to (d) at different voltages vs. Li/Li<sup>+</sup>. Top and bottom are fresh graphite and the cycled graphite after D<sub>2</sub>O rinse.

The graphite electrodes were tested with different electrolytes: LiPF<sub>6</sub> and ethylene carbonate (EC), ethyl methyl carbonate (EMC) and EC/EMC blends (11). Generally, we would expect that for different electrolytes, the compositions of graphite SEI are different. But using the techniques mentioned above, the results show that during the initial formation of the SEI, the compositions of the interphase for graphite electrode are mainly a mixture of lithium ethylene dicarbonate (LEDC) and lithium fluoride (LiF), the schematic of which is shown in Figure 7 (11). This kind of composition remains constant as the SEI thickness increases (11), which means the SEI is structurally uniform to a certain extent.

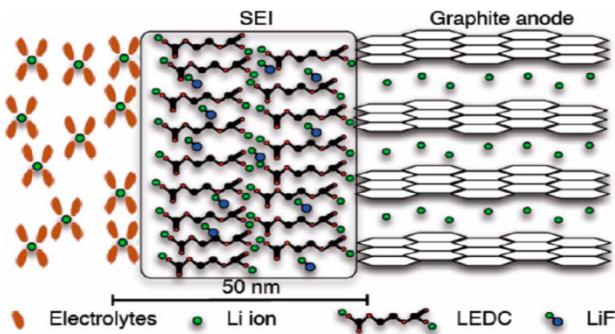


Figure 7 (11). The schematic of graphite SEI during first cycle.

The conclusion that graphite SEI structure is uniform somehow can challenge the other beliefs that SEI formation mechanism is complex and multi-staged as well as the beliefs that the structure of the SEI is multi-layered.

But from the conclusions and the experimental techniques that the researchers introduced with their conclusions, we can see that in order to understand the structure of the SEI, it is very important not to alter the SEI structure in a destructive way. For the impedance behavior reproduction method, the

inconsistency of its conclusion and the “uniform SEI structure” conclusion could due to the fact that SEI structure was disrupted during the impedance measuring process. The limitations of the popular methods investigating SEI have been mentioned in the previous part as well.

While EC, EMC, and EC/EMC electrolytes produced similar binder-free graphite electrode SEI structure, the influence of electrolytes on SEI formation is still not fully understood. Most recently, two chemical reduction methods are investigated in order to further understand the SEI structure. The synthesis of the vinylene carbonate (VC) and poly(VC) reduction products from the electrodes is investigated by Sylvie Gruegeon et al (15). Different pathways of VC reduction are compared:

- 1) “solution synthesis” through an anion
- 2) “ball milling synthesis” with the presence of lithium metal
- 3) SEI formation at the graphite surface,

and by comparing the different products of these three reduction pathways, compositions at SEI and the formation mechanisms are interpreted (Figure 8-10).

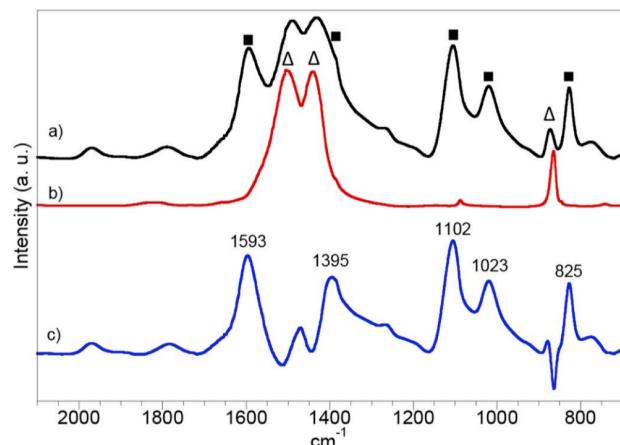


Figure 8 (15). IR spectra from ball milling synthesis of the reduced VC products.

