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Electrolyte and Solid-Electrolyte Interphase Layer in Lithium-Ion Batteries

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1. Introduction

The supply and the management of the energy are particularly at the centre of our daily concerns and represent a socio-economic priority. Indeed, while cars use fossil fuel as the main source of energy for over a century, the depletion of the oil reserves and the necessity to reduce the carbon dioxide emissions, stimulate the development of electric vehicles. Therefore, one of the main challenges for the coming decades is the development of new technologies for the storage of electrochemical energy.

Lithium-ion battery (LIB) seems to be the best choice for electric vehicles, and perhaps for the storage of electricity from wind turbines or photovoltaic cells. Even if the lithium-ion technology has known remarkable improvements over the last two decades by doubling the energy density, a technological breakthrough seems to be necessary to further increase the energy density, the charge rate, the safety and the longevity. The performances of the LIB can be improved either by optimizing the electrolyte, or by developing electrode materials more efficient in terms of energy density and cycling ability.

The internal resistance in a LIB should be maintained as low as possible throughout its life especially if the battery is dedicated to applications needing a high charge rate such as the electric vehicles. The internal resistance of a battery (R_b) can be expressed as follows:

$$R_b = R_{el} + R_{in}(N) + R_{in}(P) + R_c(N) + R_c(P) \quad (1)$$

Where R_{el}, $R_{in}(P)$, $R_{in}(N)$, $R_c(P)$ and $R_c(N)$ denote the electrolyte resistance, the interfacial resistance at the positive (P) and the negative (N) electrodes, and the resistance of the current collector at the positive (P) and the negative electrodes (N), respectively.

The resistance of the collector depends mainly on the conductivity of the material used as current collector, i.e. the conductivity of the material should be as high as possible. The electrolyte resistance depends on the distance between the positive and the negative electrodes (L), the geometric area of the electrodes (A) and the ionic conductivity of the electrolyte (κ):

$$R_{el} = L / (\kappa A) \quad (2)$$

Equation (2) shows that the electrolyte resistance can be reduced by decreasing the distance between the electrodes and by increasing the ionic conductivity (and decreasing the viscosity as conductivity and viscosity are related to each other) of the electrolyte and the geometric area of the electrodes. Nevertheless, the area of the electrodes should not be too large as the interfacial resistance (R_{in}) is proportional to A/A_{sp} where A_{sp} denotes the interfacial area at the electrode/electrolyte interface (which can be designated to the specific surface of the electrode). On the other side, the interfacial resistance can be lowered by increasing the specific surface of the electrode, i.e. by using porous electrodes with nanoparticles providing a good electrical contact between the nanoparticles.

Then, the internal resistance of a battery can be reduced by optimizing the geometry of the battery, by using porous electrodes and by increasing the ionic conductivity of the electrolyte. Nevertheless, the performances of LIBs do not depend only on the internal resistance of the battery. For instance, the longevity and the charge rate of a battery are governed by the nature of the electrode materials (diffusion coefficient of lithium ions into the host material, resistance of the material against large volume variation, etc.) and the electrode/electrolyte interface that results from the reactivity of the electrode material towards the electrolyte and especially from the reduction or the oxidation of the electrolyte on the surface of the negative or positive electrodes, respectively. These interfacial reactions are key issues for LIBs, playing a major role in the chemical and physical stability of the electrodes, the cycling stability, the lifetime and the reversible capacity of the battery. Despite numerous studies on the SEI layer, there are still lots of doubts concerning the composition of the SEI layer and its mechanism of formation.

The first part of this chapter is focused on the physicochemical properties of the electrolytes such as wettability and transport properties including the main models that were developed to predict the ionic conductivity and the viscosity of the electrolytes used in the lithium batteries. The different families of solvents and lithium salts used in LIBs are discussed in the second part of this chapter. As the electrode/electrolyte interface plays an important role in the operation of a battery, the mechanisms of formation of the SEI, the composition of the SEI on different types of negative electrodes like carbonaceous-, conversion-, and alloying-type materials as well as positive electrodes analyzed by the most appropriate techniques are also presented.

2. Physicochemical properties of electrolytes

Physicochemical properties of the electrolytes such as viscosity, ionic conductivity, thermal stability and wettability are governed by the composition of the electrolyte, i.e. the salt and the solvent. For instance, ionic conductivity and fluidity of the electrolyte should be as high as possible in order to minimize the resistance of the battery whereas the temperature range at which the electrolyte remains liquid should be as high as possible with respect to technical and safety considerations.

2.1 Transport properties

Ionic conductivity and viscosity are related to each other by the well-known Walden's product which states that the product of the limiting molar ionic conductivity (Λ_0) of an electrolyte and the viscosity (η) are constant providing that the radius of the solvated ions

remains constant [Bockris, 1970]. Thus, a decrease of the viscosity of the electrolyte results in an increase of the ionic conductivity. Therefore, the development of models for evaluating the viscosity and the ionic conductivity of an electrolyte is of great importance for the optimization of the electrolyte formulation.

2.1.1 Viscosity

Viscosity is a foremost electrolyte property that has a prominent influence on key transport properties. There are several factors that can influence electrolyte viscosity such as temperature, salt concentration, and the nature of the interactions between solvents and ions. The addition of lithium salts in dipolar aprotic organic solvents is responsible for an increase of the viscosity due to the appearance of new interactions in solution (ion-solvent and ion-ion interactions) and the solvent structuration [Chagnes, 2010]. The variation of the viscosity *vs* the salt concentration can be described by the Jones-Dole equation [Jones & Dole, 1929]:

$$\eta_r = \eta / \eta_0 = 1 + A\,C^{1/2} + BC + DC^2 \quad (3)$$

In this equation, η and η_0, are the viscosities of the solution and the pure solvent respectively and A, B and D are coefficients. This first term, in $C^{1/2}$, on the right-hand side of Eq.(3), is linked to the interaction of a reference ion with its ionic environment and may be calculated by using the Falkenhagen theory but, usually, this term is vanished in organic solvents when the salt concentration is above C≈0.05M.

The BC term is predominant at C>0.05M and has been attributed to ion-solvent interactions as well as to volume effects. These interactions can induce an increase of the viscosity due to the solvation of the ions or the effect of the electric field generated by the ions on the solvent molecules. These interactions can be also responsible for a decrease of the viscosity of structured media such as water or alcohols due to the destructuration of the solvent in the presence of big ions such as K^+ or Cs^+. In the case of the electrolytes for LIB's, the ion-solvent interactions are always responsible for an increase of the viscosity and the value of B is then always positive.

The third term in C^2, appears at the highest concentrations in salt (0.5 to 2M or more), i.e. when the mean interionic distance decreases and becomes of the order of magnitude of a few solvent molecules diameters. It is mainly related to ion-ion and/or ion-solvent interactions as it does not appear in the case of weak electrolytes. The D value is always positive in LIB electrolytes. The validity of Eq. (3) was confirmed in γ-butyrolactone, oxazolidinone, dimethyl carbonate and propylene carbonate in the presence of lithium salts [Chagnes, 2001a; Chagnes, 2002; Gzara, 2006].

Usually, the electrolytes for the LIB are mixtures of two or three solvents (ethylene carbonate-dimethylcarbonate or propylene carbonate-ethylene carbonate-dimethylcarbonate) and lithium salts. Modelling of the viscosity dependence on the concentration can be carried out by using semi-empirical equations such as the Jones-Dole equation (Eq. (3)). The physicochemical properties of the mixtures of dipolar aprotic solvents cannot be described by regular laws due to the deviation from non-ideality. In dimethylcarbonate (DMC)-ethylene carbonate (EC) and γ-butyrolactone (BL)-EC mixtures, η^E exhibits negative values over the whole range of mole fraction and the minimum of the

curve is located at x_{DMC}=0.3 and η^E=-0.37 mPa·s. [Mialkowski, 2002]. The asymmetrical shape of the curve $\eta^E = f(x_{DMC})$ indicates that the addition of a small amount of DMC to BL involves a more important effect of breaking the structure than occurs with the addition of BL to DMC. In the absence of strong specific interactions leading to complex formation, negative deviations generally occur when dispersion forces are primarily responsible for interaction, or even when they interact more strongly via dipole-dipole interactions. This means also that the interaction between pairs of like molecules is stronger than between pairs of unlike molecules like cyclic lactones and open chain carbonates [Mialkowski, 2002].

