

Characterization of lithium and electrolytes by electrochemical impedance spectroscopy

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Abstract

The electrochemical behaviour of lithium has been tested by d.c. and a.c. measurements in propylene carbonate and mixtures with 1,3-dioxolane and 1,2-dimethoxyethane using LiClO_4 and LiCF_3SO_3 as electrolytes. The solvent and the anion of the lithium salt have an influence on the properties of the formed surface layer. This influence is obvious in a change of the layer thickness, the exchange-current density, the charge-transfer resistance and the maximum frequency of the charge-transfer arc.

Keywords: Lithium; Electrolytes

1. Introduction

Since 1970 lithium has been intensively used as an anode material for low- and high-rate batteries. Since then, several kinds of lithium batteries have been developed. Serious scientific and technological research is still under development in order to improve existing types of batteries or to create new principles.

The use of lithium is only possible in aprotic solvents. The electrochemical behaviour of lithium or lithium alloys is strongly influenced by mass transport (diffusion), formation of surface layers, reduction of the electrolyte, chemical side reactions and adsorption processes in the presence of some specific additives used within the liquid or polymer solid electrolytes.

Many organic electrolyte systems have been investigated [1–6]. It is generally recognized that the composition of the electrolyte solution determines the composition of the surface layer on the top of the lithium electrode [7–9]. It is evident that in the system propylene carbonate/1 M LiClO_4 an electrolyte decomposition takes place below a voltage from 400 to 500 mV versus Li/Li^+ [9]. This surface layer was found to consist of a mixture of decomposition products of the solvent and the electrolyte used. The existence of this ‘passivating’ layer is the prerequisite for the use of lithium in modern battery systems.

2. Experimental

2.1. Materials

Propylene carbonate (PC), 1,3-dioxolane (DOL) and dimethoxyethane (DME) have been distilled and dried prior to use over a molecular sieve type 4 A. Anhydrous lithium perchlorate (LiClO_4) and lithium trifluoromethane sulfonate (LiCF_3SO_3 , Fluka) were treated under reduced pressure at 100 to 130 °C for 12 h. The solvent mixtures with PC have been made in an equi-volume ratio 1:1.

2.2. Electrochemical measurements

The impedance measurements in the frequency range from 0.001 Hz to 100 kHz were performed in a three-electrode cell using a transfer-function analyzer (Schlumberger, SI 1255). The impedance of the working electrode was determined at its equilibrium potential by means of a potentiostat/galvanostat (EG&G Princeton Applied Research, PAR 273A). The current-potential curves have been measured by the same device. As working electrodes have been used lithium ($A = 0.0314 \text{ cm}^2$, rods (Merck)). Further experimental details are described Ref. [10].

3. Results and discussion

3.1. Current–potential behaviour

The protective surface layer of the lithium electrode possess a high ionic conductivity. The composition of the layer, their thickness and kinetics of growth depend strongly on the composition of the electrolyte solution and the resting time in contact with the electrolyte solution.

The rate-determining step during the dissolution/deposition period is the migration of the Li⁺ ion through the surface layer. At higher field strength the Ohm’s law is not longer valid. The current–potential curve can be expressed in terms of a field-assisted migration process [11]:

$$i = 4zFac\nu \exp\left(-\frac{W}{RT}\right) \sinh\left(\frac{azFE}{RT}\right) \quad (1)$$

where *a* is the half-jump distance, *ν* the vibration frequency of the ion in the crystal, *c* the concentration of lattice defects, *z* the valency of the mobile ion, *W* the barrier energy for jumping, and *E* the electric field. In this case the applied overvoltage *η* is identical with the overvoltage *η*_{SEI} at the phase boundary of the solid electrolyte interface (SEI):

$$\eta = \eta_{SEI} = Ed \quad (2)$$

The exchange-current density *i*₀ follows:

$$i_0 = 2zFac\nu \exp\left(-\frac{W}{RT}\right) \quad (3)$$

For high field conditions (*azFη* > *RTd*) results a ‘Tafel’-like equation:

$$i = i_0 \exp\left(\frac{azF\eta}{RTd}\right) \quad (4)$$

or,

$$\eta = \frac{2.3RTd}{azF} \log i_0 + \frac{2.3RTd}{azF} \log i = a_i + b \log i \quad (5)$$

At room temperature the slope *b* is expressed as:

$$b \approx \frac{60d}{az} \text{ (mV)} \quad (6)$$

With a typical assumption for the tunneling range of electrons (*z* = 1 and *a* = 0.3 nm) results slope *b* from several hundred millivolts to several volts in dependence on the layer thickness [12]. The time dependence of the current–potential curves (Fig. 1) gives information on the dynamic growth of the surface layer. In general one observes a relative good coincidence of the estimated layer thickness *d* (Eq. (6)) resulting from current–potential measurements and the estimated layer thickness by impedance spectroscopy (see Eq. (11)).

