

models do not seem to be relevant to lithium battery systems since the PEIs are not thermodynamically stable with respect to lithium. Perchlorate and fluoro-anions (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 $LiClO_4/\gamma$ -BL involve LiOH or possibly some Li_2CO_3

and Li_2O , as the main products. Chlorine and oxygen were distributed uniformly over the surface film. The authors suggested that the hydrocarbon observed in the C 1s XPS spectrum can be attributed both to a hydrocarbon contaminant and to organic compounds incorporated in the surface film. The chemical composition and the depth profile of the surface film formed in $\text{LiAsF}_6+\gamma\text{-BL}$ and $\text{LiBF}_4+\gamma\text{-BL}$ electrolytes are very similar to what is observed in the case of LiClO_4 -based electrolyte. The only difference is the lithium halide present. However, the Li 1s spectra of $\text{LiPF}_6+\gamma\text{-BL}$ electrolyte were completely different from those observed for the other $\gamma\text{-BL}$ electrolytes.¹⁷ The surface film consists of LiF as the main component while close to the bottom, the SEI consists mainly of Li_2O . The depth profiles of the SEI in THF were similar to those obtained in $\gamma\text{-BL}$, but the distribution of LiOH and Li_2O was slightly different. The surface film obtained in $\text{LiClO}_4+\text{THF}$ probably has a layer of mixed $\text{LiOH}+\text{Li}_2\text{CO}_3$ that is thicker than that obtained in $\text{LiClO}_4+\gamma\text{-BL}$.²⁷ The chemical species in the surface film of lithium deposited in LiBF_4+THF electrolyte are not very different from those in $\text{LiBF}_4+\gamma\text{-BL}$. However more LiF and other fluoride compounds are formed and chemical species including elemental boron were also observed in the B 1s spectra. This means that BF_4^- ion reacts quite strongly with lithium during electrochemical deposition in THF electrolyte. According to the depth profile, the surface film comprises mainly a mixture of LiF, LiOH and Li_2CO_3 .¹⁷ The carbon content in $\text{LiAsF}_6+\gamma\text{-BL}$, probably associated with polymeric compounds, was greater than that in $\text{LiAsF}_6+\text{THF}$. This indicates high reactivity of $\gamma\text{-BL}$ (high k_c) vs Li and is in agreement with the screening-tool approach addressed above.

Because of lower volatility and higher flash point, the organic carbonates are the preferred solvent class in commercial lithium batteries. The structure and composition of the surface film on lithium in carbonate-based electrolytes has been extensively investigated.^{17, 19, 23, 27-39} High reactivity of propylene carbonate (PC) toward the bare lithium metal is expected since its reduction on an ideal polarizable electrode takes place at potentials much more positive than those for THF and 2-methyl-THF.⁴⁰ The electrochemical reduction of five organic carbonates, EC, PC, DEC, DMC and VC were studied by cyclic voltammetry at a gold electrode in $\text{THF}/\text{LiClO}_4$ supporting electrolyte.⁴¹ The reduction potentials for all carbonates were above 1V (vs Li/Li^+), the E_{VC} being the most positive. It was shown that the preferential reduction of vinylene carbonate appears to favor SEI formation.⁴¹

Aurbach and Zaban¹⁶ have found that the lithium surface deposited on a nickel electrode in carbonate-based electrolytes is covered with Li_2CO_3 , LiOH,

Li_2O , LiOR , LiOCO_2R ($\text{R}=\text{hydrocarbon}$) and lithium halide. Their recent studies revealed that traces of oxygen, water and PC reduction products form passivating surface films on gold, platinum, silver, nickel and copper electrodes, when these are polarized to low potentials in lithium-salt solutions.⁴² These films act as solid electrolyte interphases, i.e., they allow transport of alkali metal ions through them. The study also found that the major constituent in the surface films is the PC reduction product $\text{CH}_3\text{CH}(\text{OCO}_2\text{Li})\text{CH}_2\text{-OCO}_2\text{M}$. The analytical tools used in these studies included cyclic voltammetry, electrochemical quartz-crystal microbalance, surface-sensitive Fourier transform spectroscopy and X-ray photoelectron spectroscopy. When a small amount of HF is added to PC containing 1.0 M LiClO_4 , the lithium deposited on a nickel substrate is covered with a thin $\text{LiF/Li}_2\text{O}$ surface film. However, without the addition of HF, the surface of electrodeposited lithium is covered with a thick film (mainly LiOH and Li_2O). These data also support our previous statement on the importance of relatively constant rates of salt-anion and solvent reduction when choosing an electrolyte for rapid SEI formation.