The investigation of the excess volume, the excess dielectric constant and the excess Gibbs energy of activation of flow shows that the interaction between BL and DMC is such that the basic networks of intermolecular association in the pure solvents are disrupted and that the individual BL and DMC molecules are loosely bound together to give rise to a less structured solution. The loss in association of molecules gives rise to a better molecular packing as the molecular volumes are different (V_m^E is negative) and a slight negative deviation in the variation of viscosity (η^E is negative) is observed [Mialkowski, 2002].

The study of other excess thermodynamics functions [Mialkowski, 2002] gives evidence of weak dipole-dipole interactions in DMC rich mixtures and stronger interaction in BL rich mixtures. The dipole-dipole interactions are more important in (PC+DMC) or (EC+DMC) mixtures which exhibit large values of the Kirkwood parameter (g_K). The Kirkwood parameter, which provides the correlation between dipoles, is in fair agreement with XRD structure of BL at low temperature [Papoular, 2005], dielectric fraction model and excess Gibbs energy for the activation flow.

Then, the non-ideality of the viscosity should be taken into account to model the viscosity of solvent mixtures. Gering [Gering, 2006] developed such a model (tested for aqueous systems and organic electrolytes such as EC-DMC+$LiPF_6$, EC-EMC+$LiPF_6$, EC-PC+$LiClO_4$ and EC-DEC+$LiClO_4$) based on the exponentially modified associative mean spherical approximation [Barthel, 1998; Anderson & Chandler, 1970; Chandler & Anderson, 1971; Anderson & Chandler, 1971] that gives an accurate description of ion-ion interactions even at very high salt concentration. In this model, input parameters include solvated ion sizes, solution densities, permittivity, temperature, ionic number densities, and governing equations covering ion association (e.g. ion pair formation) under equilibrium conditions. Effects from ion solvation are explicitly considered in terms of solvent residence times and average ion-solvent ligand distances, both of which influence the effective solvated ionic radii.

In this model, Eq. (4) governs the viscosity:

$$\eta = \eta_{mix}^{\circ}\,(1 + f_{pos,h} - f_{neg,h} + f_{coul,h})f_{DS} \tag{4}$$

The salt-free viscosity (η_{mix}°) of each solvent in the mixture at the system temperature T towards a reference temperature T_r=298.15 K can be expressed as follows:

$$\eta_{mix}^{\circ} = \exp\left[y_1 \ln(\eta_1^{\circ}) + y_2 \ln(\eta_2^{\circ}) + y_1 y_2 a(1 + 2y_1 b)(1 + 2y2c)(T_r / T)^5\right] \tag{5}$$

Where in η_i° is the pure component viscosity of each solvent at the system temperature, y_i the mole fractions, a–c are adjustable mixing parameters. Subscripts 1 and 2 denote first and

second solvents. For simple mixtures, a=1 and a-c=0 whereas for non ideal mixing behaviour a≠1 and a-c≠0 and depends on the nature of the interactions between the molecules.

Eq. (4) is divided into (i) a positive contribution ($f_{pos,\eta}$) due to association as contact ion pairs, solvent-shared ion pairs and triple ion species, (ii) a negative contribution ($f_{neg,\eta}$) due to the solvent structure breaking in the presence of ions and (iii) a positive or negative contribution ($f_{coul,\eta}$) due to a net attraction or repulsion between ions that increases or decreases the viscosity depending on the sign of this term. For more information about this model and the exact mathematical expression of these terms, the reader could read the paper written by Gering [Gering, 2006].

Viscosity depends also drastically on the temperature. The variation of the viscosity as a function of the temperature follows the Eyring theory as viscosity is an activated process:

$$\eta = hN_a / V_m \exp(\Delta S^{\neq} / R).\exp[\Delta H^{\neq} / RT)] \quad (6)$$

In Eq.(4), h is the Planck's constant, V_m the molar volume of solvent, $\Delta S^{\neq}$ the activation entropy and $\Delta H^{\neq}$ the activation enthalpy, generally identified to the activation energy of the viscous flow $E_{a,\eta}$. Non-associated solvents and non glass-forming ionic and molecular liquids, usually confirm this equation.

A linear relation between the activation energy for the viscous flow $E_{a,\eta}$ and the salt concentration C has been proposed [Chagnes, 2000]:

$$E_{a,\eta} = E_{a,\eta}{}^{0} + V_m E_{a,\eta}{}^{salt} C \quad (7)$$

Where $E_{a,\eta}{}^{0}$ and $E_{a,\eta}{}^{salt}$ are respectively, the energy of activation for the pure solvent and the contribution of the salt (per mole of the solute) to the activation energy for the transport process.

As $E_{a,\eta}$ is always positive, the increase of the salt concentration in the solvent is responsible for an increase of the sensibility of the viscosity towards a variation of the temperature. Therefore, a good electrolyte for LIB is an electrolyte with a low value of $E_{a,\eta}{}^{salt}$ in order to avoid a high increase of viscosity when the temperature decreases.

2.1.2 Ionic conductivity

The Debye-Hückel-Onsager theory can be used to calculate quantitatively the dependence of the molar ionic conductivity ($\Lambda=\kappa/C$ with κ the specific conductivity) on concentration [Hamman et al., 2007]. For a completely dissociated 1:1 electrolyte:

$$\Lambda = \Lambda^{0} - kC^{1/2} \quad (8)$$

Where C is the electrolyte concentration and k is a constant which can be calculated by using the Debye-Hückel theory.

Nevertheless this relationship can only be used in very diluted electrolytic solutions (C<0.001 M) due to the limitation of application of the Debye-Hückel theory for evaluation of the non-ideal behaviour in electrolytes. The Debye-Hückel theory was modified by

adding empirical terms for the calculation of the activity coefficients at higher concentration or other theories were developed such as the Specific Interaction Theory (SIT) or the Pitzer theory but too few data are available in the literature concerning lithium salts dissolved in the dipolar aprotic solvents used in lithium ion batteries.

Another approach was provided by the pseudo-lattice theory adapted for the conductivity. This theory assumes that, the ions are placed in the nodes of a pseudolattice, and that even at moderate to high concentrations, the classical Debye–Hückel random picture of ionic solutions can be preserved if Debye's length is replaced by the average distance between ions of opposite charge. The conductance of electrolyte solutions thus follows a linear $C^{1/3}$ law instead of the Debye-Hückel-Onsager $C^{1/2}$ one, reflecting the underlying pseudo-lattice structure. This model was tested successfully by Chagnes et al. [Chagnes, 2001; Chagnes (2002); Gzara, 2006] in electrolytic solutions containing a lithium salt dissolved in a dipolar aprotic solvent such as $LiPF_6$, $LiAsF_6$, $LiBF_4$, $LiClO_4$ or LiTFSI (Lithium Bis(Trifluoromethanesulfonyl)Imide) dissolved in γ–butyrolactone, carbonate propylene or 3-methyl-2-oxazolidinone. When the concentration in salt is raised, the number of charge carriers increases but, at the same time, the viscosity increases and the competition between the increase in number of charges and the decrease of their mobilities lead to a maximum in the conductivity-concentration curve [Lemordant, 2002].

Conductance also depends strongly on the temperature as described by the Eyring theory that leads to the following relationship:

$$\Lambda = A\exp(E_{a,\Lambda}) / RT \tag{9}$$

Where $E_{a,\Lambda}$, A, R and T represent the activation energy for the conductivity, a constant, the ideal gas constant and T the absolute temperature, respectively.