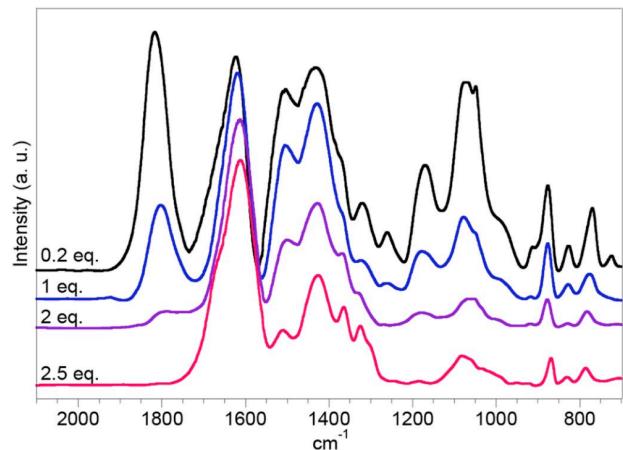


Figure 9 (15). IR spectra from solution synthesis of the reduced VC products.

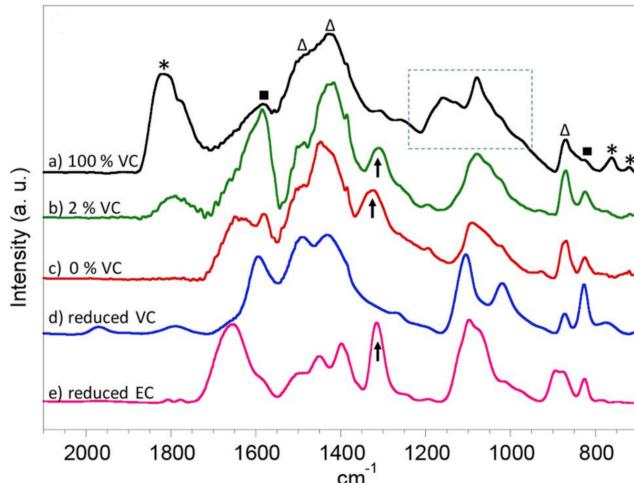


Figure 10 (15). IR spectra from SEI formation with VC at different concentration.

For the solvent-less approach, the ball milling approach mixed VC with Li metal inside the argon-filled glovebox to minimum the exposure to air (15). Poly(VC) was mixed under hexane. All the mixing reactions were not complete but the residual reagents were evaporated under conditions with minimum exposure to air as well. This procedure has the advantage of avoiding the side reactions from reagent-washing procedures (15). For the solution reduction approach, the anion used was a Li-DBB radical anion and THF solution was used as a reducing agent. The results suggest that VC-rich electrolyte tends to generate lithium alkyl carbonates and lithium carbonates and poly(VC) tends to form at subsequent cracks of the initial SEI layer (15).

The techniques and conclusions mentioned above are all experiment-based approach to investigate SEI structure and formation mechanism. However, new computational approaches are being developed as well.

With some experimental data as foundations, the field of computational materials can predictively analyze or construct the SEI structure. And since experiment-based methods are less efficient in trying out new types of electrolytes-electrode combination, computational approach might also be helpful in pre-selection of the materials and design. Review on the computational approach by Aiping Wang et al. (2). shed some light on the possibility of compensating experimental approach by computational approach. However, the correct computational model is dependent on the correct experimental data, which, as we have stated earlier, needs non-disruptive way of investigating the SEI composition and structure.

### Artificial SEI

The intention of analyzing the formation mechanism as well as the structure of the solid-electrolyte interphase is to provide a guideline in what kind of SEI is in favor of good battery performance.

In short, a good SEI has the following qualities:

- 1) minimum electronic conductivity
- 2) maximum lithium ion conductivity
- 3) fast formation of SEI before the intercalation of lithium ion to prevent further lithium loss during operation

4) uniform composition and electrochemically inert

5) good strength and elasticity to accommodate possible electrode volume growth due to intercalation process

6) good adherence to the anode.

If existing electrolytes/electrode combination cannot provide the ideal SEI structure, then artificial SEI might better improve the battery performance. Instead of letting SEI growth at the initial cycle, a pre-applied film of ideal materials acting as SEI could restrain the dendrite growth during lithium ion battery operation as well as other undesired battery problems. Nian-Wu Li et al. proposed a stable SEI layer of  $\text{Li}_3\text{PO}_4$  in organic electrolyte as well as the deposition/dissolution process (Figure 11) (12).

