Passivity of lithium in organic solvents

D. Rahner *, S. Machill, K. Siury

Dresden University of Technology, Institute of Physical Chemistry and Electrochemistry, 01062 Dresden, Germany

Abstract

A short overview concerning the nature of lithium 'passivity' and the use of in situ techniques in lithium research will be given in order to emphasize the important role of the properties of the phase-boundary metal/electrolyte. The electrochemical behaviour of lithium is strongly influenced by the formation of a surface layer due to the reduction of the solvent and of the electrolyte. A kinetic model for the layer formation at uncovered lithium surfaces will be suggested. © 1997 Elsevier Science S.A.

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1. The 'passive' layer on lithium

Lithium is the most reactive metal. It reacts immediately and irreversibly with a lot of organic and inorganic solvents and electrolytes under formation of an inhomogeneous surface layer [1-8]. In electrolyte solutions it is generally recognized that the composition of the electrolyte solution determines the composition of the layer on the top of the lithium electrode [9,10]. The existence of this 'passivating' layer is the prerequisite for the use of lithium in battery systems. If we speak about the 'passivity' of lithium we shall keep in mind that we speak about a kinetically hindered system. From a thermodynamic point of view the lithium system is not stable.

Electrochemical in situ techniques such as impedance measurements or potentiostatic or galvanostatic transients combined with optical and surface analytical methods have been used to investigate the behaviour of the phase-boundary lithium/electrolyte. It was found by Fourier-transform infrared (FTIR), infrared (IR), X-ray spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), Raman and X-ray measurements [11-17] that lithium forms, for instance in contact with propylene carbonate (PC) electrolytes, a surface layer of decomposition products of the solvent and the anion of the electrolyte. Lithium alkyl carbonates have been detected as the main component of the layer. In the presence of traces of water the alkyl carbonates react to lithium carbonate, alcohol and carbon dioxide. It was found by electro-

chemical in situ techniques [18] that the surface layer is formed instantly upon contact of the metal with the solution. This means that metallic lithium also reacts with the anions of the electrolyte and traces of other components (e.g. H_2O, O_2, CO_2, N_2O, N_2, etc.) forming a lot of decomposition products [19-24].

The thickness of the freshly formed layer is determined by the electron-tunnelling range, and changes with time. This layer acts as an interphase between the metal and the solution and has the properties of a solid electrolyte with high electronic resistivity.

The results of these investigations have been summarized in two models of the 'passive' layer:

- SEI model (solid electrolyte interface). According to Peled [18,25,26] the surface layer consists of a thin lithium-ion conducting solid electrolyte of inorganic nature without electronic conductivity.
- PEI model (polymer electrolyte interface). This model takes into account the polymerization of organic solvent molecules induced by metallic lithium [27,28]. The reaction products form an oligomeric and/or polymeric surface layer which is permeable for solvated lithium ions and its corresponding anions. The layer is gel-like and porous.

Combining both models, the 'passive' layer of metallic lithium was described as a combination of the above-mentioned two models: (i) an inner inorganic dense film, and (ii) an outer porous organic layer [29,30].

The existing models describe only rough the manifold experimental observations. Most of the investigations in order to improve the reversibility of the lithium electrode during cycling have been done by the trial-and-error princi-

* Corresponding author: Tel.: +49-351-4634 369; Fax: +49-351-4637 164; e-mail: rahner@cech01.chm,.tu-dresden.de

ple. This means, proven concepts coming from the galvano-techniques (influence of inhibitors and other additives on the metal dissolution and deposition processes) have been transformed from the interacting system metal ↔ water to the interacting system lithium ↔ aprotic solvent, hoping, that the kinetics of the lithium dissolution and deposition processes can be influenced positively in terms of a long-time reversibility. According to our knowledge [31] these concepts are doomed to failure because:

1. the reactive interaction between lithium and the solvent or the anion of the electrolyte leads to an irreversible formation of a surface layer in a time domain less than 100 ms;

2. the solvent molecule and the electrolyte anion are decomposed by metallic lithium at different potentials and/or with different velocities;

3. the reaction products exhibit an inhomogeneity with respect to their chemical composition, and

4. the 'passive' layer shows therefore a lot of regions with variations in the electronic and ionic conductivity causing a variation in the local layer thickness.

2. The kinetics of the lithium electrode

2.1. Current–potential behaviour

The protective surface layer of the lithium electrode is very thin with cation-conducting properties ($t_+ \approx 1$). The rate-determining step during the dissolution/deposition period is the migration of the Li^+ ion through the surface layer. The kinetics of the lithium electrode has been described by Peled [18], assuming that the current density i is given by the high field equation [32] and the ion transport can be interpreted in terms of a field-assisted, thermally activated hopping mechanism [33].

