

# Recent studies of the lithium-liquid electrolyte interface Electrochemical, morphological and spectral studies of a few important systems

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## Abstract

Our recent studies on the correlation between Li-cycling efficiency, morphology, interfacial properties and surface chemistry in a variety of Li battery electrolyte solutions are reviewed. The solvent systems include alkyl carbonate mixtures, ether and ether alkyl carbonate mixtures, and methyl formate solutions. The techniques include surface sensitive Fourier-transform infrared spectroscopy, both in situ and ex situ modes, energy dispersive analysis of X-rays, scanning electron microscopy, impedance spectroscopy and standard electrochemical techniques. The principal points are: (i) the surface chemistry of Li is determined by a delicate balance between reduction processes of the solvents, salts and common contaminants; (ii) the surface films initially formed are subjected to ageing processes which gradually change their structure and properties; (iii) the heterogeneous chemical structure of the Li electrode's surface films induces non-uniform Li deposition; (iv) the cycling efficiency is high in systems where Li deposition is smooth and/or the Li deposited is efficiently passivated by the surface species instantaneously formed on it, and (v) it is evident that less hygroscopic surface species passivate the active metal in solution (e.g.,  $\text{Li}_2\text{CO}_3$ , LiF) more effectively.

*Keywords:* Rechargeable lithium batteries; Lithium; Electrolytes

## 1. Introduction

While most of the attention of both industrial and academic research groups in the field of Li batteries has focused in recent years on Li-carbon rocking-chair systems and/or Li-polymer electrolyte systems, rechargeable Li battery systems of Li metal anode and liquid electrolyte solutions still possess a higher potential energy density, capacity and voltage and a wider temperature range of operation. Safety considerations and limited cycle life of battery prototypes based on Li metal and liquid electrolyte solutions have detracted from the interest in these systems. The key factor in utilizing Li metal anodes in commercial liquid electrolyte rechargeable batteries remains the control of the electrochemical behaviour of the Li-electrolyte solution interface in terms of stability, uniformity and morphology. It is generally accepted that the electrochemical behaviour of Li electrodes in solutions is determined by the nature of the surface films which are spontaneously formed on the metal upon exposure to at-

mospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ) and many solvents and salts anions [1]. In fact, all polar aprotic solvents which may form conductive solutions of Li salts contain C–O, C–S, C–N, N–S and O–S bonds which should be cleaved by Li metal to form thermodynamically stable Li oxide, Li alkoxide, Li sulfide or Li nitride species. Therefore, most of the solvents relevant to Li battery systems should undergo thermodynamically favourable reduction by Li metal to insoluble, stable Li salts (organic or inorganic). This is also true for many salt anions such as  $\text{ClO}_4^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ , etc., which should be reduced by Li to stable, insoluble Li halides. Thus, the surface films formed on Li may be composed of species resulting from reduction of solvents, salts and atmospheric contaminants. The actual combination of species formed on the Li surface in a specific solution determines the electronic properties of the Li-solution interphase in terms of resistivity, thickness and uniformity, and hence also the current distribution of Li dissolution/deposition processes and thus the electrode morphology. In many respects, the electrode morphology

determines both the cycle life and safety of the system since the more dendritic the Li deposition the higher the surface area of the electrode and its reactivity in accidents, such as exposure to air, overall or local heating due to shorting, etc. The cycle life also depends on the effectiveness of the passivation developed on the Li deposits in solutions (determined by the specific surface chemistry). Therefore, in order to develop safe and reliable rechargeable Li battery systems with Li metal anodes and liquid electrolyte, one has to understand properly the correlation between the solution composition and the Li surface chemistry, and also the correlation between the composition of the surface films, the electronic properties of the Li–solution interface and the electrode morphology in deposition/dissolution cycles. In this way, the relationship between the solution composition and the anode performance may be understood and leads to a judicious optimization of systems for practical battery systems [2]. Consequently, many research groups investigated the Li surface chemistry [3], Li morphology [4] or the electrical properties of the Li–solution interface (mostly by impedance spectroscopy) [5]. Many of these groups were involved in the study of only one of the above-mentioned aspects in a single study.

The present paper reviews our recent work which is aimed at understanding the correlation between the surface chemistry (resulting from the solution composition), morphology, interfacial electrical properties and the electrode cycle life. This was obtained in a single study by the application of several surface sensitive techniques in conjunction with electrochemical methods to Li electrodes in solutions of a wide spectrum of solvents, salts and additives. The surface chemistry was studied using surface sensitive *in situ* and *ex situ* Fourier-transform infrared spectroscopy (FT-IR) and energy dispersive analysis of X-rays (EDAX) (X-ray microanalysis), the morphology was studied using scanning electron microscopy (SEM), the electrical interfacial properties were studied using impedance spectroscopy and potentiodynamic techniques, and the electrode performance was measured in half-cell testing that imitated various situations in practical batteries.