Chagnes et al. used the quasi-lattice theory to write a new relationship between the activation energy for the conductivity ($E_{a,\Lambda}$) and the salt concentration [Chagnes, 2003b; Lemordant, 2005]:

$$E_{a,\Lambda} = E^0_{a,\Lambda} + \frac{2N_{av}^{4/3}e^2MV_m}{4\pi\varepsilon_0\varepsilon_r Z^{1/3}}C^{4/3} + E_{id} \tag{10}$$

Where $E_{a,\Lambda}^0$ is the activation energy for the conductivity at infinitesimal dilution and is closed to the activation energy for the viscosity of the pure solvent and E_{id} is the ion-dipole energy. M is a Madelung-like constant (the value M=1.74, corresponding to fcc lattice, is often used), N_{av} the Avogadro number, e=1.6 10^{-19} C, ε_r the static dielectric constant of the solvent, ε_0=8.82 10^{-12} S.I, and Z is the number of ions in a unit cell of the anion or cation sub-lattice (Z=4 in a fcc lattice). In Eq. (4), only ion-ion interactions were hitherto taken into account. The experimental $E_{a,\Lambda}$ values follow effectively a $C^{4/3}$ dependency on the salt concentration

($E_{a,\Lambda}=E_{a,\Lambda}^0 + b\ C^{4/3}$), but the slope value (b) has been found to differ significantly from the calculated values. This has been attributed to the fact that the interaction energy between ions and solvent dipoles has been neglected as confirmed by a mathematical algorithm that permits to calculate the value of E_{id} in the quasi-lattice framework. By accounting the ion-dipole interaction, the quasi-lattice model successfully describes the variation of the activation energy for the conductivity *vs* the salt concentration [Chagnes, 2003b].

Later, Varela et al. [Varela, 1997; Varela, 2010] used a statistical mechanical framework based on the quasi-lattice theory to model satisfactorily experimental values of ionic conductivity *vs* salt concentration in conventional aqueous electrolytes. In this approach, the ion distribution is treated in a mean-field Bragg–Williams-like fashion, and the ionic motion is assumed to take place through hops between cells of two different types separated by non-random-energy barriers of different heights depending on the cell type. Assuming non-correlated ion transport, this model permits to observe the maximum of conductivity of $\kappa=f(C)$. This model could be likely extended to the electrolytes used in LIB and provide another theoretical background that confirm the validity of the quasi-lattice theory.

2.1.3 Thermal behaviour

The lithium-ion technology is efficient in term of specific energy and energy density compared to other technologies but efforts should be made to enhance the safety at high temperature and the performances of the LIB at low temperature. The charge capacity of LIB's decreases at low temperature due to the increase of the resistance of the battery (the ionic conductivity decreases and the viscosity increases) and the decrease of the lithium diffusion coefficient in the electrode materials. At high temperature, the decomposition of the electrolyte onto the positive electrode can lead to safety problems such as thermal runaway causing explosion, overpressure due to the generation of gas, etc. Therefore, the formulation of an electrolyte should take into account these aspects.

At low temperature, the wettability of the electrolyte towards the separator and the electrodes, the ionic conductivity of the electrolyte and the crystallisation point of the electrolyte mainly limit the operation of a battery. Basically, the electrolyte would have a low crystallisation point providing that the crystallization point of the solvents mixture used in the composition of the electrolyte is low. Phase diagrams of mixtures of dipolar aprotic solvents used in LIB give useful information about the low temperature behaviour of electrolytes.

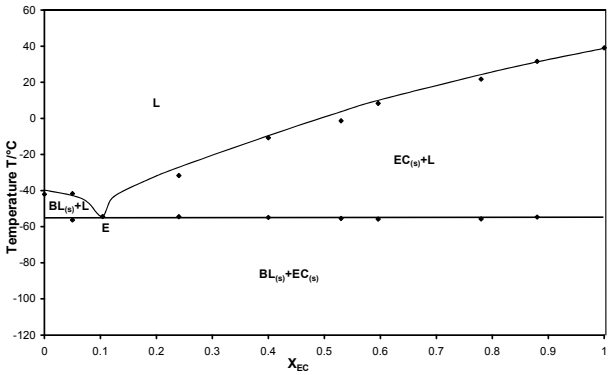


Fig. 1. Phase diagram of BL-EC mixture [Chagnes, 2003].

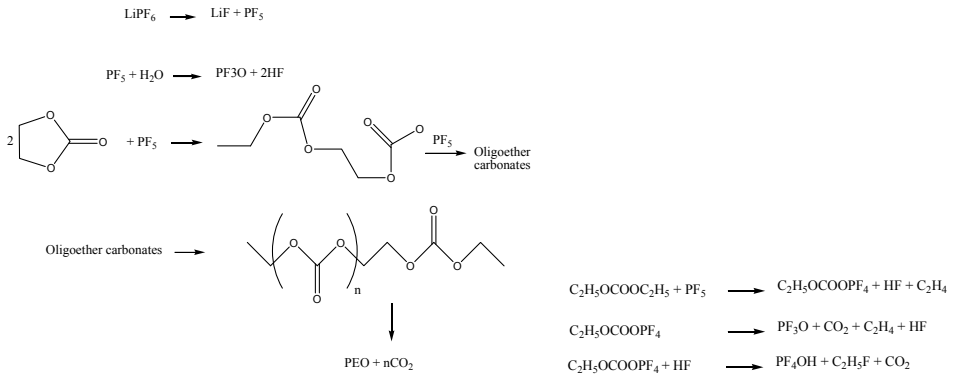
For instance, the phase diagrams of mixtures of cyclic ethylene carbonate (EC) and linear carbonates as dimethylcarbonate (DMC) or ethylmethylcarbonate (EMC) have been studied by Ding [Ding, 2000; Ding, 2001]. The obtained phase diagrams are simple and characterised

by an eutectic point which is close to the compound having the lowest melting point. Besides, there is no miscibility gap in the liquid state whereas in solid state there is no mutual solubility. For a sake of illustration, Figure 1 shows a phase relation between γ-butyrolactone and ethylene carbonate [Chagnes, 2003a] determined by using differential scanning calorimetry (DSC) coupled with X-ray diffraction (XRD) at low temperatures.

This phase diagram shows the presence of an eutectic point for x_{EC} =0.1 and T=-56.3 °C as it was already observed for EC-DMC (eutectic point at x_{DMC}=0.12 and T=-57.5 °C) [Chagnes, 2001]. No significant influence of the carbonate co-solvent on the composition of the eutectic point was observed in BL-carbonate mixtures. Then, from a thermal viewpoint, it seems that the most interesting composition for this kind of solvent mixtures corresponds to a mole fraction of carbonate close to 0.1.

At high temperature due to outside warm or thermal runaway under abuse conditions, the electrolyte can react with the positive electrode and feed up the runaway process. Lithium hexafluorophosphate is the most used salt in lithium battery though its poor thermal stability.

Indeed, this salt decomposes to LiF and PF_5 and the latter readily hydrolyzes to form HF and PF_3O [Ravdel, 2003; Yang, 2006]. Ping et al. [Ping, 2010] confirmed that the addition of lithium salt reduces drastically the thermal stability of the solvent due to the strong Lewis acidity of PF_5 in the case of $LiPF_6$ and BF_3 in the case of $LiBF_4$ even if BF_3 is a weaker Lewis acid than PF_5. The following mechanism of degradation was proposed according to different works reported in the literature [Ping, 2010; Sloop, 2003; Wang, 2005 ; Gnanaraj, 2003a ; Gnanaraj, 2003b] :



The results of the thermal stability studies show that the thermal stabilities of lithium salt in inert atmosphere can be ranked as LiTFSI (lithium bis(trifluoromethylsulfonyl)imide) <$LiPF_6$<LiBOB (lithium bis(oxalate)borate)<$LiBF_4$ and the thermal stabilities of EC electrolytes follows this order: 1 M $LiPF_6$/EC + DEC<1 M $LiBF_4$/EC + DEC<1 M LiTFSI/EC + DEC< 0.8 M LiBOB/EC + DEC. Nevertheless, it may be pointed out that electrocatalytic reactions onto the positive electrode associated with high reactivity of the electrolyte at high temperature can significantly reduce the thermal stability compared to the thermal stability of the electrolyte without any contact with a positive electrode.