The current–potential curves for metallic lithium and for the lithium intercalation into aluminium in different electrolytes (1 M $LiClO_4$ in propylene carbonate (PC) with or without addition of dilithiumphthalocyanine (Li_2PC)) are shown in Fig. 1 as an example. In recent time we studied the
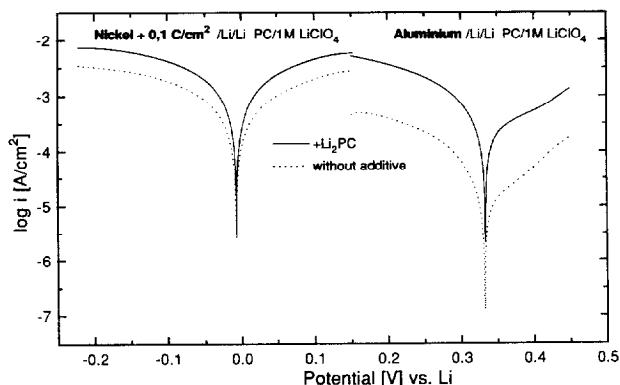

Fig. 1. Current–potential curve of lithium and aluminium vs. electrolyte composition (sweep rate 0.16 mV/s).

effect of dilithiumphthalocyanine on cycling efficiency, cycle life and corrosion behaviour of different anodes in 1 M $LiClO_4$/PC solution [34]. It was shown by electrochemical impedance spectroscopy and current–potential measurements that the addition of dilithiumphthalocyanine reduces the thickness of the surface layer and a modified film with enhanced migration properties for lithium ions is growing. In the case of lithium–aluminium alloy anodes, the addition of dilithiumphthalocyanine has a positive influence on long-time cycling. In the electrolyte without additive a 'normal' behaviour of the aluminium electrode is observed.

The process of layer formation is very dynamic. It can be observed that the presence of the Li_2PC additive increases continuously the exchange current density. The estimated characteristic parameters of the surface layer (apparent thickness, d, exchange current density, i_0, and resistivity, ρ) are compared with known values in other electrolytes and have been tabulated in Table 1 [18,35].

Unfortunately, interpretations of current–potential curves give no information on the first stages of the layer formation process. In the meantime we know, that the first contact between a 'bare' lithium surface and the electrolyte solution switches the points for the desired homogeneous layer formation. These processes can be studied on a 'clean' lithium surface, monitoring the rest potential after exposure to the electrolyte solution.

2.2. Potential–time behaviour of the bare lithium surface

In order to create a bare lithium surface it is necessary to perform cutting experiments in the electrolyte solution. It was shown by Odziemkowski and Irish [36,37] that the surface film reproduces in less than 1 s. The open-circuit voltage–time transients suggest a very rapid reaction of the lithium surface with the solvents and the electrolytes used. The findings reveal that the reactivity of the solvents and the electrolytes versus lithium are different. The most reactive solvent of the compared solvents was PC, the most reactive anion the AsF_6^- anion.

The corrosion reaction of freshly cut lithium can be interpreted in terms of the corrosion theory by superimposing the partial current densities of the occurring anodic and cathodic reactions. In order to describe this process we will discuss a very simple model (Fig. 2(a)).

Immediately after cutting the anion (curve 4) and the solvent (curve 3) the electrolyte react with lithium and form a blocking film of decomposition products on top of the lithium surface. Therefore, lithium (curve 1) is polarized from $U = 0$ V (versus Li/Li^+) to a more positive value $U(t)$ (Fig. 2(b)) depending on the existing current–potential curves. We will assume for a first approximation the current–potential curve of lithium in this potential region to be linear and the cathodic decomposition processes as nearly constant and potential independent (Fig. 2(a)), knowing that the last assumption is not totally correct.