Another important source of information is the study of non-active electrodes at low potentials in the various solutions. Non-active metals polarized to low potentials in Li salt solutions develop surface chemistry similar to that of lithium. The role of additives and the stability of the surface films can be better understood by this study. The solvents studied include alkyl carbonates (propylene, ethylene, dimethyl and diethyl carbonates – PC, EC, DMC and DEC), ethers (tetrahydrofuran (THF), 2-methyltetrahydrofuran (2MeTHF) 1,3-dioxolane (1,3DN) and 1,2-dimethoxyethane (DME) and esters (methyl formate (MF),  $\gamma$ -butyrolactone ( $\gamma$ -BL)). The salts include  $\text{LiAsF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,

$\text{LiSO}_3\text{CF}_3$ ,  $\text{LiN}(\text{SO}_2\text{CF}_3)$ ,  $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ ,  $\text{LiI}$  and  $\text{LiBr}$ . The influence of all active atmospheric contaminants such as  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{N}_2$  and  $\text{CO}_2$  was also explored.

## 2. Experimental

The experimental considerations are as follows:

(i) the use of highly pure solvents and salts under highly pure argon atmosphere (glove box operation);

(ii) developing the appropriate spectroscopic techniques for the highly reactive Li electrodes and the proper method of transferring the samples for measuring;

(iii) the judicious use of impedance spectroscopy on well-defined electrode surfaces (prepared *in situ* in solutions), the development of models for the Li–solution interphase and testing their validity, and

(iv) the use of Li electrode performance tests which will be short enough and yet meaningful for practical battery systems.

The glove box operation and solvent purification methods have already been reported [6]. Three different complementary methods for *in situ* FT-IR measurements of Li and noble metals at low potentials in solutions were developed [7]. A method to investigate authentic surface films formed on Li by use of *ex situ* FT-IR (external reflectance) was also developed [8]. The electrode preparation procedure for impedance spectroscopy, the instrumentation, the model fittings and the experimental sequences for the proof of their validity have already been described [9].

The tests for measuring Li-cycling efficiency based on *in situ* Li electrode preparation and cycling at practical depth-of-discharge (DOD) and current densities were also reported [10]. Electrolysis of several important solvents using tetrabutyl ammonium salt solutions and noble metals electrodes and identification of bulk products as reported [6] also contributed a great deal towards the understanding of the Li surface chemistry in these systems. The procedures used in the complementary work with non-active electrodes in these solutions have already been described [11].

## 3. Results and discussion

### 3.1. General experimental considerations

The combination of Li electrodes and non-aqueous solvents forms highly sensitive and complicated systems. Li electrodes are highly reactive and react readily with all atmospheric components except noble gases. Li reacts readily with organic solvents with C–Cl, C–O, C–N, C–S, S–O or N–S bonds to form Li salts. Polar aprotic

organic solvents are never completely clean of atmospheric contaminants. Therefore, the choice of the appropriate surface sensitive techniques and the related transfer methods from the electrochemical systems to the spectrometers is essential for understanding these systems. The arsenal of surface sensitive techniques which are capable of following the complicated Li surface chemistry is very limited and includes FT-IR [6–8], Auger electron spectroscopy (AES) [12], X-ray photoelectrospectroscopy (XPS) [12], Raman spectroscopy [13], and EDAX [14]. There are other novel methods such as extended X-ray absorption fine structure (EXAFS) that may be applicable to Li systems in the future. XPS, AES and EDAX have the disadvantage in that they are ex situ methods. AES and EDAX are not specific for identifying oxidation states and functional groups.

XPS, on the other hand, is specific and provides useful information about oxidation states of elements on the examined surfaces. However, in the case of Li it is quite possible that further reduction will take place due to the X-ray radiation, the flow of electrons and sputtering. Raman spectroscopy (which can be used as an in situ technique for the analysis of functional groups and bonds of the surface species [13]) was also found to be a problematic method for the study of Li surface chemistry since we discovered that the laser beam focused on the studied Li surfaces (which is essential for this technique) damages the surface during the measurement, probably because of local heating [15]. Consequently we chose FT-IR spectroscopy and EDAX as the major techniques for surface analysis of Li electrodes. EDAX provided surface element analysis and FT-IR provided identification of the functional groups and the chemical bonds of the surface species. The following was the strategy of the research:

(i) Li surfaces after being treated in solutions were studied ex situ using surface sensitive FT-IR in external reflectance mode [8].

(ii) Surface films formed on noble metal electrodes polarized to low potentials in the same solution (as (i)) were also investigated using surface sensitive FT-IR (ex situ, external reflectance mode) [11]. Usually the surface chemistry of noble metal electrodes polarized to potentials close to that of Li deposition is quite similar to that of Li in the same solutions. However, spectra of a better quality could usually be obtained from the noble metals. Thus, (i) and (ii) provided complementary spectral information.

(iii) It was possible to electrolyze PC, EC, BL, MF, DMC and DEC using tetrabutylammonium (TBA) salt solutions and gold electrodes. Reduction products of the above solvents are soluble in them when the cation is the bulky TBA<sup>+</sup> instead of Li<sup>+</sup>. Thus, bulk electrolysis products could be collected by precipitation as Li salts followed by identification using nuclear magnetic res-

onance (NMR), mass spectroscopy (MS) and FT-IR. In addition, a library of FT-IR spectra of possible expected Li surface species such as Li hydroxide, Li oxide, Li peroxide, Li nitride, Li alkoxides, Li carboxylates and Li alkyl carbonates was prepared. (Most of these species were specially synthesized for this study.) Comparison of their FT-IR spectra as well as those of the solvent electrolysis products with the spectra obtained from Li and noble metal electrodes enabled identification of the surface species formed on Li in most of the electrolyte systems of interest [6].

