

Neutron Radiography have been recently adapted to the study of the electrode surface and the chemical and physical properties of the SEI.

This chapter addresses several issues dealing with the mechanism of SEI formation on inert substrates, lithium, carbonaceous materials and tin-based alloys. Attention is currently focused on the correlation between the composition and morphology of the solid-electrolyte interphase forming on the different planes of highly ordered pyrolytic graphite (HOPG) and different types of disordered carbon electrodes in lithium-ion cells.

2 SEI Formation Processes and Morphology

2.1 The Main Principles and Routes of SEI Formation

The deposition-dissolution process of an electrode covered by an SEI involves three consecutive steps, which are described schematically as follows:

Electron transfer at the metal/SEI interface



Migration of cations from one interface to the other when $t_M^+ = 1$ (or migration of anions when $t_x^- = 1$)



Ion transfer at the solid-electrolyte interphase/solution (SEI/sol). For $t_M^+ = 1$



In principle, any one of these could be the rate-determining step (r.d.s.). However, it was found, by the use of a variety of experimental techniques, that ionic migration through the SEI is the rate-determining step for many systems. In addition, it was found that the rate of nucleation of the metal deposit is affected by the interfacial resistance.^{5,6} This transport process is a key factor in the operation of non-aqueous SEI batteries.

The standard reduction potential of lithium is more negative than that of the solvated-electron system (at least in highly purified ammonia, amines and ethers). This results in the formation of the well known blue solutions of solvated electrons (e^-_{sol}).^{9,10} In rechargeable batteries under prolonged dissolution, a process of breakdown and repair may take place. Mechanical breakdown can be caused by both local preferential dissolution of the anode and by stresses in the SEI due to uneven retreat of the anode. The new anode surface, exposed to the electrolyte, immediately reacts with it to form a fresh

thin protective film that slows further local corrosion. Because the solvated electron may take part in the early stages of SEI formation and in the break-and-repair healing processes during lithium plating and stripping, it is necessary that the formation and the healing of the SEI take place very quickly. This is especially important on graphite, during the first intercalation step. In addition, the SEI building materials must have extremely low solubility. Thus the electrolyte must be designed to contain one or more SEI precursors having high standard electrode potential (E^0) and high exchange-current density (i_0) for reduction. However, the data bank of i_0 for such reactions is limited. It was therefore suggested to use the data bank for the bimolecular rate constant (k_c) for the reaction:¹¹



where e_{aq}^- is a hydrated electron and S is an electron scavenger and a candidate material for a lithium-battery electrolyte. The reactivity of materials toward e_{aq}^- (in aqueous solutions) is expected to be quite close to that for e_{sol}^- in organic solutions. The data bank for k_c in aqueous solutions contains information on more than 1500 materials.^{12,13} The first factor to take into account is that rate constants higher than $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ relate to diffusion-controlled reactions, which are expected to proceed very quickly at the lithium-electrode potential. Therefore SEI precursors should be chosen from this group or at least from the group having rate constants higher than $10^9 \text{ M}^{-1} \text{ sec}^{-1}$. For instance, AsF_6^- and CO_2 , which are good SEI precursors,¹⁴⁻¹⁶ have values of k_c that approach those for diffusion-controlled reactions. Liquid electrolytes typically used in lithium batteries consist of a lithium salt dissolved in an organic solvent, or a mixture of solvents. The solvents fall into two general classes: ethers or alkyl esters of carbonic acid. "Inert" electrolyte components — for example ethers, which are chosen because of their very slow reaction with lithium (or with the Li_xC_6 anode) must be taken from the group that has the smallest rate constant — preferably smaller than 10^7 (or even 10^5) $\text{M}^{-1} \text{ sec}^{-1}$.