2.1.4 Wettability

The wettability of the electrolytes towards the separator or the electrodes in a LIB is of great importance for the performances of the battery, especially at low temperature. Lowering the viscosity and increasing the surface tension improve the wettability. For instance, it was observed that increasing the amount of EC and/or lithium salts decreases the wettability of $LiCoO_2$ electrodes due to poorer electrolyte spreading and penetration [Wu, 2004].

The cycling ability of BL-EC+$LiBF_4$ at -20 °C in a full-cell (graphite as negative electrode and $LiCoO_2$ as positive electrode) was improved by adding a surfactant (tetraethylammonium perfluorooctanesulfonate) [Chagnes, 2003c]. This additive at 0.014 M does not perturb the quality of the solid electrolyte interphase (SEI) at the negative electrode and increases the wettability on the electrodes and the Celgard® separator by lowering the surface tension of the electrolyte.

Another approach for improving the wettability of an electrolyte on a separator consists to modify its surface by plasma treatment or by grafting acrylic acid and diethyleneglycol-dimethacrylate onto the surface of the separator [Gineste & Pourcelly, 1995].

3. Electrolyte formulation

The electrolytes for LIB are composed of a lithium salt dissolved in a dipolar aprotic solvent or a mixture of dipolar aprotic solvents. This electrolyte must meet the following specifications:

- high conductivity even at low temperature (-20 °C for electric vehicle),
- low viscosity,
- good wettability towards the separator and the electrodes,
- low melting point (T<<-20 °C) and high boiling point (T>180 °C),
- high flash point,
- large electrochemical window,
- environmentally friendly,
- low cost.

Usually, all of these criteria cannot be gathered by one solvent and the formulation of the LIB's electrolytes involves a mixture of two or three solvents and one lithium salt.

3.1 Solvents

3.1.1 Dipolar aprotic solvents

Solvents compatible with LIB are dipolar aprotic solvents because dipolar molecules can dissolve inorganic salts such as lithium salts due to the existence of ion-dipole interactions. Furthermore, aprotic solvents do not react violently with lithium as there is no proton in solution.

The main relevant solvents properties for LIB are the dipolar moment, the permittivity, the melting point, the boiling point, the flash point and the viscosity. The dipolar moment should be high to get easy the solubilisation of the lithium salt by complexing lithium ions. Usually, solvents for LIB contain electronegative atoms such as oxygen, nitrogen or sulphur to favour the complexation of lithium ions. The permittivity should be high to dissociate the

lithium salt and limit the formation of ion pairs in the electrolyte as ion pairs do not participate to the ionic conductivity (neutral species). The flash point should be as high as possible for safety considerations and the viscosity should be as low as possible to facilitate the mobility of the ions in solution and ensure a good conductivity. These properties vary significantly from one category of solvents to another. The main categories of solvents used or studied for LIB's electrolytes are alkycarbonates, ethers, lactones, sulfones and nitriles. The physiscochemical properties of these solvents are collected in Table 1. Alkylcarbonates are usually used as electrolyte in lithium batteries. Propylene carbonate (PC) and ethylene carbonate (EC) exhibit a high permittivity due to the high polarity of these solvents but they are very viscous due to strong intermolecular interactions. On the other side, dimethyl carbonate (DMC) and diethyl carbonate (DEC) have a low permittivity and a low viscosity due to their molecular structure (linear carbonate) that permits to increase the degree of freedom of the molecule (rotation of alkyl groups). Besides, alkylcarbonate solvents such as ethylene carbonate form a stable passivating film (solid electrolyte interphase, *vide infra*) required for reversible intercalation at the graphite electrode. Electrolytes for LIB are mostly constituted of mixture of solvents with high permittivity (such as EC) and low viscosity (DMC, DEC) in order to promote simultaneously ionic dissociation and ion mobility. Asymmetric alkylcarbonates such as methylpropylcarbonate or ethylpropylcarbonate are promising solvents to replace conventional alkylcarbonates such as EC, DMC or PC because

Category of solvent	Solvent	T_m (°C)	T_b (°C)	ε_r	η (cP)	μ_D (D)
AlkylCarbonates	Ethylene carbonate	39-40	248.0	89.6[b]	1.860[b]	4.80
	Propylene carbonate	-49.2	241.7	64.4	2.530	5.21
	Dimethylcarbonate	3	90	3.12	0.585	0.76
	Diethylcarbonate	-43	127	3.83	0.750	0.96
	Methylpropylcarbonate	-49	130	5	1.08	4.84
	Ethylpropylcarbonate	-81	148	5	1.13	5.25
Ethers	Diethylether	-116.2	34.6	4.3	0.224	1.18
	1,2-dimethoxyethane	-58.0	84.7	7.2	0.455	1.07
	Tetrahydrofurane	-108.5	65.0	7.25[a]	0.460[a]	1.71
	Diglyme	-64.0	162.0	6.25	0.98	-
	2-methyltetrahydrofurane	-137	80.0	6.2	0.457	1.6
Lactones	γ-butyrolactone	-42.0	206.0	39.1	1.751	4.12
	γ-valerolactone	-31	208	34	2	4.29
Sulfones	Sulfonomethane	28.9	287.3	42.5[a]	9.870[a]	4.70
Nitriles	Acetonitrile	-45,7	81,8	38,0	0,345	3,94
	Adiponitrile	2	295	30	6	-

Table 1. Physicochemical properties of the main families of dipolar aprotic solvents for LIB's electrolytes. T_m : melting point, T_b: boiling point, μ_D: dipolar moment, η: absolute viscosity (25 °C), ε: permittivity (25 °C). [a] : à 30°C ; [b] : à 40°C ; [c] : à 20°C. [Hayashi et al., 1999; Hayashi et al., 1999; Smart et al., 1999; Wakihara, M., 1998; Geoffroy et al., 2000 ; Xu (2004); Abu-Lebdeh & Davidson, 2009].

these solvents suffer from their poor low temperature behaviour and exhibit low flash point (18 and 31°C, respectively) [Geoffroy et al., 2002]. In spite of their relatively low permittivity (ε_r=3-8), asymmetric alkyl carbonate solvents present promising properties such as low melting points, relatively high boiling points (>100°C), low viscosities and large electrochemical windows.

Ethers was studied as solvent for LIB to replace PC because they exhibit a low viscosity (<1 cP at 25 °C) and a low melting point. This category of solvent seems to be less and less interesting as their oxidation potentials are lower than 4V, especially on traditional positive electrodes for LIB. Electrolytes containing γ-butyrolactone (BL) or γ-valerolactone (VL) are very promising because these solvents have a large electrochemical window, a high flame point, a high boiling point, a low vapour pressure and a high conductivity at low temperatures in spite of a moderate permittivity and an absolute viscosity of 1.75 cP at 25°C. Sulfones such as ethylmethylsulfone (EMS), methoxy-methylsulfone (MEMS) or tetramethylsulfone (TMS) are good candidates for the high voltage electrolytes (electric vehicles) as their electrochemical stability in the presence of $LiPF_6$ remains good up to 5 V *vs* Li/Li^+ on platinum electrode [Watanabe et al., 2008; Sun & Angel, 2009; Abouimrane et al., 2009]. Unfortunately, these solvents cannot be used with graphite electrodes as they do not form a stable and protective SEI onto graphite. Nitriles solvents have a low viscosity and a good anodic stability (about 6.3 V *vs* Li/Li^+). Nagahama et al. [Nagahama, 2010] showed that the electrochemical window of dinitrile based electrolytes such as sebaconitrile mixed with EC and DMC in the presence of $LiBF_4$ can reach 6V at a vitreous carbon electrode and promising result were obtained with $LiFePO_4$ electrode.