In addition, three different in situ methods for FT-IR spectroscopy of Li and noble metals in Li battery electrolyte solutions under potential control have been developed [7]. The results thereby obtained were also compared with those of the ex situ studies. Thus, it was verified that the above ex situ results were indeed authentic and reflected the situation in solutions. Usually, the FT-IR spectra obtained in situ from the active surfaces in solutions suffered from the masking effect of solution absorbance. Therefore, each part of the spectral studies including the ex situ and the in situ measurements, Li and noble metal electrodes investigation and the solvent electrolysis products' identification was essential for obtaining a complete picture. Table 1 summarizes the identification of electrolysis products of a few important solvents. Table 2 summarizes the identification of the surface species formed on Li in a variety of electrolyte systems including different solvents, solvent mixtures, salts, contaminants and additives.

Another important experimental aspect is the Li surface preparation. Glove box operation is not adequate for obtaining initially clean Li surfaces. Argon atmosphere containing traces of H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> even at the ppm level should be considered reactive for Li. Indeed, Li electrodes in practical batteries are covered with native films. However, during charge/discharge cycling the native films are removed and fresh Li is exposed to the solution. Consequently, we developed methods for in situ preparation of fresh Li surfaces in solutions. These served both surface sensitive FT-IR and impedance spectroscopic studies of Li electrodes.

The last experimental point to be discussed is that of Li-cycling efficiency measurements. Testing cycle life of practical AA-size Li batteries requires many months. Optimization of electrolyte solution for rechargeable Li batteries requires much faster tests. The method chosen by us was an in situ preparation of Li anodes by Li deposition on copper or nickel substrates (usually 5–10 C/cm<sup>2</sup>) in the tested solution followed by 10 to 20 charge/discharge cycling at 25% DOD and practical charge/discharge currents (0.5–5 mA/cm<sup>2</sup>) versus Li counter electrode. The residual Li was then dissolved electrochemically. The loss per cycle and thus the Li-cycling efficiency was calculated from the difference

Table 1  
Products of the electrolysis of several solvents (reduction products, gold cathode, tetrabutylammonium/perchlorate solutions)

Solvent	Dry (20 ppm H <sub>2</sub> O)	Wet (0.01 M H <sub>2</sub> O)
Propylene carbonate	CH <sub>3</sub> CH(OCO <sub>2</sub> <sup>-</sup> )CH <sub>2</sub> (OCO <sub>2</sub> <sup>-</sup> ), CH <sub>3</sub> CH=CH <sub>2</sub> ↑	CO <sub>3</sub> <sup>2-</sup> , CH <sub>3</sub> CH(OCO <sub>2</sub> <sup>-</sup> )CH <sub>2</sub> (OCO <sub>2</sub> <sup>-</sup> ), CH <sub>3</sub> CH=CH <sub>2</sub> ↑
Ethylene carbonate	(CH <sub>2</sub> OCO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , CH <sub>2</sub> =CH <sub>2</sub> ↑	CO <sub>3</sub> <sup>2-</sup> , (CH <sub>2</sub> OCO <sub>2</sub> <sup>-</sup> ) <sub>2</sub> , CH <sub>2</sub> =CH <sub>2</sub>
γ-Butyrolactone	$  \begin{array}{c}  \text{Li}^+ \\    \\  \text{O} \quad \text{O} \\     \quad    \\  \text{HO}(\text{CH}_2)_3\text{C} \quad \text{C} \quad \text{O} \\    \quad   \\  \text{C} \quad \text{C} \\    \quad   \\  \text{CH}_2 \quad \text{CH}_2  \end{array}  $	HO(CH <sub>2</sub> ) <sub>3</sub> COO <sup>-</sup>
Methyl formate	CH <sub>3</sub> O <sup>-</sup> , HCO <sub>2</sub> <sup>-</sup> , CO↑, H <sub>2</sub> ↑ alkenes and/or alkanes	HCO <sub>2</sub> <sup>-</sup>
Ethers	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, butane, butene tetrabutylammonium salt reduction products	(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N, butene, (reaction of the salt cation with OH <sup>-</sup> )

between the initial deposition and the final dissolution charges [10].

Note that in these experiments there is no stack pressure on the Li electrodes and the ratio between the solution volume and the electrode surface area is several orders higher than in practical Li batteries. Therefore, the Li-cycling efficiencies so measured are much lower than would be obtained using the same electrolyte solutions in practical battery systems (a thin-layer configuration and stack pressure). The difference in Li-cycling efficiency measured using different solutions in these experiments was therefore very pronounced and a comparison of the various electrolyte systems was meaningful despite the short tests performed. Solutions, in which Li-cycling efficiency above 95% was measured in these short tests, should perform very well in practical Li batteries.

### 3.2. The correlation between morphology and surface chemistry and the performance of Li anodes

After being cycled in solutions, SEM observation of Li electrodes always shows pronounced differences in the morphology of the electrode surfaces treated in different solutions [10]. In general, it can be said that in electrolyte systems where Li deposition was highly dendritic the cycling efficiency measured was poor. However, dendrite formation is not necessarily a guarantee for poor anodic performance. There are several cases in which Li deposition is highly dendritic while Li-cycling efficiency is high. Typical examples are solutions containing CO<sub>2</sub> as an additive. The poor cycle life of an anode is due to Li mass losses during cycling. When Li deposition is dendritic the high Li surface area facilitates more irreversible reactions with solution component and corrosion in the dendrites' bottle necks which disconnect them electrically from the bulk.