Because no external current, I, is flowing, the condition

Table 1
Characteristic parameters of the surface layer on lithium in different electrolytes

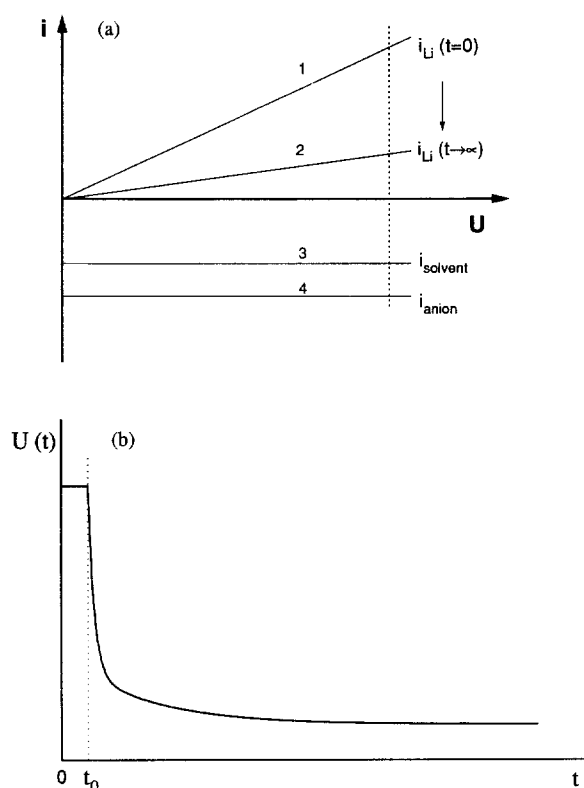| Electrolyte	Ref.	d (nm)	i_0 (mA/cm^2)	ρ (Ωcm)
SOCl$_2$/LiAlCl$_4$	[18]	2		10^7–10^9
THF/LiClO$_4$	[18]	10		10^8
2-MeTHF/THF/1 M LiAsF$_6$	[35]	1.1	3.1	
PC/1 M LiClO$_4$	[18]	2.5		0.5–2.5×10^8
PC/1 M LiClO$_4$	[35]	1.18	3.0	
PC/1 M LiClO$_4$		7.3	5.95	7.2×10^7
PC/1 M LiClO$_4$ + 10^{-3} M Li$_2$phthtalocyanine		5.6	10.9	4.1×10^7

Fig. 2. Kinetic model of corrosion and layer formation processes on a freshly cut lithium surface: (a) (curve 1, 2) partial current–potential curves of anodic lithium dissolution; (curve 4) cathodic anion decomposition; (curve 3) cathodic solvent decomposition, and (b) expected potential–time transient
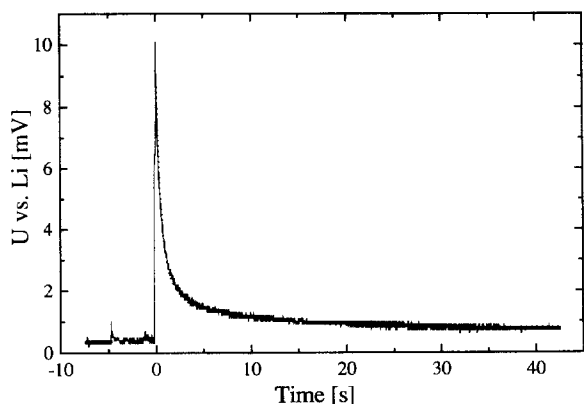

Fig. 3. Potential–time behaviour of a freshly cut lithium surface 1 M LiClO$_4$ solution in PC.

$$I = I_+ + I_- = I_{Li} + I_S + I_A = 0 \tag{1}$$

must be fulfilled, where I_{Li}, I_S and I_A are the partial currents of lithium dissolution, solvent decomposition and anion decomposition, respectively. With constant current densities i_{Li} and $i_S + i_A$ at the areas A_{Li}, A_S and A_A we will get

$$i_{Li}A_{Li} = |i_S|A_S + |i_A|A_A \tag{2}$$

Under the assumption that the anodic and cathodic areas are blocked simultaneously in the same way, only the corrosion current will diminish by time. The corrosion current densities at the unblocked surface area remain constant leading to a constant corrosion potential $U(t)$. The surface will be covered by the decomposition products of the solvent and the anion with the fractional coverage Θ_S and Θ_A respectively

$$\Theta = \Theta_S + \Theta_A \tag{3}$$

The formation rate of the surface layer is given by

$$\frac{d\Theta}{dt} = k_S|i_S| + k_A|i_A| = k|i_-| \tag{4}$$

with k as the rate constant for the formation of a dense, nonporous layer. The layer dissolution will be neglected. With constant current densities follows

$$\Theta = k|i_-|t \tag{5}$$

The time t_0 for fully surface coverage ($\Theta \cong 1$) is given by

$$t_0 = \frac{1}{k|i_-|} \tag{6}$$

From our experiments (Fig. 3) and the data of Odziemkowski and Irish [36,37] one should conclude, that t_0 is smaller than 100 ms and therefore could not be observed experimentally. For instance, to cover the whole lithium surface with LiCl in an LiClO$_4$ solution by a thickness of 1 nm the time of 24 ms is necessary under the assumption, that $i_- = -200$ mA/cm^2.