Room temperature ionic liquids (RTIL) belong to another category of "solvent" which are more and more studied for various applications including the LIB's electrolytes. RTIL's are liquid at room temperature and contain big organic cations associated with small inorganic or organic anions by strong electrostatic interactions. They are popular because they have a low vapour pressure, a large electrochemical window and a high conductivity in spite of a high viscosity [Galinski, 2006]. Furthermore, they can be mixed with numerous organic solvents. For instance, the electrochemical and thermal behaviours of 1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium hexafluorophosphate mixed with BL were studied by Chagnes et al. [Chagnes, 2005a; Chagnes et al., 2005b]. They showed that these mixtures exhibit a very good thermal stability (>350 °C) and remains liquid at very low temperature (<-110°C) providing that the molar fraction of BL was greater than 0.3. Unfortunately, these ionic liquids mixed with BL and lithium salts undergo an easy reduction at a graphite electrode near 1V that leads to the formation of a blocking film which prevents any further cycling. However, the titanate oxide electrode can be cycled with a high capacity without any significant fading but cycling at the positive cobalt oxide electrode was unsuccessfully owing to an oxidation reaction at the electrode surface that prevents the intercalation or de-intercalation of Li ions in and from the host material. Then, less reactive positive material than cobalt oxide must be employed with this kind of RTIL's. Furthermore, the high viscosity and poor wettability of RTIL's seems to get impossible to apply them directly as electrolyte for LIB if they are not mixed with an organic solvent.

3.1.2 Additives

Numerous additives can be added to the electrolyte to improve the performance of LIB:

Category of additives	Molecules
SEI forming improver	Vinylene carbonate, vinyl ethylene carbonate, allyl ethyl carbonate, 2-vinyl pyridine, maleic anhydride, etc.
SEI forming improver and poisoning electrocatalytic effect	SO_2, CS_2, polysulfide, ethylene sulfite, propylene sulfite aryl sulfites.
SEI stabilizer (cycle life improvement)	B_2O_3, organic borates, trimethoxyboroxine, trimethylboroxin, Lithium bis(oxalato) borate.
Cathode protection agent	Butylamine, N,N′ -dicyclohexylcarbodiimide, N,N-diethylamino trimethyl- silane, Lithium bis(oxalato) borate.
$LiPF_6$ salt stabilizer	tris(2,2,2-trifluoroethyl) phosphite, amides, carbamates, and fluorocarbamates pyrrolidinone, hexamethyl-phosphoramide.
Fire retardant	Trimethyl phosphate, triethyphosphate
Overcharge protection	Tetracyanoethylene,tetramethylphenylenedi-amine, dihydrophenazine, Ferrocene.

Table 2. Electrolyte additives. [Zang, 2006]

However, the use of such additives can be responsible for negative effects if they are used at high concentration or if they interfere with other compounds. Table 2 gathers the main additives reported in the literature. The reader could have more information in the paper of Zang [Zang, 2006].

3.2 Salts

Lithium salts for LIB must be soluble in dipolar aprotic solvents at a concentration close to 1 M. Such lithium salts should usually have a large anion to ensure a good dissociation in the solvents and limit the formation of ion pairs. Furthermore, these salts should be safe, environmentally friendly and they must exhibit a high oxidation potential especially for high energy applications such as the electric vehicle while they should participate in the formation of a good passivative layer at the negative electrode if necessary. In the literature, the most studied salts are lithium perchlorate ($LiClO_4$), lithium hexafluorophosphate ($LiAsF_6$), lithium tetrafluoroborate ($LiBF_4$), lithium Bis(Trifluoromethanesulfonyl)Imide (LiTFSI), lithium triflate (LiTf) and lithium hexafluorophosphate ($LiPF_6$), the most commercialized salt.

It is well known that $LiAsF_6$ and $LiClO_4$ cannot be used in LIB because these salts are not safe as $LiAsF_6$ can release toxic gases and $LiClO_4$ is an explosive material at high temperature. LiTFSI exhibits an interesting ionic conductivity in dipolar aprotic solvent but it can be responsible for the corrosion of the collectors whereas $LiBF_4$ has a low ionic conductivity in dipolar aprotic solvents. $LiPF_6$ is the most used lithium salts in LIB because it forms a good SEI when dissolved in EC-DMC or PC-EC-DMC electrolytes and the ionic conductivity of such electrolytes is high enough to minimize the internal resistance of the battery. Indeed, the success of $LiPF_6$ is mainly due to a combination of well-balanced properties such as ion mobility, ion pair dissociation, solubility, chemical inertness, surface chemistry (SEI) and collector passivation. Nevertheless, this salt is expensive and it reacts

with trace of water in the solvent to form HF, a corrosive product that can degrade the SEI. A major drawback of $LiPF_6$ solutions is its poor stability at elevated temperatures. The decomposition reaction may be written as:

$$LiPF_6 = PF_5 + LiF \text{ and } PF_5 + H_2O = 2\,HF + POF_3$$

which may be summed up as:

$$LiPF_6 + H_2O = LiF + POF_3 + 2\,HF$$

The properties of $LiPF_6$ are compared to those of other lithium salts and are classified from best to worse in table 3 [Marcus, 2005].

Property	From best			to		worse
Ion mobility	$LiBF_4$	$LiClO_4$	$LiPF_6$	$LiAsF_6$	LiTf	LiTFSI
Ion pair dissociation	LiTFSI	$LiAsF_6$	$LiPF_6$	$LiClO_4$	$LiBF_4$	LiTf
Solubility	LiTFSI	$LiPF_6$	$LiAsF_6$	$LiBF_4$	LiTf	
Thermal stability	LiTFSI	LiTf	$LiAsF_6$	$LiBF_4$	$LiPF_6$	
Chem. Inertness	LiTf	LiTFSI	$LiAsF_6$	$LiBF_4$	$LiPF_6$	
SEI formation	$LiPF_6$	$LiAsF_6$	LiTFSI	$LiBF_4$		
Al corrosion	$LiAsF_6$	$LiPF_6$	$LiBF_4$	$LiClO_4$	LiTf	LiTFSI

Table 3. Classification of lithium salts.

The properties of LiBOB were enhanced by adding fluorine atoms to LiBOB. The corresponding salt, lithium difluoromono(oxalato)borate (LiDFOB), shows excellent Al-corrosion-protection properties, excellent cycling behavior of lithiated carbon anodes and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ positive electrode, no HF formation by hydrolysis, and a good solubility in dipolar aprotic solvent [Zugmann et al., 2011].

4. Solid Electrolyte Interphase Layer (SEI)

This part of the chapter is designed to present of the passivation layer formed on the surface of electrode materials due to electrolyte decomposition (solvent and salt) in Li-ion battery systems. The understanding of the electrodes surface chemistry (Fig. 2) *i.e.* the electrochemical behaviour of the electrolyte (salt and solvent) including the formation of the passivating layer is prerequisite for a good battery design and functioning. Electrochemical processes taking place at the surface of a noble electrode (in this case Au) in a typical Li-salt/alkyl carbonate solution ($LiClO_4$/PC) are schematically presented in Fig.2.

The schema was plotted on the basis of the voltammetric studies and EQCM (Electrochemical Quartz Crystal Microbalance) presented by Aurbach et al. [Aurbach et al., 2001]. The numerous cathodic (reduction) and anodic (oxidation) processes undergoing on the electrode surface can have a big influence on the LIBs performance. In a case of some undesirable water and oxygen traces in the electrolyte, the reduction of both (oxygen at around 2V and water at around 1.5 V *vs* Li/Li^+) can take place which is

then followed by reduction of electrolyte (solvent and salt) starting at potential inferior to 1 V *vs* Li/Li^+. Another important irreversible process which has a significant influence on the LIB system stability and the formation of a passive layer on surface of positive electrode is electrolyte oxidation at potentials superior to 3.5 V *vs* Li/Li^+. Other reversible processes, such as gold oxidation or lithium underpotential deposition (Li UPD), which also appear in the scheme, are irrelevant to our discussion.