However, if the Li passivation in an electrolyte system is efficient, it is quite possible that Li losses are largely avoided and a high performance is obtained despite dendritic Li morphology. There are thus two independent factors related to the Li-solution interactions:

(i) the specific surface chemistry and the nature of the surface films formed which determine the uniformity of Li deposition and dissolution, and

(ii) the passivity of the Li deposits, which also depends on the nature of the surface films (which are formed spontaneously on bare Li in solutions), determining the resistance of Li to corrosion and thus the degree of Li loss upon cycling.

In practical Li battery systems the detrimental effect of dendrite formation with bottle necks, fractures and high surface area is largely avoided because the electrodes are pressed to the separator and Li deposition takes place under pressure. Li deposits in practical battery systems are thus much flatter than those observed in usual laboratory testing [16]. Therefore, pronounced differences in Li anode performance measured in laboratory testing due to detrimental morphological effects in many electrolyte solutions should considerably contract in practical battery systems.

Nevertheless, the morphological studies are important and relevant to the real world because they provide an indication of the efficiency of the Li passivation in solution and Li deposition uniformity (which obviously affects prolonged cycle life).

### 3.3. Impedance spectroscopy

Impedance spectroscopy is one of the most sensitive in situ techniques for the study of Li electrodes in the electrolyte solutions. However, the usefulness of this method depends mostly on the electrode surface preparation. When electrodes are introduced to solutions

Table 2  
Reaction products of solvent salts and atmospheric contaminants with lithium

Solvent type	Specific solvent	Dry	Contaminants		
			H <sub>2</sub> O	O <sub>2</sub>	CO <sub>2</sub>
<b>Alkyl carbonates</b>					
	PC	CH <sub>3</sub> CH(OCO <sub>2</sub> Li)CH <sub>2</sub> OCO <sub>2</sub> Li ↓ propylene ↑	ROCO <sub>2</sub> Li	ROCO <sub>2</sub> Li	ROCO <sub>2</sub> Li
	EC	(CH <sub>2</sub> OCO <sub>2</sub> Li) <sub>2</sub> ↓ ethylene ↑	Li <sub>2</sub> CO <sub>3</sub>		+
	DMC	ROCO <sub>2</sub> Li ↓ (CH <sub>3</sub> OCO <sub>2</sub> Li)	(reaction of	Li <sub>2</sub> O	Li <sub>2</sub> CO <sub>3</sub>
	DEC	CH <sub>3</sub> CH <sub>2</sub> OCO <sub>2</sub> Li ↓ + CH <sub>3</sub> CH <sub>2</sub> OLi ↓	ROCO <sub>2</sub> Li + H <sub>2</sub> O)	Li <sub>2</sub> O <sub>2</sub>	
			LiOH–Li <sub>2</sub> O		
<b>Esters</b>					
	MF	Mostly HCO <sub>2</sub> Li, ROLi (CH <sub>3</sub> OLi?)	HCO <sub>2</sub> Li	Li oxides +	HCO <sub>2</sub> Li + Li <sub>2</sub> CO <sub>3</sub>
	γ-BL	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOLi, cyclic β-keto ester, anion, di-Li salt <sup>a</sup>	LiO(CH <sub>2</sub> ) <sub>3</sub> COOLi	RCOOLi species	
<b>Ethers</b>					
	THF	ROLi (CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OLi)	LiOH	Li oxides	Li <sub>2</sub> CO <sub>3</sub>
	2MeTHF	Li pentoxides	Li <sub>2</sub> O	+	+
	DME	ROLi (CH <sub>3</sub> OLi)	Li alkoxides	ROLi species	ROLi species
	1,3DN	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> OLi, HCO <sub>2</sub> Li Poly DN species			
<b>Mixtures</b>					
	EC–PC	EC reduction products dominate			
	EC–DEC	EC reduction products dominate			
	MF–EC	HCO <sub>2</sub> Li, ROCO <sub>2</sub> Li species			
	MF–PC	HCO <sub>2</sub> Li, ROCO <sub>2</sub> Li species			
	MF–DMC	HCO <sub>2</sub> Li dominates, ROCO <sub>2</sub> Li (minor)			
	MC–DEC	HCO <sub>2</sub> Li dominates, ROCO <sub>2</sub> Li (minor)			
	MF–ethers	HCO <sub>2</sub> Li dominates			
	EC or PC with ethers	ROCO <sub>2</sub> Li species dominate, ROLi (minor)			
	THF–2MeTHF	THF reduction products dominate			
<b>Salt</b>		<b>Contaminants</b>			
	LiAsF <sub>6</sub>	LiF, Li <sub>x</sub> AsF <sub>y</sub>			
	LiClO <sub>4</sub>	Li <sub>2</sub> O, LiCl, LiClO <sub>3</sub> , LiClO <sub>2</sub> , etc.			
	LiBF <sub>4</sub>	LiF, Li <sub>x</sub> BF <sub>y</sub> , Li <sub>x</sub> BF <sub>y</sub> O <sub>z</sub> ?			
	LiPF <sub>6</sub>	LiF, Li <sub>x</sub> PF <sub>y</sub> , Li <sub>x</sub> BF <sub>y</sub> O <sub>z</sub> ?			
	LiSO <sub>3</sub> CF <sub>3</sub>	Li <sub>2</sub> S <sub>x</sub> O <sub>y</sub> , LiF			
	LiN(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	LiF, Li <sub>2</sub> S <sub>x</sub> O <sub>y</sub> , Li <sub>3</sub> N, etc.			