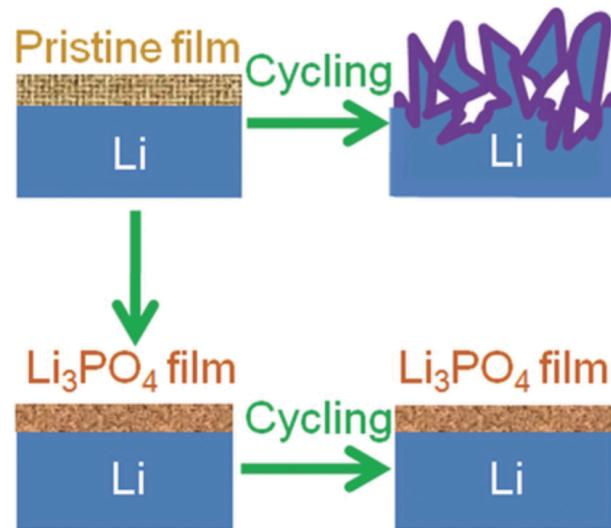


Figure 11 (12). Schematic of the effects of artificial SEI.

Yayuan Liu et al. proposed another artificial SEI with several desirable characteristics such as high strength, good flexibility as well as high lithium-ion conductivity (17). This is a coating composed of  $\text{Cu}_3\text{N}$  nanoparticles joined with styrene butadiene rubber (SBR). In this layer,  $\text{Cu}_3\text{N}$  basically functioned as the lithium-ion conducting particles while the SBR provides good mechanical properties such as high strength and good elasticity (17).

Artificial SEI design can also utilize the computational methods as well to predict interphase performance.

### Non-aqueous to Aqueous Electrolyte

Through the development of lithium-ion batteries, battery safety is another major concern due to the widely application of commercial rechargeable batteries. The problem with non-aqueous organic electrolytes is that they are flammable and toxic. Alternatively, aqueous electrolytes can avoid those issues. But for aqueous electrolytes, their electrochemical stability window is too narrow.

However, SEI model can also be used in this type of electrolytes. Lumin Suo et al. proposed an electrode-electrolyte interphase which enables the window to expand to ~3.0 volts (8-9). The electrolyte is highly concentrated  $\text{LiTFSI-H}_2\text{O}$  (8-9). This interphase formation is also investigated (Figure 12), which consists of anion reduction and dissolved  $\text{O}_2/\text{CO}_2$  reduction (8-9).

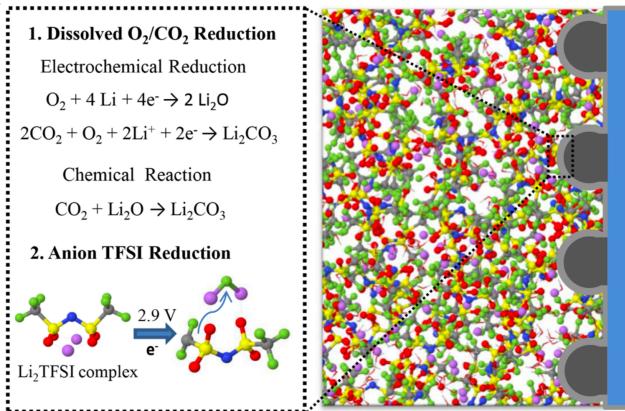


Figure 12 (8-9). Proposed SEI formation mechanism in Water-in-Salt electrolyte.

The application of the concept SEI on aqueous electrolyte shows that the formation mechanism of SEI is rather complex. More advanced techniques are required to fully understand especially the kinetics of the SEI formation. However, artificial SEI somehow shed light on approaches of improving battery performance.

### Conclusion

The introduction of the SEI model is a vital step towards understanding the working mechanism of rechargeable batteries. Investigations on formation mechanism and consequent structure of SEI are conducted based on the improvement of the techniques. It is important to know the limits of the techniques so as not to draw incorrect conclusions. While SEI formation is not fully understood, the ideal SEI is desirable through artificial coatings on the electrodes, which have been proved to improve the battery performance.