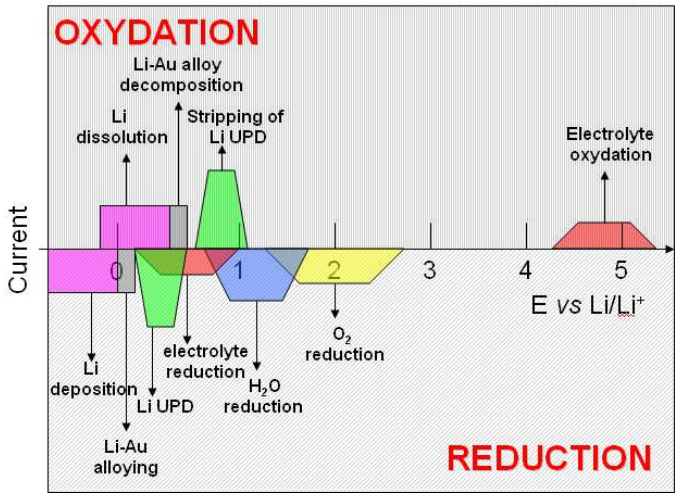


Fig. 2. Schematic presentation of reactions taking place on a noble metal electrode (Au) in alkyl carbonate/Li salt solution depending on the applied potential.

The passivating layer formed on the electrode surface due to reductive decomposition of electrolyte was named Solid Electrolyte Interphase (SEI) layer by Peled [Peled 1979]. The properties of the SEI layer affect the LIBs cyclability, life time, power and rate capability, and even their safety. Therefore, the comprehension of the formation of the SEI layer and the possibility of tuning the quality of the SEI layer on the surface of the negative as well as on the positive electrodes are essential for optimising the LIB systems.

To understand the mechanisms of the SEI formation and to control the quality of the SEI layer, it is necessary to correctly analyse the chemical composition of this layer as well as its morphology. The most appropriate techniques for the SEI analysis are the surface analytical techniques. When studying the bibliography, one can notice that the most popular analytical techniques used for the SEI analysis are the FTIR and XPS but other new techniques complementary to XPS and FTIR can be used, like in situ microscopic techniques and spectroscopic techniques (time-of-flight secondary ion mass spectrometry - ToF-SIMS).

4.1. SEI formation on negative electrodes

4.1.1 Role of the SEI

The SEI layer is formed onto the electrode surface due to electrolyte decomposition (solvent and salt) at potential below 1 V *vs* Li/Li^+ (typically 0.7 V *vs* Li/Li^+ for most electrolytes). For

instance, in the case of carbonaceous electrodes, the formation of the SEI layer proceeds from the deposition of organic and inorganic compounds during the first five charge-discharge cycles. The role of the SEI layer is to prevent further decomposition of the electrolyte in the successive cycles in order to ensure a good cycling ability of the electrode, low irreversible capacity (constant and high reversible capacity) all along the charge/discharge cycles. Therefore, the SEI layer should be well adhered onto the electrode material, be insoluble in the electrolyte even at high temperatures, and also be a good electronic insulator and a good ionic conductor for lithium ions, while removing the solvation shell around the lithium ions to avoid solvent co-intercalation which is associated to exfoliation of active material [Besenhard et al., 1995]. The potential of formation, the composition and the stability of the SEI depend on numbers of factors like the formulation of the electrolyte (solvent, additives and salt) [Ein-Eli et al. 1994; Liebenow et al. 1995], the charge and discharge rate, *etc*. Few strategies can be implemented to improve the cycling ability of LIB systems. For instance, it is possible to modify the electrolyte formulation (see above) or the electrode surface in order to decrease the reactivity of the material towards the electrolyte. Recently, some studies have shown an improvement of the electrochemical performances of the graphite electrodes after modification of the surface structure by mild oxidation [Buka et al., 2001], deposition of metals oxides [Lee et al., 2000], polymer coatings [Wang et al., 2002] and coatings with other kinds of carbons [Fu et al., 2006]. Another approach for improving the electrical performances of negative material for lithium-ion batteries could be a deposition of a "synthetic" passivating layer on the graphite electrode as it was investigated by Swiatowska et al., where a thin ceria layer was deposited onto graphite electrode by electroprecipitation [Swiatowska et al., 2011].

4.1.2 SEI formation on lithium, carbonaceous electrodes, conversion and alloying-type electrodes

The composition of the SEI depends on the nature of the electrolyte and the type of active material on which the SEI is formed. The proportion of the electrolyte decomposition products can vary depending on the electrode material. For instance, in the case of carbonaceous electrode materials, the type of carbon affects the composition and the quality of the SEI [P. Verma et al., 2010]. In addition of surface specific area, particle morphology, crystallographic structure of graphite which influence the formation the SEI layer, edges and surface imperfections like defects, crevices, and active sites act as catalytic sites for electrolyte reduction [Peled at al. 2004]. The formation of the SEI layer can be also dependent on the surface finishing of the carbonaceous electrodes. Thus different kind of pre-treatments can be applied in order to modify the morphology and the chemical composition of the electrode like chemical reduction [Scott et al. 1998] or oxidation [Ein-Eli et al. 1997], electrochemical [Liu et al. 1999] or thermal treatment [Ohzuku et al., 1993].

Various spectroscopic techniques allowed for identification of the SEI layer components formed on electrode materials of LIBs. Numerous spectroscopic studies have been performed on the SEI layer in classical organic electrolytes like ethylene carbonate based electrolytes in the presence of $LiPF_6$ which resulted in proposition of different mechanisms of SEI formation. The very recent study performed by Swiatowska et al. [Swiatowska et al., 2011] the graphite-type electrodes by means of XPS showed that the SEI layer is composed of polymeric compounds such as poly(ethylene oxide) PEO ($-CH_2-CH_2-O-)_n$), ROLi (e.g.

$LiOCH_3$), R–CH_2OCO_2Li and R–CH_2OLi, and fluorinated carbons –CF_2– in agreement with previous studies [Fong et al., 1990; Aurbach et al., 1995; Laruelle et al., 2004; Andersson et al., 2001; Peled et al., 2001; Lee et al., 2000]. The formation of some SEI products like the fluorinated carbon results from reaction between the PVDF binder of the graphite and the electrolyte [Stjerndahl et al., 2007]. The decomposition of the lithium salt ($LiPF_6$) can lead to the formation of LiF, but also some other products like $Li_xPF_yO_z$ [Andersson et al., 2001; Herstedt et al. 2004] and polymer compounds *i.e.* organic-fluorinated and/or organofluoro-phosphorous (*i.e.* $C_2H_4OF_2P$) as already reported by Aurbach et al. can be formed [Aurbach et al. 2002].

Much less information can be found in the literature about the formation of the SEI layer on negative electrodes that undergo conversion/deconversion reactions. These types of electrodes (for example Sn-, Si-based and several transition metal oxide materials like Fe, Cr, Ni, Co, Cu, etc.) have attracted intense scientific attention as LIB negative electrode materials due to much higher capacities than commercially used graphite materials and no problem with so-called co-intercalation present in graphite electrodes [Bosenhard et al. 1997]. The conversion-type materials exhibit an outstanding initial irreversible capacity in comparison to the intercalation-type materials (i.e. graphite) which is always higher than it can be expected [Binotto et al., 2007]. The irreversible capacity is related to the reductive decomposition of the electrolyte, which leads to the formation of the SEI layer. Besides, the first deconversion reaction is incomplete which contributes to a large initial irreversible capacity, and the SEI layer is unstable on transition oxide materials due to volume change effects induced by the conversion/deconversion reaction [Hu et al., 2006].

The formation of the SEI layer on thin film of Cr_2O_3 in PC-1M $LiClO_4$ and its evolution during the cycling was studied by Li et al. [Li et al. 2009]. The cycling voltammetry data showed that the reductive decomposition of the electrolyte resulting from the formation of the SEI layer on the surface of the Cr_2O_3 film starts at 1.1 V *vs* Li/Li^+ and gives a cathodic peak at 0.59 *vs* Li/Li^+ in the first scan. The initial irreversible capacity due to the electrolyte reduction and the incomplete deconversion process during the first cycle is 70% of the first discharge capacity. A stable charge/discharge capacity of 460 $mAhg^{-1}$ was obtained between the 3rd to 10th cycles. XPS and PM-IRRAS reveal that the main composition of the SEI layer grown on the Cr_2O_3 film by reductive decomposition of PC is Li_2CO_3. The XPS data show that the chemical composition of the SEI layer is stable and the thickness and/or density changes in a function of the conversion/deconversion process. The formation of the Li_2CO_3 can be also confirmed from the analysis of the Li1s binding energy peak which can be found at around 55.3 ± 0.2 eV. The significant presence of Li_2CO_3 compound on the conversion-type electrodes cycled in PC-$LiClO_4$ can be justified by a reductive decomposition of PC. From the analysis of the O1s peak observed at around 533.2±0.2 eV it can be deduced that some other SEI layer components like Li-alkoxides (R-CH_2OLi) are present on the electrode surface. The XPS analysis can also give an approximate estimation of the SEI layer thickness. In the case of the thin Cr_2O_3 film the SEI homogenous layer is already well formed after one cycle of conversion/deconversion process and the thickness exceeds the 5 nm as the Cr2p core level signal (coming from the electrode surface) is completely attenuated.