<sup>a</sup> (See structure in Table 1).

PC=propylene carbonate; EC=ethylene carbonate; DMC=dimethyl carbonate; DEC=diethyl carbonate; MF=methyl formate; γ-BL=γ-butyrolactone; THF=tetrahydrofuran; 2MeTHF=2-methyltetrahydrofuran; DME=dimethoxyethane; 1,3DN=1,3-dioxolane.

covered with native films resulting from Li reactions with atmospheric components, the ability to sense solution effects and to compare electrolyte systems decreases considerably. Consequently, there are research groups who have tried to prepare fresh Li surfaces in solutions by electrochemical dissolution or deposition processes [17]. These surface preparations are also very problematic since the electrode area thus formed is not determined and there is no basis for the interfacial resistance measurements. In our studies, fresh, smooth Li surfaces are prepared in solution allowing the electrode area to be calculated precisely and the solution impact to be fully influential and measurable [9].

Impedance spectra obtained from Li electrodes reflect the contribution of several time constants of interfacial processes including Li<sup>+</sup> diffusion in solution phase, Li<sup>+</sup> migration through surface films and charge transfer through the Li–film interface, as well as double-layer and film capacitances charging.

The important time constants are obviously related to Li<sup>+</sup> migration through the surface films and the film capacitances. These elements form the semicircle that characterizes all Nyquist plots which are usually obtained from impedance spectroscopy of Li electrodes.

The Li–solution interphase is formed instantaneously when fresh Li is exposed to the solutions [18]. It has

a multilayer structure because the driving force for its formation changes during its formation. Thus, the first layers are formed under the highest Li–solution potential difference. This potential difference then falls gradually on the films formed and the reduction of solution species therefore becomes more selective. This obviously leads to a change in the chemical and physical structure of the Li–solution interphase from the Li to the solution sides. The impedance spectra obtained reflect this multilayer structure very well. There are several different time constants related to  $\text{Li}^+$  migration through the surface films because of this structure. Nyquist plots obtained thereby are flat semicircles. Because of the above, the Li–solution interface and the related impedance spectra can be modeled very precisely by an equivalent circuit analog of several resistance-capacitance ( $R\parallel C$ ) circuits in series, all of which related to different layers of the Li–solution interphase [9].

One should note that the main Li–solution interphase in all electrolyte solutions is formed very quickly (time-scale of seconds) [18]. Therefore, the changes usually measured in the interfacial behaviour by impedance spectroscopy relate mostly to ageing of the initially formed surface films, generally because of secondary reactions with solution species and dissolution/deposition of surface compounds.

Fig. 1 presents some Nyquist plots obtained from Li electrodes prepared identically in different solutions after 48 h of storage at 25 °C and reflects the sensitivity of this technique to the solution composition (which determines the structure of the surface films).

Fig. 2 presents variations in the interfacial resistance upon storage of Li electrodes prepared identically in

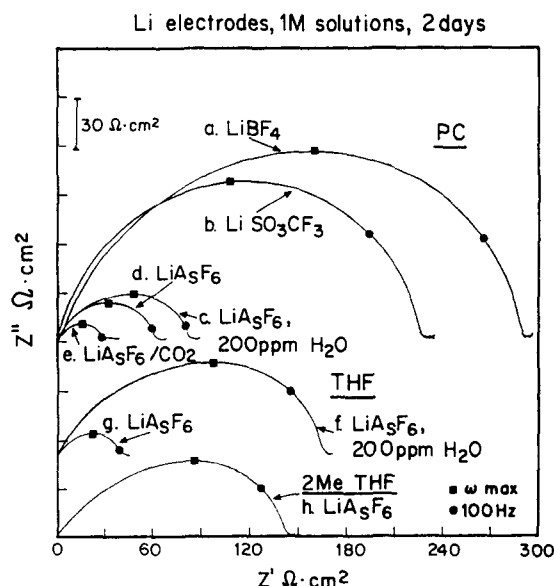


Fig. 1. Typical Nyquist plots obtained from Li electrodes stored for 48 h in several Li salt solutions;  $\omega_{\max}$  values (Hz): (a) 100; (b) 316; (c) 1000; (d) 1000; (e) 1995; (f) 316; (g) 1259, and (h) 355.