### REFERENCES

- [1] A. N. Dey, in *Proceedings of the workshop on Lithium non-aqueous battery electrochemistry*, Vol. 80–87, edited by E. G. Yeager, B. Schumm, G. Blomgren, D. R. Blankenship, V. Leger, and J. Akridge, The Electrochemical Society, Princeton, New Jersey, 1988.
- [2] A. Wang; S. Kadam; H. Li, S. Shi; Y. Qi. Review on modeling of the anode solid electrolyte interphase for lithium-ion batteries. *Computational Materials*. 2018, 4, 15.
- [3] E. Peled. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* 1979, 126(12), 2047-2051.
- [4] E. Peled; D. Bar Tow; A. Merson; A. Galaktion; L. Burstein; D. Goldnitsky. Composition, depth profiles and lateral distribution of materials in the SEI built on HOPG-TOF SIMS and XPS studies. *J. Power Sources*. 2001, 97-98, 52-57.
- [5] E. Peled; H. Yamin. Solid Electrolyte Interphase (SEI) Electrodes. Part 1. The Kinetics of Lithium in LiAlCl<sub>4</sub>-SOCl<sub>2</sub>. *Isr. J. Chem.* 1979, 18, 131-135.
- [6] E. Peled; S. Menkin. Review-SEI: Past, Present and Future. *J. Electrochem. Soc.* 2017, 164(7), A1703-A1709.
- [7] J.G. Thevenin; R. H. Muller. Impedance of Lithium Electrodes in a Propylene Carbonate Electrolyte. *J. Electrochem. Soc.* 1987, 134(2), 273-280.
- [8] L. Suo; O. Borodin; T. Gao; M. Olguin; J. Ho; X. Fan; C. Luo; C. Wang; K. Xu. “Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* 350(6263), 938-943.
- [9] L. Suo; D. Oh; Y. Lin; Z. Zhuo; O. Borodin; T. Gao; F. Wang; A. Kushima; Z. Wang; H. Kim; Y. Qi; W. Yang; F. Pan; J. Li; K. Xu; C. Wang. How Solid-Electrolyte Interphase Forms in Aqueous Electrolytes. *J. Am. Chem. Soc.* 2017, 139, 18680-18680.
- [10] M. B. Pinson; M. Z. Bazant. Theory of SEI Formation in Rechargeable Batteries: Capacity Fade, Accelerated Aging and Lifetime Prediction. *J. Electrochem. Soc.* 2013, 160(2), A243-A250.
- [11] M. Nie; D. Chalasani; D. P. Abraham; Y. Chen; A. Bose; B. L. Lucht. Lithium Ion Battery Graphite Solid Electrolyte Interphase Revealed by Microscopy and Spectroscopy. *J. Phys. Chem.* 2013, 117(3), 1257-1267.
- [12] N. Li; Y. Yin; C. Yang; Y. Guo. An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Adv. Mater.* 2015, 28(9), 1853-1858.
- [13] P. Verma; P. Maire; P. Novak. A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries. *Electrochimica Acta*. 2010, 55 6332-6341.
- [14] S. B. Brummer, in *Proceedings of the workshop on Lithium non-aqueous battery electrochemistry*, Vol. 80–87, edited by E. G. Yeager, B. Schumm, G. Blomgren, D. R. Blankenship, V. Leger, and J. Akridge, The Electrochemical Society, Princeton, New Jersey, 1988.
- [15] S. Grugeon; P. Jankowski; D. Caillet; C. Forestier; L. Sannier; M. Armand; P. Johansson; S. Laruelle. Towards better understanding of vinylene carbonate derived SEI-layers by synthesis of reduction compound. *J. Power Sources*. 2019, 427, 77-94.
- [16] S.-H. Kang; D. P. Abraham; A. Xiao; B. L. Lucht. Investigating the solid electrolyte interphase using binder-free graphite electrodes. *J. Power Sources*. 2008, 175, 526.
- [17] Y. Liu; D. Lin; P. Y. Yuen; K. Liu; J. Xie; R. H. Dauskardt; Y. Cui. An Artificial Solid Electrolyte Interphase with High Li-Ion Conductivity, Mechanical Strength, and Flexibility for Stable Lithium Metal Anodes. *Adv. Mater.* 2016, 29(10).