The exact mechanism of the SEI layer formation on the negative electrode materials made of transition metal oxides is not well known. Some recent studies performed by Li et al. [Li et

al. 2009] using ToF-SIMS analyses show possible reconstruction of the SEI layer on the electrode surface during the following cycles of conversion/deconversion process. The analysis of the SEI layer and bulk composition of the thin Cr_2O_3 film during lithiation/delithiation process performed by ToF-SIMS using negative and/or positive ion depth profiles evidences volume expansion and contraction of the electrode material. The volume expansion on the lithiated sample presumably generates cracks in the SEI layer that are filled by the immediate adsorption of the electrolyte products decomposition at low potential, thus increasing the surface content in Li_2CO_3. The volume shrink of the delithiated oxide, also evidenced by ToF-SIMS after deconversion, is thought to generate the loss of fragments of the SEI layer due to compressive stress.

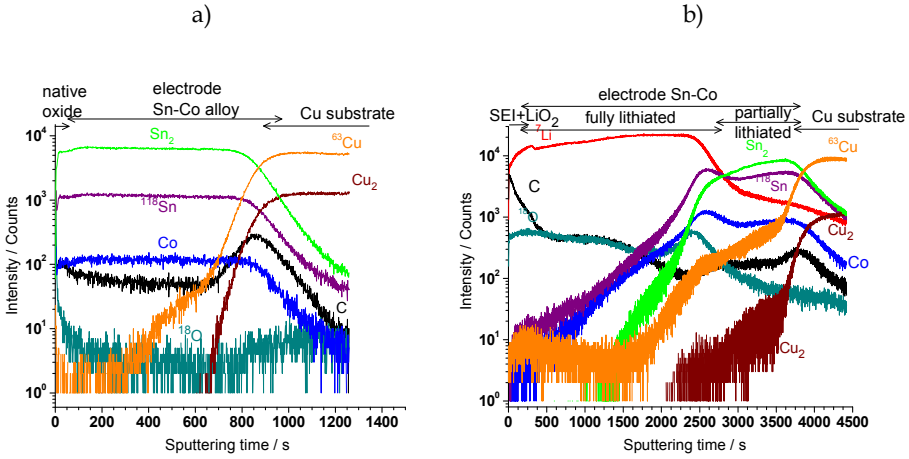


Fig. 3. ToF-SIMS negative ion depth profiles of (a) pristine and (b) lithiated Sn–Co alloy electrode at 0.02 V *vs* Li/Li^+ in 1M $LiClO_4$/PC.

Alloying-type materials are considered to be very promising alternative negative electrodes for LIBs due to their high capacity and good cycling ability [Winter et al., 1999; Huggins, 1999; Mao et al., 1999]. Despite the progress of electrochemical performance of alloying materials such as Sn-Co electrodes, the mechanisms of interfacial reactions, especially the formation, the stability, the variation and the composition of the SEI layer are not yet completely known. The formation of the SEI layer on the electrode surface and bulk modification of the alloys Sn-based electrodes deposited on a metallic copper substrate by electroplating was studied by Li et al. [Li et al. 2010; Li et al. 2011] using XPS and ToF-SIMS. A significant chemical surface modification can be observed by the changes of the C1s and O1s core level peaks which indicate that the SEI layer formed on the Sn-Co electrode is composed of Li_2CO_3, lithium alkyl carbonate $ROCO_2Li$ and alcoholates (ROLi). These findings are supported also by XPS analysis of other research groups [Ehinon et al. 2008; Dedryvere et al. 2006; Naille et al. 2006; Leroy et al. 2007]. As evidenced by the XPS data [Li et al. 2010], the quantity of Li_2CO_3 in the SEI layer increases with increasing the number of cycling. Similarly to conversion-type electrodes, the SEI layer formed on the alloying-type electrodes is thicker than the detection limit of XPS in depth, which means that it exceeds 5 nm. Tof-SIMS analysis performed on the Sn-Co electrode sample reveals some

complementary information about the composition and distribution of the SEI layer on this type of electrode. Comparing the ToF-SIMS negative ion profiles performed on Sn-Co sample before and after lithiation (Fig. 3a and 3b), significant differences are observed concerning the surface and the bulk of the Sn-Co thin electrode.

Apart significant volume expansion of the electrode material (thin Sn-Co layer) after lithiation evidenced by the increase of sputtering time, significant changes can be observed in the first seconds of sputtering. The Tof-SIMS results confirm the formation of the SEI layer on the extreme surface of the alloy-type electrode and then the presence of a second layer composed of Li_2O. The products of the electrolyte decomposition are also present in the bulk and in the cracks of the alloyed (Li_xSn) electrode.

4.1.3 Influence of the SEI on the electrochemical performances of LIBs

It is well known that graphite electrode cannot be cycled in propylene carbonate electrolyte ($PC+LiPF_6$ or $LiClO_4$) because the SEI layer is not able to prevent the co-intercalation of solvent molecules in the graphite leading to the formation of gas responsible for an increase of the pressure in graphene layers and then electrode destruction by exfoliation. The exfoliation phenomenon is governed by low quality SEI layer which depends on its composition and morphology. The use of ethylene carbonate (EC) as co-solvent with PC increases significantly the cycling ability. Indeed, the composition of the SEI influences the electronic insulating properties of the SEI layer and its chemical stability. The morphology of the SEI layer, its porosity and thickness, will govern the conduction of lithium ions through the SEI layer. Therefore, the charge capacity and the irreversible capacity will depend strongly on the quality of the SEI layer. For instance, Chagnes et al. studied the influence of the composition and the morphology of the SEI layer on the cycling ability in a function of salt nature ($LiPF_6$ or $LiBF_4$) in γ-butyrolactone (BL)-ethylene carbonate (EC) [Chagnes et al., 2003c].

This study shows that the graphite electrode can be successfully cycled in the electrolyte of $LiBF_4$ used as a salt in a mixture of BL-EC solvent. Indeed, the galvanostatic charge/discharge tests show that the $LiPF_6$ used as a salt is responsible for an important ohmic resistance that prevents lithium insertion/deinsertion. This behaviour has been explained by a different SEI layer morphology and its chemical composition formed in presence of $LiPF_6$ or $LiBF_4$. SEM micrographs show that the SEI layer formed onto graphite in the presence of $LiBF_4$ is more dense and thicker than the SEI layer obtained in electrolyte containing $LiBF_4$. The XPS analyses of these SEI layers show the presence of Li_xPF_y and Li_xPO_y when $LiPF_6$ is used as salt in BL-EC and Li_xBF_y and Li_xBO_y when the electrode is cycled in $LiBF_4$+BL-EC electrolyte. Besides, in both cases, LiF is present in the whole width of the SEI layer. Therefore, Li_xPF_y and Li_xPO_y might be responsible for the ionic insulating properties of the SEI.

4.2 SEI formation on positive electrodes

Numerous research efforts are still focused on the formation of SEI layer on negative electrode material. Even the SEI layer formation on the surface of negative electrode is so extensively studied since decades it should be noted that especially its formation mechanism and chemical composition are still controversial. Contrary to negative electrode materials, the positive electrode materials were not thoroughly studied in the meaning of interfacial electrode/electrolyte processes due to difficult experimental implementation

resulting from very thin SEI layer on positive electrodes. The most appropriate techniques can be the *in situ* measurements like Fourier transform infrared (FTIR), Raman spectroscopy chemical analysis or Atomic Force Microscopy (AFM). However, these techniques present numerous disadvantages due to difficulties in interpretation of origin of molecules having, for example, similar FTIR signature etc. One of the most appropriate and powerful tool for analysis of thin layers is the XPS technique by combination of core and valence band spectra as it has been already proposed by Dedryvère et al. [Dedryvère et al., 2005].