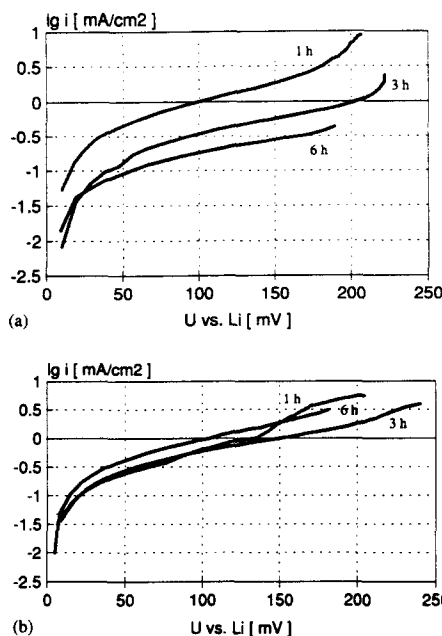


Fig. 1. Current–potential curve of lithium vs. electrolyte (*dU/dt* = 0.5 mV s⁻¹): (a) 0.5 M LiClO₄ in PC–DME, and (b) 0.5 M LiCF₃SO₃ in PC–DME.

Under low field conditions, Eq. (1) reduces to Ohm’s law:

$$i = \frac{4.6i_0 \eta}{b} \quad (7)$$

The estimated resistance is the resistance of the surface layer *R*_{SEI}. Under the assumption of a homogeneous layer the specific resistivity *ρ* is given by:

$$\rho = \frac{R_{SEI}}{d} = \frac{b}{4.6i_0d} \quad (8)$$

The results of the time dependence on the current–potential curve of lithium in different electrolytes (0.5 M LiClO₄ in PC–DME and 0.5 M LiCF₃SO₃ in PC–DME, respectively) are shown in Fig. 1(a) and (b). The process of layer formation is very dynamic. It can be observed that the presence of the ClO₄⁻ ion decreases continuously the exchange-current density. In the presence of CF₃SO₃⁻ ion the exchange-current density is nearly constant within the error limit. At overvoltages from about 150 to about 200 mV, in all cases, the surface layer will be broken and the dissolution process of lithium is enhanced. The estimated characteristic parameters of the surface layer (apparent thickness, exchange-current density and resistivity) are tabulated in Table 1. In the presence of ClO₄⁻ ions the layer thickness is increasing up to about 1.3 nm causing a decrease in the exchange-current density. In the presence of CF₃SO₃⁻ ions the layer thickness and the exchange-current density is nearly constant (about 1 nm and 0.2 mA/cm²).

Table 1
Characteristic parameters of the surface layer on lithium in propylene carbonate–dimethoxyethane vs. electrolyte

Salt	Time (h)	b (mV)	d (nm)	i_0 (mA cm ⁻²)	ρ (Ω cm)
LiClO ₄	1	150	0.8	0.32	1.4×10^9
	3	200	1.0	0.10	4.3×10^9
	6	250	1.3	0.06	7.2×10^9
LiCF ₃ SO ₃	1	200	1.0	0.25	1.7×10^9
	3	200	1.0	0.18	2.4×10^9
	6	200	1.0	0.18	2.4×10^9

3.2. Kinetic properties of the surface layer

Electrochemical in situ techniques like impedance spectroscopy or potentiostatic and galvanostatic transients can be used to investigate the electrochemical behaviour of lithium or lithium-inserting anodes, electrodes and cathode material. Especially the protective surface layer at lithium and lithium-inserting anodes immersed in liquid aprotic organic media undergoes dynamic alterations during polarization or wet standing at the rest potential and causes changes in the behaviour of the electrolyte solution.

Using a.c. impedance spectroscopy, it is often possible to divide an overall reaction into its partial reactions due to their different frequency responses. The 'time window' of this method is 'open' from slow diffusion processes up to fast charge-transfer or migration processes. The electrical equivalent is expressed in terms of different time constants resistance–capacitance (RC) which contain information related to rate constants, surface layer composition and thickness, diffusion parameters and transport numbers of moving charged species. The so-discussed models will describe the electrochemical behaviour of the surface layer correctly, and the layer properties can be monitored.

A general treatment of the a.c. impedance behaviour of a binary dilute electrolyte placed between parallel non-blocking electrodes has been given by MacDonald [13,14] and was used to investigate the mass-transport properties of lithium surface layers formed in several electrolytes [15–17]. Following the suggestions of Sørensen [17] and Garreau and co-workers [15], three elementary processes related to the mass transport (migration process = arc <1>), the charge-transfer process (arc <2>) and the diffusion process (arc <3>) should be expected (Fig. 2).