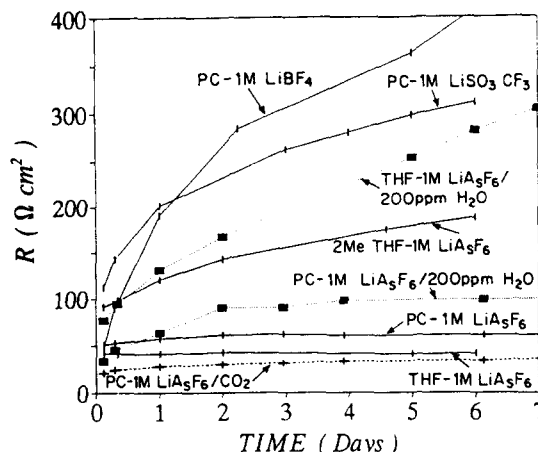


Fig. 2. The interfacial resistance of Li electrodes as a function of storage time, in several electrolyte solutions (calculated from their impedance spectra).

several Li–salt solutions (calculated from impedance spectroscopy). All the changes upon storage shown in Fig. 2 are attributable only to the ageing process and not to the build-up of the surface films.

Consequently, this technique and the related calculations of parameters such as interfacial resistance, film resistivity and film thickness as a function of storage time and solution composition are ideal tools for the study of ageing processes of the Li–solution interphase.

### 3.4. Electrolyte systems of interest

When reviewing recent papers and reports on Li battery systems with Li metal intercalation cathodes and organic liquid electrolytes one realizes that there are several electrolyte solutions which were the main focus of attention in recent years. These include combinations of alkyl carbonates: (i) EC–PC, DMC and EC–DEC with electrolytes such as  $\text{LiAsF}_6$  and  $\text{LiPF}_6$ , combinations of ethers and alkyl carbonates, especially 2MeTHF and EC (with  $\text{LiAsF}_6$ ) [19]; (ii) combinations of MF and alkyl carbonates (DEC, DMC) with  $\text{LiAsF}_6$  and  $\text{LiBF}_4$  [20], and (iii) the combination of THF–2MeTHF–2Mefurane with  $\text{LiAsF}_6$  [21]. Other points of interest are the use of non-poisonous Li salts such as  $\text{LiPF}_6$ ,  $\text{LiSO}_3\text{CF}_3$  or  $\text{Li}(\text{SO}_2\text{CF}_3)_2$  instead of  $\text{LiAsF}_6$ , and the role of additives.

The additives of interest are primarily atmospheric components because they are unavoidably present, and it is important to understand their impact on both the interfacial parameters and on the performance. In addition, some additives were found to have a very positive impact on the Li anode performance in a variety of solutions. A typical example is  $\text{CO}_2$  [20,22].

Studies of several important electrolyte solutions are reported below.

### 3.5. Alkyl carbonate solvents

The basic Li surface chemistry in these solvents as summarized in Tables 1 and 2 involves the reduction of the solvents to Li alkyl carbonates (ROCO<sub>2</sub>Li compounds) [22]. In the case of PC or EC, the surface species are alkylene di-Li carbonates [23] while in the case of DMC or DEC they are alkyl mono-Li carbonates [23,24]. In the case of DEC the CH<sub>3</sub>CH<sub>2</sub>OCO<sub>2</sub>Li formed is soluble and therefore Li is not passivated in this solvent. However, in mixtures of DEC with EC or PC, the surface chemistry is dominated by the reduction of the cyclic alkyl carbonates to the di-Li carbonate species which are insoluble in DEC. Therefore, Li is apparently stable in systems such as EC–DEC. The interfacial properties such as resistance, film resistivity, thickness and uniformity (as reflected by the uniformity of Li deposition) are highly dependent on the Li salt and the contamination level.

All commonly used Li salt anions participate in the build-up of the Li–solution interphase (Table 2). However, the importance and impact change from salt to salt. When the salts are LiAsF<sub>6</sub> or LiClO<sub>4</sub> which can be regarded as ‘non-reactive’, the major ageing process of the surface films initially formed is the reaction of the ROCO<sub>2</sub>Li with trace water to form Li<sub>2</sub>CO<sub>3</sub>, ROH and CO<sub>2</sub>. The enrichment of the interphase with the inorganic carbonate causes its stabilization and reduces its resistivity slightly [9]. At a water concentration above 100 ppm, the ageing processes also include hydration of the surface species initially formed, diffusion of water to the Li film interface and reduction of water to form LiOH–Li<sub>2</sub>O species in the inner part of the surface films. These processes cause an increase in the thickness and resistivity of the surface films, and thus the interfacial resistance increases upon storage [9]. The growth of film thickness in time is parabolic. When the salts are LiBF<sub>4</sub> or LiPF<sub>6</sub>, the interfacial ageing process is vastly different. The ROCO<sub>2</sub>Li and Li<sub>2</sub>CO<sub>3</sub> initially formed, as discussed above, dissolve [25].

As suggested by Kanamura and co-workers [26], the mechanism for this may be the reaction of these salts with trace water to form HF. HF reacts with both Li<sub>2</sub>CO<sub>3</sub> or ROCO<sub>2</sub>Li to form LiF and protonated carbonates, which are soluble. Upon storage, therefore, the surface films become inorganic, consisting of LiF and species of the Li<sub>x</sub>BF<sub>y</sub>, Li<sub>x</sub>BF<sub>y</sub>O<sub>z</sub>, Li<sub>x</sub>PF<sub>y</sub> or Li<sub>x</sub>PF<sub>y</sub>O<sub>z</sub>-type. These processes may be followed by FT-IR and EDAX spectroscopic studies and by impedance spectroscopy [25]. The surface film's resistance (in the case of LiPF<sub>6</sub> or LiBF<sub>4</sub> solutions) increases considerably upon storage and becomes two orders of magnitude higher than that of the Li–solution interphase formed in alkyl carbonate solutions of LiClO<sub>4</sub> or LiAsF<sub>6</sub> [25].