In many cases there is a good correlation between the SEI composition and the reactivity of electrolyte components toward e_{aq}^- . LiF and As-F-O species are found in the SEI formed in electrolytes containing LiAsF_6 ,^{14,17,18} BF_4^- and ClO_4^- are much less reactive toward e_{aq}^- ($k_c < 10^6$) and LiCl and B^0 are rarely found in the SEI in γ -BL solutions.¹⁷ γ -BL is expected to have a high k_c , similar to that of acetone. Ether is kinetically stable vs e_{aq}^- ($k_c < 10^7$), thus in ether-based solutions, the anion may be reduced. Indeed, in ether-based solutions containing LiBF_4 , B^0 was found in the SEI.¹⁷ When CO_2 , which has a high k_c , is added to the electrolyte, more Li_2CO_3 is found in the SEI.¹⁹ EC is so far the best SEI-forming

precursor. We attribute this (in part) to its high i_0 , which is expected to be similar to that of DMO. Esters such as ethyl acetate and semicarbonates like propylene glycol carbonate have moderate rate constants (10^7 - 10^8 $\text{M}^{-1}\text{sec}^{-1}$). This suggests that semicarbonate is not stable with respect to lithium and that the part of the SEI, which is close to the lithium (or the Li_xC_6) anode cannot consist of semicarbonate as already reported^{14, 20} and as was confirmed in Ref. 11.

The voltage of SEI formation (V_{SEI}) correlates with the reactivity of the electrolyte components towards e_{aq}^- as well; this reactivity, in turn, is directly related to i_0 . In the case of reactive components like AsF_6^- , CO_2 and EC, V_{SEI} is more positive. However, for more kinetically stable (lower k_i) substances, like ClO_4^- (and probably PF_6^- and imide), V_{SEI} approaches the Li/Li^+ potential, i.e. the overpotential of the SEI formation process is higher. In order to estimate the relative contribution of the EMF and i_0 to the value of V_{SEI} , let us consider the following example. The OCV of the $\text{Li}/\text{SO}_2/\text{C}$ ²¹ cell and of the Li/EC , PC , DEC , DMC/C cells is about the same, 2.8-3 V. However, the SEI formation voltage on a carbonaceous (Li_xC_6) electrode in the SO_2 -containing electrolyte is 2.4 V, almost 1 V more positive than that in EC, PC, DEC, DMC solutions (where V_{SEI} varies from 0.6 to 1.5 V). This indicates that the kinetics has a more profound effect on the SEI formation voltage than does the thermodynamic parameter (OCV).

On the basis of the data presented in Refs. 11 and 22, it was suggested that the rate constants for the reactions of solvated electrons with electrolyte and solvent components and impurities be used as a first screening tool for the selection of electrolyte components for use in lithium and lithium-ion batteries.

A brief overview of experimental data supporting the above suggestion (namely the selection of precursors for rapid SEI formation from a group of materials having high rate constants) is presented below (see sub-chapters 3 and 4).

2.2 Structure of the SEI

The transport of ions through the SEI, which consists mainly of polycrystalline material,⁵ takes place by mobile point (Schottky or Frenkel) defects. As a result, the contribution of the grain boundaries must be taken into account. In the first models describing the SEI,^{3, 4} its structure was represented as comprising two or more separate layers of different composition and properties. The first (the SEI itself), is thin and compact, while the second one (if it exists) on top of the SEI

is a more porous, or structurally open layer, that suppresses the mass transport of ions in the electrolyte filling its pores. According to this model, the SEI is made up of ordered or disordered crystals, which are thermodynamically stable with respect to lithium.