When the surface is covered completely ($\Theta = 1$, $t = t_0$) at least one of the partial corrosion processes will be diminished. A hindrance of the anodic process will cause a more positive potential shift $U(t)$, this was not observed experimentally. A decrease in the cathodic processes will cause a potential shift $U(t)$ in negative direction.

The cathodic processes of solvent and anion decomposition are influenced by the electronic conductivity of the formed layers with coverage Θ_S and Θ_A. A growth of both layer parts will cause a decrease in the number of charge carriers N_i in the different layer parts. Under the assumption of a first order decay with the rate constant k_i results

$$N_i(t) = N_i(t=0) \exp(-k_i t) \tag{7}$$

and the decomposition current density $i_-(t)$ can be expressed as

$$i_-(t) = i_S(t) + i_A(t) = i_S(t=t_0) \exp(-k_S t)$$
$$+ i_A(t=t_0) \exp(-k_A t) \tag{8}$$

and corresponds to $i_{Li}(t)$ of the current–potential curve of anodic lithium dissolution

$$|i_-|(t) = i_{Li}(t) = i_0 \frac{zF}{RT} U(t) \tag{9}$$

With Eq. (8) the time dependence of the corrosion potential $U(t)$ of freshly cut lithium can be described approximately by

$$U(t) = \frac{RT}{zF} \frac{1}{i_0} [\, |i_S|(t=t_0) \exp(-k_S t)$$
$$+ |i_A|(t=t_0) \exp(-k_A t)\,] \tag{10}$$

Fig. 3 shows the results of our experiments in a solution of 1 M LiClO$_4$ in PC.

The expected time t_0 (Eq. (6)) for the growth of the surface could not be observed in all experiments. The decomposition reaction is so fast that only growing processes within the formed layer determine the potential–time transients.

The mathematical approximation of Eq. (10) to the experimental results gives information about two different time constants

$$\tau_S = \frac{1}{k_S} \quad \text{and} \quad \tau_A = \frac{1}{k_A}$$

for the layer formation process, caused by different diminution velocities of the electronic conductivity. The extrapolation to zero time contains information on the relationship between the exchange current density of the uncovered lithium surface and the total decomposition current density i_- (Table 2)

Table 2
Characteristic data for decomposition and corrosion processes on a 'fresh' lithium surface in different electrolyte solutions

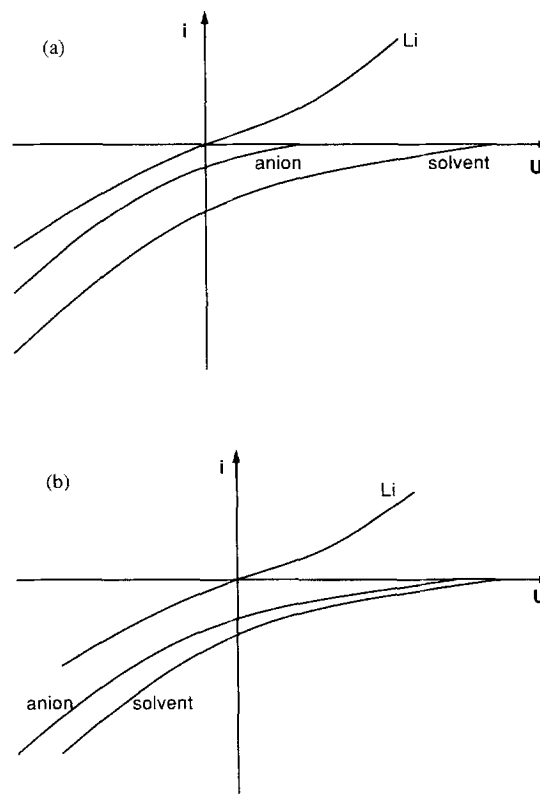| Electrolyte	$U(t=0)$ (mV)	$|i_-|/i_0$	τ_1 (ms)	τ_2 (ms)
1 M LiClO$_4$ in PC	9.2	0.35	565	7350
0.1 M LiClO$_4$ in PC	17.1	0.66	62	2111
1 M LiAsF$_6$ in PC	7.3	0.28	19	1140
1 M LiPF$_6$ in EC:DMC (1:1)	7.6	0.29	27	2831

Fig. 4. Schematically model of partial currents in the reactive system lithium–solvent–anion: (a) stable anion, and (b) instable anion.

$$U(t=0) = \frac{RT}{zF} \frac{|i_-|}{i_0} \tag{11}$$

By the above assumptions one is not able to predict whether the surface layer formed by solvent decomposition or by anion decomposition gives information on τ_1 or τ_2. However, a decrease in the electrolyte concentration leads to a higher value of $U(t=0)$ and an enlarged ratio of $|i_-|/|i_0|$.