The migration impedance is determined by the resistance of the surface layer R_b (or R_{SEI}) and the geometric capacitance C_g (normally some $\mu\text{F}/\text{cm}^2$). Knowing the layer thickness from independent methods (ellipsometry, scanning electron micrographs, current–

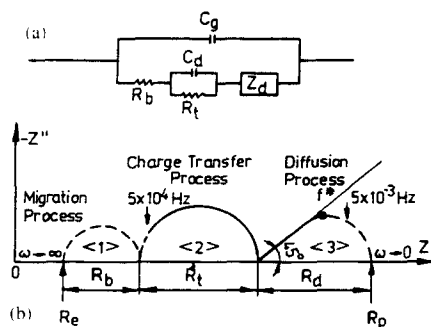


Fig. 2. Impedance behaviour of a surface layer according to Ref. [15]: (a) equivalent electrical circuit, and (b) impedance diagram in the complex plane. R_e = electrolyte resistance; R_p = polarization resistance; R_b = bulk resistance; R_t = charge-transfer resistance; C_d = double-layer capacitance; Z_d = diffusion impedance; R_d = diffusion resistance, and f^* = frequency at the maximum of the imaginary part.

potential curves) one can calculate the average specific resistivity ρ of the layer:

$$R_b = \rho \frac{d}{A} \quad (10)$$

If the model of the plate condenser is valid, the layer thickness will be given by:

$$d = \frac{\epsilon \epsilon_0 A}{C_g} \quad (11)$$

where $\epsilon_0 = 8.86 \times 10^{-12}$ As V⁻¹ m⁻¹, absolute dielectric constant, ϵ the relative dielectric constant (~ 12), and A the area. In case of a linear diffusion, the diffusion impedance is the Warburg impedance, Z_w :

$$Z_w = (1-j)\sigma\omega^{-1/2} \quad (12)$$

where $w = 2\pi f$ and f the frequency. For 1,1-valent electrolytes [15] the Warburg constant σ is given by:

$$\sigma = \frac{2\sqrt{2}RT(1-t^+)^2}{F^2c\sqrt{D_s}} \quad (13)$$

and is influenced by the diffusion coefficient of the mobile species, D_s , and the transfer number, t^+ .

The film formed on the lithium surface (cut from a rod and foiled in the argon-filled glove box) strongly depends on the solvent and electrolyte used (Fig. 3). The diagrams are composed of a semicircle in the high-frequency region (maximum frequency f_2 from about 200 to 2000 Hz) and a small arc in the low-frequency region (maximum frequency f_3 from about 1 to 200 mHz) on the complex plane.

According to the above-discussed models, the high-frequency arc is considered to represent the charge transfer to a less conductive film at the lithium surface. The low-frequency arc results from a slow diffusion process at the interface. Both arcs are time dependent, especially the maximum frequency is shifted to higher

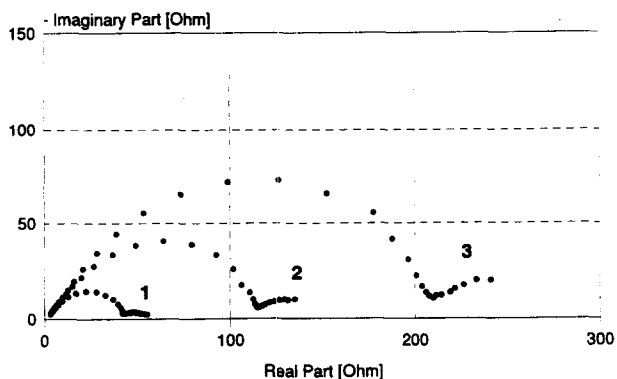


Fig. 3. Cole-Cole plot of lithium in 1 M LiClO₄/PC vs. immersion time: (1) 15 min; (2) 3 days, and (3) 7 days.

frequencies when the system is stored in the electrolyte solution. The expected migration process is not visible within the frequency range investigated (100 kHz to 1 mHz). During the measurements of the current-potential curves in the mixed electrolyte PC-DME, it was observed that the solvent as well as the anion of the lithium salt strongly influence the properties of the surface layer (Fig. 1(a) and (b)). Impedance measurements show, in agreement with these findings, that in the presence of CF₃SO₃⁻ anions the surface layer is formed quickly. After one day wet standing in the solution no further change is observed in the impedance spectra. In the presence of ClO₄⁻ anions a one-day immersion causes an increase in the charge-transfer resistance from 1 Ω cm² (1 h immersion) to 25 Ω cm² (24 h immersion). The measured impedance spectra are therefore similar to these measured in an LiCF₃SO₃ solution. The difference in the charge-transfer resistance is only small but evident in the diffusion process (Fig. 4).