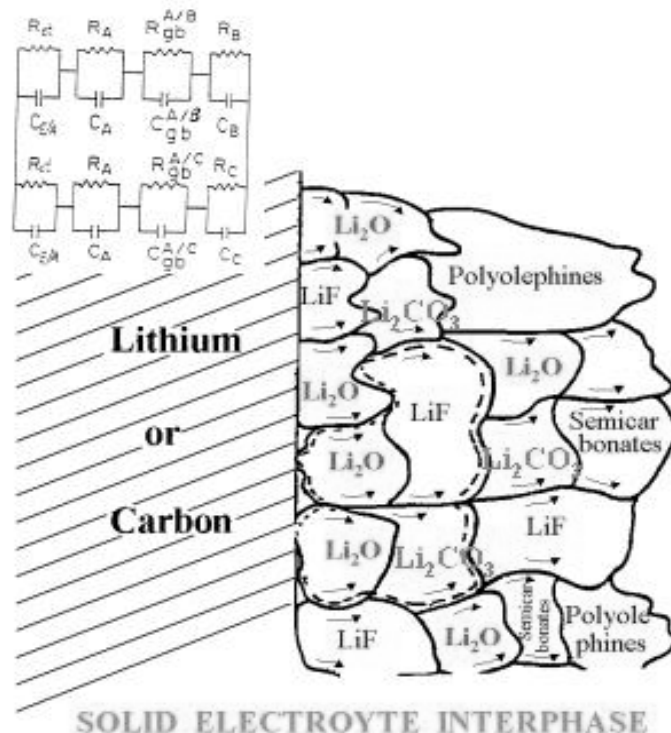


Figure 1 Schematic presentation of Polyhetero Microphase SEI. Reproduced from [8] by permission of The Electrochemical Society, Inc.

Later Thevenin and Müller²³ suggested several modifications to the SEI model: (1) the polymer-electrolyte interphase (PEI) model in which the lithium in PC electrolyte is covered with a PEI composed of a mixture of Li_2CO_3 , $\text{P}(\text{PO})_x$ and LiClO_4 . $\text{P}(\text{PO})_x$ is polypropylene oxide, formed by reduction-induced polymerization of PC; (2) the solid-polymer-layer (SPL) model, where the surface layer is assumed to consist of solid compounds dispersed in the polymer electrolyte; (3) the compact-stratified layer (CSL) — in this model the surface layer is assumed to be made of two sublayers. The first layer on the electrode surface is the SEI, while the second layer is either SEI or PEI. The first two

models do not seem to be relevant to lithium battery systems since the PEIs are not thermodynamically stable with respect to lithium. Perchlorate and fluoroanions (but not halides) were found to be reduced to LiCl and LiF.^{8, 17, 19, 22-25} Aurbach *et al.*²⁶ carried out an intensive electrochemical and spectroscopic study of carbon electrodes in lithium-battery systems. On the basis X-ray photoelectron spectroscopy measurements they suggested multi(3 or 5)-layered SEI structures.

In our recent SEI study, we assumed that reduction of salt anions and solvents proceeds simultaneously and both organic and inorganic materials precipitate on the electrode as a mosaic of microphases.^{8, 25} These phases may, under certain conditions, form separate layers, but we believe that it is more appropriate to treat them as polyhetero microphases (Fig. 1). The equivalent circuit for a mosaic-type SEI electrode is extremely complex. However, to a first approximation, a single-layer SEI is characterized by at least four RC elements in series and a Warburg impedance. These RC elements represent two interfaces-electrode/SE and SE/solution-SEI ionic resistance and capacitance, and grain-boundary resistance and capacitance. Each additional sublayer adds another three RC elements. The total SEI resistance (R_{SEI}) in battery electrolytes is typically in the range of 10-1000 ohm cm². The expected value for R_{gb} at 30°C for a 10 nm SEI is between 10-100 ohm cm², i.e. it cannot be neglected and R_{gb} and C_{gb} must be included in the equivalent circuit of the SEI, for both metallic lithium and for Li_xC_6 electrodes.⁸ We believe that in polymer electrolytes, lithium-passivation phenomena are similar to those commonly occurring in liquid electrolytes.

3 Chemical Composition and Properties of the SEI on Inert Substrate and Lithium

3.1 Inert Metal Substrate

Much information about lithium deposition/dissolution on inert electrodes has been obtained over the past twenty years. Thorough studies of the chemical composition of surface films of lithium deposited on a nickel substrate in γ -butyrolactone (γ -BL) and tetrahydrofuran electrolytes, containing various salts, such as LiClO_4 , LiAsF_6 , LiBF_4 and LiPF_6 were carried out by Kanamura *et al.*¹⁷ With the use of XPS it was found, that the outer and inner layers of the surface film covering lithium in LiClO_4/γ -BL involve LiOH or possibly some Li_2CO_3