The highest Li-cycling efficiency is measured in LiAsF<sub>6</sub> solutions [22] (about 90%). In solutions of LiPF<sub>6</sub>,

LiClO<sub>4</sub>, LiSO<sub>3</sub>CF<sub>3</sub> or LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> the Li-cycling efficiency is much lower [25] (<80%). The morphology of Li deposition in all alkyl carbonate solutions is usually dendritic and this may be attributed to the fact that the surface films formed are highly inhomogeneous as there are so many types of surface species involved in their build-up [14,22] (ROCO<sub>2</sub>Li, Li<sub>2</sub>CO<sub>3</sub>, LiF, LiOH, Li<sub>2</sub>O, etc.). Li-cycling efficiency can be considerably increased by using CO<sub>2</sub> as additive. CO<sub>2</sub> reacts with Li to form Li<sub>2</sub>CO<sub>3</sub> and CO. Li<sub>2</sub>CO<sub>3</sub> is an excellent passivating agent, mostly because it is the least hygroscopic compound of all other possible surface species formed. The interfacial resistance of Li electrodes in solutions containing CO<sub>2</sub> is lower than in uncountaminated solutions and remains constant upon storage [9]. Li deposition in CO<sub>2</sub> containing alkyl carbonate solutions is highly dendritic [22]. However, the dendrites formed are efficiently passivated by Li<sub>2</sub>CO<sub>3</sub> and remain electrically connected to the bulk because of this corrosion protection (due to the Li<sub>2</sub>CO<sub>3</sub> films) [22].

### 3.6. Alkyl carbonate–ether mixtures

In general, alkyl carbonates are more reactive towards Li than ethers. This is also clearly shown in the difference of reactivity towards Li amalgam or in electrolysis of these solvents on noble metal electrodes with tetrabutylammonium salts (TBA<sup>+</sup>) as the electrolyte. While alkyl carbonates react with Li/Hg and are electrolyzed, ethers are apparently stable with Li/Hg, and in their electrolysis the cation TBA<sup>+</sup> is reduced rather than the solvent [6] (see Table 1). It is therefore not surprising that the surface species formed on Li in practical ether–alkyl carbonate solutions are mostly ROCO<sub>2</sub>Li compounds – the alkyl carbonate reduction products [14]. However, the spectral studies clearly show that even at a solvent ratio of 1:1 the ethers also participate in the build-up of the Li–solution interphase, and thus the surface films also contain ROLi compounds [14]. Their relative amount depends on the solvent ratio and the specific solvent used. For example, THF is more reactive than 2Me–THF, and therefore the Li surfaces formed on Li in THF–PC mixtures contain more ROLi species than those formed in 2MeTHF–PC [14]. One of the major advantages of the use of these mixtures is that the conductivity of the solution thus increases [14] (as compared with the single-solvent solutions). However, when examining combinations of PC or EC with THF, 2MeTHF or DME, the Li morphology is rougher and the Li-cycling efficiency is lower in the mixtures than in the single-solvent solutions [14]. This is attributed to the heterogeneous character of the Li–solution interphase formed in the mixtures which consists of several surface species (ROCO<sub>2</sub>Li, ROLi, Li<sub>2</sub>CO<sub>3</sub>, Li halides and LiOH–Li<sub>2</sub>O). It is assumed that this heterogeneous structure induces more non-uniform

Li deposition (dendrite formation) and the passivation of the Li deposits is not very efficient. However, it is impossible to ignore reports from the Jet Propulsion Laboratories in which the mixture of 2MeTHF–EC/LiAsF<sub>6</sub> is described as a very good electrolyte system for rechargeable Li/TiS<sub>2</sub> batteries [19]. It is possible that in practical configuration when the electrodes are pressed towards the separator and stack pressure is applied, the above effect of the solvent mixture on Li morphology, and thus on cycling efficiency, becomes marginal, while the increase in conductivity remains a considerable advantage.

### 3.7. Ether mixtures

There are reports which describe the electrolyte system 2MeTHF, THF, Me-furane (a few percent) and LiAsF<sub>6</sub> as a very good solution for rechargeable Li batteries [21]. It is interesting and important to explore why this system is so good and what is the contribution of each of its elements to the high performance reported. Therefore, we explored this system using a variety of techniques [27]. In general, the morphology of Li deposition is fairly smooth and Li-cycling efficiency is high (about 95% in our test experiments as described above) with any combination of 2MeTHF, THF and a salt concentration of 1.5 M. However, Li-cycling efficiency is slightly higher, and Li morphology is slightly smoother in 2MeTHF than in THF solutions. Addition of Me-furane up to 5% by volume does not change the picture too much. It can be said that Li-cycling efficiency measured at high 2MeTHF ratio (> 70%) is much more sensitive to the presence of contaminants, such as water, than that measured in solutions of lower 2MeTHF content. The surface films formed on Li in these mixtures are composed of Li alkoxides – reduction products of the solvents [11] – and LiF and Li<sub>x</sub>AsF<sub>y</sub> species resulting from salt reduction [7]. The addition of Me-furane suppresses both the solvent and salt reduction, as is evident from FT-IR and EDAX studies [27]. The interfacial resistance of Li in THF solutions is much lower than that measured in 2MeTHF (as calculated from impedance spectroscopy). Addition of Me-furane to THF does not affect the interfacial resistance considerably, but slightly increases the thickness of the surface films (calculated from impedance spectroscopy). Addition of either THF, Me-furane or both of them to 2MeTHF considerably decreases the interfacial resistance of Li electrodes in solutions (compared with that calculated for Li in 2MeTHF).