It was confirmed by surface-enhanced Raman scattering (SERS)⁴³ that the main stable species of the SEI film on the surface of the discharged silver electrode in 1M $\text{LiPF}_6/\text{EC}:\text{DEC}$ electrolyte are $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 . However, SERS cannot indicate the presence or absence of LiF in the SEI since this substance is inactive in the Raman spectrum. ROCO_2Li was found in 1 M LiClO_4 PC:DMC electrolyte. In PC-based solutions the order of the interfacial resistance of the SEI for different salts was as follows: $\text{LiPF}_6 \gg \text{LiBF}_4 > \text{LiSO}_3\text{CF}_3 \gg \text{LiAsF}_6 > \text{LiN}(\text{SO}_2\text{CF}_3)_2 > \text{LiBr}, \text{LiClO}_4$.¹⁹ The R_{SEI} values for LiPF_6/PC and $\text{LiN}(\text{SO}_2\text{CF}_3)_2/\text{PC}$ were about 800 and 23 ohm cm^2 , respectively. Such high R_{SEI} may be caused by the presence of highly reactive HF in the LiPF_6 electrolyte. The addition of CO_2 to solutions considerably reduced the interfacial resistance.

A comparison of the SEI properties on bare lithium in four electrolytes, LiClO_4/PC , $\text{LiClO}_4/\text{PC-DME}$, $\text{LiAsF}_6/\text{EC-2MeTHF}$ and $\text{LiAsF}_6/\text{THF-2MeTHF}$ was made by Montesperelli *et al.*³⁴ using impedance spectroscopy. After 10 days of storage, the resistance of the passivating film in LiAsF_6 -based solutions was found to be twice that in LiClO_4 electrolyte. High values of R_{film} (~45 ohm cm^2) in THF-containing electrolyte were explained by the high reactivity of this solvent towards lithium, followed by the formation of a thick (~220 Å) surface film. It was found that the SEI in $\text{LiPF}_6/\gamma\text{-BL}$ electrolyte is much thinner than those formed in LiAsF_6 , LiClO_4 or $\text{LiBF}_4/\gamma\text{-BL}$ -based electrolytes.¹⁷ The SEI thickness was found to be less than a few tens of angstroms in $\text{LiPF}_6 + \gamma\text{-BL}$,

while for other electrolytes it exceeds 200 Å. Moreover, the film formed in the LiPF₆-containing electrolyte was very uniform and sufficiently compact. The thickness of the lithium surface layer in a lithium perchlorate/propylene carbonate solution, as calculated from the apparent resistance according to the CSL interface model, was found to increase exponentially with storage time from 100 to 1000 Å.²³ The values obtained are in good agreement with those deduced from ellipsometric measurements.³⁵