The rest potential of the lithium electrode follows the Nernst equation [38,39]. Therefore, in this case the current potential curve of lithium is shifted towards negative direction. This means that the new rest potential corresponds to a higher decomposition current of the solvent and the anion (Fig. 4). Both processes seem to be coupled.

It is not excluded that a solvated electron [40] is trapped in the growing layer. In this case the life time of the trapped electron should depend on the donor properties of the incorporated solvent molecules. These places are the origin of 'metallic' lithium clusters within the forming layer. Their growth will lead to the lithium dendrites.

Eq. (10) is only a very rough approximation. We neglected the time dependence of the exchange-current density of the anodic lithium dissolution, the potential dependence of all cathodic processes (solvent and anion decomposition and lithium deposition) and the influence of a possibly porous layer and the diffusion of lithium ions away from the surface. The velocity of lithium-ion migration through the surface layer is influenced by the change in composition and thickness of the growing blocking layer. Nevertheless, the above-suggested model is able to describe the first steps in layer

formation at the reactive surface of uncovered lithium and gives information on the electronic properties of different layer parts.

2.3. The 'passive' layer on lithium — a kinetic model

The main concept for creating a secondary lithium cell with metallic lithium as the negative electrode is in general the demand for a stable solvent and a stable anion of the electrolyte. But cycling of the lithium electrode is achieved in the potential region of solvent and anion decomposition [24] depending on the stability of all components. It will be shown, that the different stabilities of the solvents and anions versus lithium are the reason for the insufficient cycleability of the metallic lithium electrode.

The solvents used are not stable in contact with metallic lithium and undergo a decomposition with different potential dependencies and velocities. The anions used in contact with metallic lithium can be divided roughly into two groups:

1. stable anions (ClO_4^-, PF_6^-, ...) decomposition starts approximately near the rest potential of lithium or lower, and
2. instable anions (AsF_6^-, ...) decomposition begins to start in the same potential region like the solvent decomposition.

2.4. Stable anion

In the case of a stable anion lithium cycling occurs in different potential regions with respect to the solvent and anion decomposition (Fig. 4(a)). This means that during the discharge process (dissolution of metallic lithium) the solvent is mainly decomposed forming an organic/inorganic polymeric surface layer. The result is an irreversible increase in the layer resistivity (see Fig. 1(b) in Ref. [41]). During the charge process (deposition of metallic lithium) the anion decomposes additionally under formation of an mostly inorganic decomposition layer with ionic conducting properties. The result of these processes is the formation of a very inhomogeneous layer with respect to the ionic conductivity, resistivity and thickness. The cycling performance is strongly decreasing by time.

2.5. Instable anion

In the case of an instable anion lithium cycling occurs more or less in the same potential region with respect to the solvent and anion decomposition (Fig. 4(b)). This means that during discharge and charge both the solvent and the anions are decomposed forming a more or less homogeneous surface layer with respect to the ionic conductivity, resistivity and thickness (see Fig. 1(b) in Ref. [41]). The cycling performance is sufficient high. This principle is realized when choosing $LiAsF_6$ as the electrolyte in a solvent mixture.

If one is not able to use the instable $LiAsF_6$ (high toxicity), the addition of hydrofluoric acid [42] may transform parts

of the surface layer into LiF with pronounced ionic conductivity. The addition of very reactive additives (fluorinated hydrocarbons, etc.) will also substitute instable anions in order to improve the layer homogeneity and the cycleability.

2.6. Formation of a homogeneous passive layer

From the above findings we will derive an improved concept for the formation of a homogeneous passive layer:

1. the solvent molecule and the anion should be decomposed with similar velocities;
2. lithium cycling should never occur in different potential regions with respect to the solvent and anion stability, and
3. the negative influence of a stable anion can be compensated by the addition of a very reactive additive.

3. Conclusions

The processes of solvent and anion decomposition in contact with metallic lithium play an important role during passive layer formation. A kinetic model for the layer formation at uncovered lithium surfaces was suggested.

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