All the above information converges to the picture: Li-cycling efficiency is basically very high and Li morphology very smooth in 2MeTHF/LiAsF<sub>6</sub> solutions. In fact, this electrolyte system is one of the best ever tested for rechargeable Li battery systems. However, since 2MeTHF is one of the least reactive solvents

mentioned in connection with Li batteries, the performance of Li electrodes in these solutions is highly sensitive to contamination, e.g., the presence of water considerably increases the Li interfacial resistance and reduces Li-cycling efficiency. Addition of the more reactive components, THF and Me-furane stabilizes the Li–solution interphase formed and decreases its resistivity, making it much less sensitive to the presence of contaminants. The penalty for increasing roughness and decreasing cycling efficiency due to the use of solvent mixture instead of pure 2MeTHF is low. It is believed that 2Me-furane may act as a scavenger for trace Lewis acids that may be formed on the cathode and are detrimental to the stability of ether solvents [28].

It should be emphasized that only non-reactive salt such as LiAsF<sub>6</sub> can be used with ether solvents. Other salts such as LiBF<sub>4</sub>, LiSO<sub>3</sub>CF<sub>3</sub> and LiN(SO<sub>2</sub>CF<sub>3</sub>) cannot be used because they are too reactive on the Li surface. The surface films thus formed induce a very rough and dendritic Li deposition and, therefore, poor Li-cycling efficiency. LiPF<sub>6</sub> may polymerize ethers, due to acidic contaminants it contains, and obviously cannot be used as an electrolyte in them [25].

### 3.8. Solution of methyl formate

MF has many advantages for use in Li batteries. It is easy to clean, highly polar, and therefore its solutions are highly conductive and can be used at very low temperatures. As its electrochemical window is wide (> 4.5 V), this solvent is suitable for batteries with cathodes such as Li<sub>x</sub>CoO<sub>2</sub>, Li<sub>x</sub>NiO<sub>2</sub> or Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>. The major surface chemistry of Li in this solvent is Li formate – HCO<sub>2</sub>Li formation. Due to its high polarity and reactivity towards Li, Li-cycling efficiency measured in MF solutions or in MF with co-solvents such as alkyl carbonates or ethers is very poor. However, using CO<sub>2</sub> which is highly soluble in MF, as an additive, enables very high Li-cycling efficiency to be obtained.

As mentioned above, CO<sub>2</sub> reacts on Li surfaces to form Li<sub>2</sub>CO<sub>3</sub> which is insoluble, even in MF. When the surface films are composed of Li<sub>2</sub>CO<sub>3</sub> they are highly protective and passivating and therefore the corrosion of Li during charge/discharge cycling, no matter how rough the morphology, is minimal. The preferred salt for MF–CO<sub>2</sub> solutions seems to be LiAsF<sub>6</sub>.

## 4. Conclusions

The chemical structure of the surface films formed on Li in the commonly used electrolyte solutions is determined by a delicate balance amongst reduction processes of solution components on the active metal. All solution components including solvents, salts and



trace water, CO<sub>2</sub>, O<sub>2</sub> etc., participate in the build-up of the Li–solution interphase. It is assumed that as the surface films are more heterogeneous in their chemical structure, they induce more non-uniform Li deposition and, therefore, dendrites formation. Li-cycling efficiency depends not only on the electrode morphology but also on the degree of passivity, i.e., to what extent the surface species formed are stable, impermeable to solution components and insoluble. In this respect, CO<sub>2</sub> may be a desirable additive for rechargeable Li batteries since it reacts to form Li<sub>2</sub>CO<sub>3</sub> on the Li surface. Li<sub>2</sub>CO<sub>3</sub> films are highly stable and protective on Li in most non-aqueous solvents of interest.

It was also found that the behaviour of Li electrodes in solutions depends not only on the surface films initially formed but rather on ageing processes of these films. These depend on the presence of contaminants such as water and the salt used. For instance, the surface films formed initially on Li in alkyl carbonates which consist mostly of ROCO<sub>2</sub>Li react with trace water to form Li<sub>2</sub>CO<sub>3</sub>, and upon ageing the surface films become a mixture of the organic and inorganic carbonates. When the salts are LiPF<sub>6</sub> or LiBF<sub>4</sub>, these carbonates dissolve (this may be due to a reaction with trace HF), allowing salt reduction processes to dominate in the build-up of the Li–solution interphase. This substitution process considerably increases the Li interfacial resistance in solutions and the cycling efficiency obtained is lower as compared with solutions of more stable salts (LiAsF<sub>6</sub>).

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