3.2 *Lithium Covered by a Native Film*

The presence of a native film on lithium does not significantly affect the surface chemistry of the SEI formation. The outer part of the lithium native film consists of Li₂CO₃ or LiOH and the inner part is Li₂O.²⁹ As with lithium deposited on an inert substrate, the XPS spectra of lithium electrodes, covered by native film and treated in fluorine-containing salts such as LiAsF₆, LiBF₄, LiPF₆, Li-imide and Li-triflate dissolved in THF, always show fluorine, oxygen and carbon peaks.¹⁹ Methyl formate is the most reactive solvent toward lithium, as compared to other polar aprotic solvents including ethers, BL, PC and EC. Even in the presence of trace amounts of water and methanol contaminants, it is reduced to lithium formate as a major precipitate.³⁰ The presence of CO₂ in MF causes the formation of a passivating film containing both lithium formate and lithium carbonate. In PC solutions, the lithium solid electrolyte interphase was shown to be mainly a matrix of Li alkylcarbonates.¹⁶ In PC-based electrolytes, LiPF₆, LiBF₄, LiSO₃CF₃, LiN(SO₂CF₃)₂ were found to be more reactive toward lithium than were LiClO₄ and LiAsF₆.¹⁹ In LiAsF₆ PC/THF electrolyte, the concentrations of As and F in the SEI decrease. This indicates that the addition of reactive PC to the ether suppresses salt reduction by competing with it, and the film becomes more organic in nature, containing less LiF. In the case of EC/PC or EC/ether mixtures, the reduction of EC by lithium seems to be the dominant process, followed by the formation of lithium alkyl carbonates.³³ Addition of cyclic compounds with heteroatoms and conjugated double bonds, such as 2-methyl-thiophene (2MeTp) 2-methylfuran (2MeF), and aromatic compounds like benzene are very effective in electrolyte solutions for rechargeable lithium batteries.^{37, 38} In the presence of surfactants like polyethylene glycol dimethylether and a mixture of dimethyl silicone and propylene oxide in EC/DMC solutions, the smooth surface morphology and almost constant thickness of the lithium passivating film was detected.⁴⁴ Several techniques have been applied to the electrochemical analysis of lithium

electrodes in a large variety of electrolyte solutions. These include chronopotentiometry,²⁶ cyclic voltammetry, transient methods, fast OCV measurements and impedance spectroscopy. An important finding as a result of these studies is that the passivation of fresh lithium in polar aprotic electrolytes may be completed less than one second. Using a Voigt-type analog model, Aurbach calculated the thickness and resistivity of the SEI. The average thickness of the interphase next to the lithium is about 30-50 Å and the resistivity is on the order of $0.1-0.2 \cdot 10^8$ ohm cm. The resistivity of the more porous part of the SEI on the solution side is estimated to be $3-4 \cdot 10^8$ ohm cm. The higher resistivity of the SEI in LiPF_6 and LiAsF_6 solutions as compared to other salts, was explained by the replacement of the ROCO_2Li surface species by LiF . The author concluded that it is not an increase in the SEI thickness, but rather resistivity changes that lead to the high interfacial impedance of the lithium anode in LiPF_6 and LiAsF_6 electrolytes. Li_2CO_3 is stated to be one of the best passivating agents for the enhancement of lithium cycling efficiency.

3.3 SEI Formation in Solid Polymer and Gel Electrolytes

The major differences between polymer (PE) and liquid electrolytes result from the physical stiffness of the PE. PEs are either hard-to-soft solids, or a combination of solid and molten-phase equilibrium. As a result, wetting and contact problems are to be expected at the Li/PE interface. In addition, the replacement, under OCV conditions, of the native oxide layer covering the lithium by a newly formed SEI is expected to be a slow process. Aside from these differences it seems likely that in polymer electrolytes, especially in the gel types, lithium-passivation phenomena are similar to those commonly occurring in liquid electrolytes. Results obtained with PEGDME electrolytes containing different salts showed that the formation of LiF as a result of the reduction of anions like AsF_6^- or CF_3SO_3^- , plays a key role in the lithium-passivation mechanism.⁴⁵ The authors showed that SEI formation was apparently complete in just 2-3 minutes. The increase in the SEI resistance (R_{SEI}) over hours and days is apparently due to the relaxation of the initially formed passivating films or to the continuation of the reaction at a much slower rate. The formation and properties of the lithium SEI was studied in different types of hybrid and gel electrolytes based on polymers and organic solvents combined with organic or inorganic gelation agents.⁴⁶

LiI-tetraglyme-based hybrid electrolytes with PVDF-silica membrane form SEIs that are highly stable for more than 3000 hours. The three-fold increase in