The Warburg constant σ was estimated in ClO₄⁻ media to $\sigma=5.4 \Omega \text{ cm}^2 \text{ s}^{-1/2}$ and in CF₃SO₃⁻ media to $\sigma=38.0$ and $8.8 \Omega \text{ cm}^2 \text{ s}^{-1/2}$. The overall diffusion process seems to consist of two partial processes. The bigger CF₃SO₃⁻ anion obviously causes a very 'porous' structure on top of a dense surface layer.

These findings show that one is able to characterize electrolyte systems for lithium batteries by impedance measurements. A lot of several electrolytes and mixtures has been investigated. Only a few results demonstrate the possibilities. As electrolyte mixtures have been used a solution of 1 M LiClO₄ in: (i) PC as standard; (ii) PC:DME (1:1), and (iii) PC:DOL (1:1).

The impedance spectra are similar to those given in Fig. 3. The characteristic data (charge-transfer resistance and maximum frequency) are shown in Fig. 5(a) and (b). The following trend can be observed:

(i) the surface layer in pure PC possesses a nearly constant value of the charge-transfer resistance. The characteristic maximum frequency of the charge-transfer arc is increasing monotonously to a limiting value of

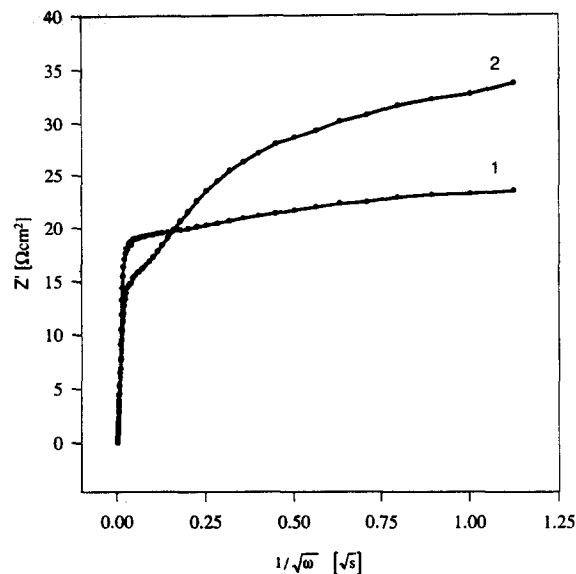


Fig. 4. Impedance of lithium (diffusion part) at open-circuit voltage after 2 days immersion in: (1) 0.5 M LiClO₄ in PC-DME, and (2) 0.5 M LiCF₃SO₃ in PC-DME.

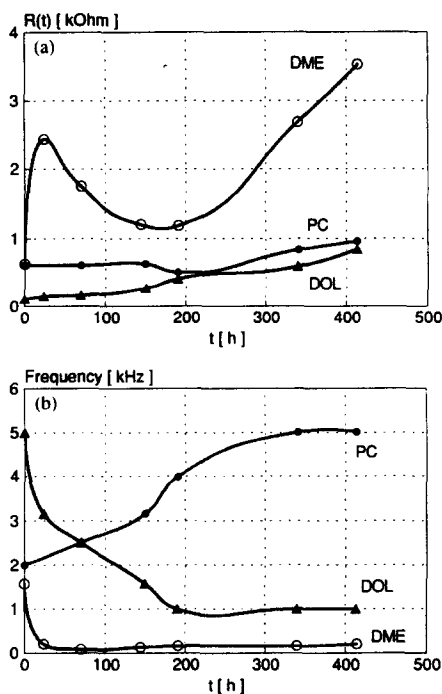


Fig. 5. Time dependence of the charge-transfer impedance of lithium at open-circuit voltage in different solvent mixtures (1 M LiClO₄ in PC, PC-DME and PC-DOL): (a) charge-transfer resistance, and (b) maximum frequency of the charge-transfer arc.

about 5000 Hz. The time constant RC is measured to the region from 1 to 2 ms.

(ii) The presence of DOL causes a change in the charge-transfer resistance and in the maximum frequency. The charge-transfer resistance is increasing with time and reaches the value of the pure PC solution. The maximum frequency is strong decreasing with time

and reaches a constant value of about 1000 Hz. The time constant RC is measured to 0.5–1 ms.

(iii) The addition of DME causes a considerably growing charge-transfer resistance. No constant value could be observed during the measuring period. The maximum frequency is sharply decreasing to constant values from about 100 to about 200 Hz. The time constant RC is measured to 4–6 ms.

4. Conclusions

The comparison of the measured impedance data and the data measured by d.c. current allows the following conclusions. The surface layer in PC seems to be homogeneous and more or less dense. The addition of ether to PC causes a dynamic alteration of the surface layer. The structural and chemical compositions are changing and a porous sub-layer is formed.

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