Formation of the surface layer on the positive electrode material has different properties and origins. Thus, it has been proposed that this layer can be called Solid Permeable Interface (SPI) rather than a Solid-Electrolyte Interphase (SEI) [Balbuena & Wuang, 2004]. This layer formed on the positive electrode material has some limits to passivate the electrode surface as is principally composed of organic compounds rather than inorganic compounds [Levi et al., 1999].

4.2.1 Oxidation potentials of the electrolytes

The formation of the SEI layer on the positive electrode surface depends on the anodic stability of the electrolyte. The oxidation potentials increase with a following order: alkyl carbonates > esters > ethers. To study the anodic stability of organic solvents one should take into account that the solvent reactivity depends on the nature of the electrode and even solvents with relatively high anodic stability, like alkyl carbonates, undergo anodic reactions on noble metal (Au, Pt) at potentials below 4V versus Li/Li^+ [Moshkovich et al., 2001], whereas these solvents are stable on the classical cathodes ($LiNiO_2$, $LiCoO_2$, $LiMn_2O_4$, etc.). Nevertheless, the stability of the electrolytes with 4V positive electrodes is assured due to formation of a film at the surface of the positive electrode [Aurbach, 2000]. In-situ FTIR and EQCM measurements do not show the formation of passive layer on the surface of metallic electrode, hence it can be concluded that the oxidation products of these systems are formed in the solution phase and do not precipitate as surface films. Various possible reaction mechanisms of oxidation of DMC and EC were proposed where one the final reaction product can be $CH_3OCO_2CH_2CH_2OCO_2CH_3$ as observed by the nuclear magnetic resonance (NMR) analysis. Gas chromatographic mass spectroscopy (GCMS) analysis of an oxidized EC-DMC solution shows the formation of an oxidation product issue of EC-DMC combination which is $CH_3OCO_2CH_2CH_2OCO_2CH_2CH_2$-$OCO_2CH_3$. The following both products have been detected by NMR, GCMS and FTIR analysis $HOCH_2CH_2OCO_2CH_2CH{=}O$, and $O{=}CH$-$CH_2OCO_2CH_2CH_2OCH{=}O$ [Moshkovich et al., 2001]. However, the information about oxidized alkyl carbonate solutions that can be obtained from these three experimental techniques is not fully conclusive, thus it is impossible to propose the exact reaction patterns and identify all the reaction products. The identification of the products is difficult due to impossible separation of the products of reaction and the compounds originating from the mother solution. Moreover, the solution storage can lead to formation of polymer compounds.

4.2.2 SEI formation on lithiated metal transition oxides, phosphates

As already stated above, the major reason of film formation on the positive electrode is the oxidation of electrolyte. The process could be driven by the reduction of unstable metal ions in the active electrode material (in a case of $LiMn_2O_4$ electrode it can be Mn^{4+}). The corrosion of electrode materials provoked by the electrolyte depends on the pH and it was reported

that the dissolution of spinel-type electrode decreases in the order: $LiCF_3SO_3$ > $LiPF_6$ > $LiClO_4$ > $LiAsF_6$ > LiBF [Jang et al., 1997]. The XPS spectra performed on the $LiMn_2O_4$ electrode showed that the passive layer is constituted of both organic and inorganic materials like: LiF, and Li_xPF_y-type compounds, poly(oxyethylene), $ROCO_2Li$ and Li_2CO_3 [Balbuena & Wuang, 2004]. The XPS profile performed on this electrode evidenced that the passive film has a layered structure and that the film is not dense enough to serve as a barrier between the electrolyte and the oxidizing environment which is in contrast with the properties of the SEI layer formed on the negative electrode material.

Similar compounds are found to be formed on the surface of LiNi0.8Co0.2O2, which are organic polycarbonates, polymeric hydrocarbons and salt-based products [Balbuena & Wuang, 2004].

The XPS analysis of the V_2O_5 and MoO_3 used as positive electrodes show the irreversible build-up of a surface layer including lithium carbonates and Li-alkyl carbonates ($ROCO_2Li$) and likely Li-alkoxides (R–CH_2OLi) [Swiatowska-Mrowiecka et al., 2007; Swiatowska-Mrowiecka et al., 2008]. The layer formed on the positive electrode transition metal oxides is very thin and does not exceed few nanometers in comparison to the SEI layer formed on the negative electrode materials. After multiple cycles, the composition of the passive layer formed on the V_2O_5 is modified and the lithium carbonates disappears, whereas Li-alkyl carbonates and/or Li-alkoxides remain on the surface, indicating the dissolution and/or conversion of the SEI layer [Swiatowska–Mrowiecka et al. 2007].

The formation of the passive layer on the phosphate-type electrodes is significantly different than on the spinel-type electrodes. The most typical products of electrolyte decomposition (i.e., polycarbonates, semicarbonates and Li_2CO_3) could not be detected on the carbon-coated $LiFePO_4$ surface that indicates that the phosphate group does not react with the solvents. The film formed on the $LiFePO_4$ surface consist of products issued the salt decomposition like : LiF, $LiPF_6$, Li_xF_y- and $Li_x PO_yF_z$-type compounds.

5. Conclusions

The formulation of electrolytes for lithium batteries (LIB's) is difficult as this task should take into account numerous constraints depending on the application (high energy density, temperature, etc.). Furthermore, the electrolyte must be compatible with each battery component, i.e. the electrode materials, the current collector, and the separator. The following specification must be taking into account:

- high conductivity even at low temperature (-20 °C for electric vehicle),
- low viscosity,
- good wettability towards the separator and the electrodes,
- low melting point (T<<-20 °C) and high boiling point (T>180 °C),
- high flash point,
- large electrochemical window,
- environmentally friendly,
- low cost.

These specifications cannot be reached with only one dipolar aprotic solvent in which a lithium salt is dissolved. Usually, the formulation of electrolytes for LIB implies two or three

solvents and one lithium salt. Most of the electrolytes contain ethylene carbonate because this solvent permits to enhance the cycling ability of graphite-types electrodes by improving the quality of the Solid Electrolyte Interface (SEI) formed on the electrode surface before reaction of lithium insertion. The morphology of the SEI is governed by the formulation of the electrolyte, and then by the composition of the SEI. The morphology of the SEI is of great importance as a thick SEI with a poor porosity can be responsible for insulating properties towards lithium ions and poor cycling ability of the electrode. Therefore, the electrode-electrolyte interface plays a crucial role in lithium batteries at negative electrode and at positive electrode as well. Although an electrolyte exhibits good electrochemical window on inert electrodes such as glassy carbon electrode, an oxidation can occur on the surface of positive electrode due to catalytic effects of electrode materials (i.e. lithiated transition metal oxides). The main challenges for the next generation of LIB's for the high energy density applications such as the electric vehicle will be to find material for positive electrode and the electrolyte operating at high voltages. At present, sebaconitrile seems to be a promising solvent for this application but the formulation should be adapted to be used with classical negative electrode materials.

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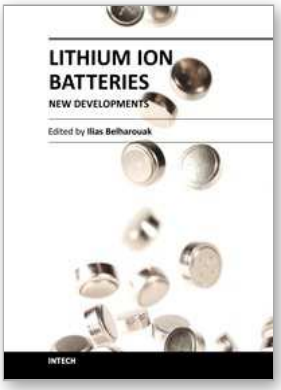

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The eight chapters in this book cover topics on advanced anode and cathode materials, materials design, materials screening, electrode architectures, diagnostics and materials characterization, and electrode/electrolyte interface characterization for lithium batteries. All these topics were carefully chosen to reflect the most recent advances in the science and technology of rechargeable Li-ion batteries, to provide wide readership with a platform of subjects that will help in the understanding of current technologies, and to shed light on areas of deficiency and to energize prospects for future advances.

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