the R_{SEI} of LiImide-HPEs after 300 hours of storage and about an order of magnitude increase after 2000 hours, provides evidence of the thickening with time of the passivating layer on lithium. The effect of salt on the stability of the SEI was similar in PVDF-SiO₂ and PVDF-Al₂O₃ HPEs of different porosities. Low and almost constant resistance of the SEI in lithium iodide-containing electrolytes, may be associated with high thermodynamic stability of the iodide anion towards metallic lithium. In hybrid electrolytes with Tefzel membranes, even the initial R_{SEI} value was twice that in HPEs with PVDF membranes, and the R_{SEI} increased sharply (up to 80 ohm cm²) after 300 hours of storage. These data support previous observations that nano-size ceramic fillers incorporated in a polymer membrane improve interfacial resistance in hybrid as well as in composite solid polymer electrolytes;^{25, 47} this is due to their ability to adsorb impurities and traces of water. In addition, inorganic fillers may prevent free diffusion of the liquid electrolyte components to the lithium surface and, as a result, inhibit the growth of the SEI. It is worth noting that the resistance of the lithium passivating film in alumina-containing HPEs is twice that in the silica-based HPEs. The same R_{SEI} difference was detected between Al₂O₃- and SiO₂ highly porous and less porous HPEs. At room temperature, the initial R_{SEI} in the LiI-tetraglyme- and LiI-PEGDME-based HPEs was about 200 ohm cm², while in LiImide it was 280 ohm cm². After 200 hours of storage the R_{SEI} increased by about 10% in the former electrolyte and by about 25% in the latter.

The initial interfacial resistance of EC: DMC-PAN-based gel electrolytes at room temperature was about the same order of magnitude as in TG-, PEGDME- and EC:DMC-based hybrid electrolytes. The R_{SEI} stability, however, was much lower than that of the hybrid electrolytes and the R_{SEI} increased up to 1.5 kΩ after 900 hours of storage.⁴⁸ Thus, doubts are raised as to the inert nature of the PAN matrix with respect to lithium passivation. The reactivity of PAN may stem from impurities in the commercial product and reactivity of the -CN group possibly leading to the formation of LiCN. Dissolution of LiCN could be followed by the breaking and thickening of the SEI. Contrary to EC:DMC solvents, lithium oxide, carbonate, fluoride compounds and alkoxides, which are the basic compounds found in the anode SEI, are highly insoluble in tetraglyme and polyethylene glycol dimethyl ether solvents similar to solid PEO.²² This property, as expected, increases the stability of the lithium passivation layer by producing a thinner and more compact film.

The morphology of lithium deposits from 1-3 M LiClO₄-EC/PC-ethylene oxide (EO)/ propylene oxide (PO) copolymer electrolytes was investigated.⁴⁹ It

was found that as the weight ratio of host polymer to liquid electrolyte increased, fewer lithium dendrites were formed, with no dendrites found in electrolytes containing more than 30% w/w host polymer. The authors emphasized that good contact between the polymer and lithium is also of great importance for the suppression of dendrites. Direct *in situ* observation of lithium dendritic growth in Li-imide P(EO)₂₀ polymer electrolyte⁵⁰ shows that dendrites grow at a rate close to that of anionic drift.

The interfacial phenomena in solid LiX/PE systems were extensively studied by Scrosati *et al.*⁵¹ For the dry PEO-based polymer electrolytes it was shown that the interfacial stability can be significantly enhanced by decreasing the ceramic particle size to the scale of nanometers.^{52,53} The mechanism of the processes leading to improved stability is not well understood and some explanations include scavenging effects and screening of the electrode with the ceramic phase.^{52,54}

4 Carbonaceous Electrodes

4.1 Principles of SEI Formation

Lithium-ion batteries occupy a large and increasing share of the rechargeable-battery market as a result of their excellent performance in terms of cycle life, energy density, power density and charge rate. However, for the successful use of carbon electrodes in secondary lithium-ion batteries, much work, such as the selection of high reversible and low irreversible capacity carbons, as well as understanding the complex mechanism of lithium-ion intercalation into lithium, has still to be done.

Surface structure and chemical composition⁵⁵⁻⁵⁷ affect the physico-chemical properties of carbon. The most important parameters determining the use of carbons as anode material are particle shape and size, pore-size distribution and pore-opening, BET surface area and content of surface species and impurities. The basic building block of carbons is a planar sheet of carbon atoms arranged in a honeycomb structure (called graphene or basal plane). These carbon sheets are stacked in an ordered or disordered manner to form crystallites. Each crystallite has two different edge sites: the armchair and zig-zag sites. The reactivity of carbon atoms at the edge sites (and near lattice defects and foreign atoms) is much higher than that of carbon atoms in the basal planes.⁵⁵⁻⁵⁷ Consequently, the physical and chemical properties of carbon vary