

FILM FORMING REACTION AT THE LITHIUM/ELECTROLYTE INTERFACE

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Summary

Active metal nonaqueous systems can be divided into three groups: (a) solid electrolyte interphase (SEI)-free, aqueous-like, active-metal nonaqueous systems, such as aluminium plating baths; (b) metal solvent blue solutions, or solvated electron systems; (c) SEI battery systems. It is concluded that the only type of system that can be applied in primary and secondary lithium batteries is the SEI electrode system. The following are presented and discussed: The deposition-dissolution mechanism and the kinetics of SEI electrodes, the effect of several parameters on the resistivity of the SEI, the growth rate of the SEI, the morphology of the overall passivating layer and the voltage delay problem.

Introduction

The electrochemistry of lithium in nonaqueous solution began about 90 years ago, at the end of the last century, when a number of workers successfully electrodeposited lithium from solutions of lithium chloride in acetone, pyridine, and aliphatic alcohols [1]. From 1920 to 1960 nothing much was done in this field. The work on lithium deposition was renewed in the early sixties because of the interest in the development of high-energy-density secondary batteries.

Although scientists have known how to electroplate lithium from many nonaqueous solutions for almost 90 years, its electrochemistry was not well understood. For example, there were no rules for the choice of a proper solvent system for efficient lithium deposition. It is well known that in contact with the electrolyte of many lithium batteries, the lithium anode becomes covered by a passivating layer (PL) [2 - 7]. This PL slows the corrosion of the lithium anode. It is generally accepted that at least some battery systems such as Li/SOCl₂ can exist only because of this anode surface layer. However, no complete agreement has been achieved among lithium battery experts regarding the necessity of the existence of this PL for the proper

operation of lithium batteries. In addition, the role it plays in the deposition-dissolution process of lithium is not well understood. While several workers emphasized its necessity for proper operation of primary lithium cells, others, such as Brummer [8] and Newman [9] recently concluded that a passivated anode can offer only a limited cycle life, and in order to obtain a deep-discharge, high-cycle-life secondary battery, the lithium anode must be PL-free and kinetically stable with respect to the electrolyte.

A very basic and important question arises: Is it possible at all to operate successfully a primary or secondary lithium battery with no PL on the surface of the anode? It will be shown later that the answer is probably negative and so another question arises: How does this PL form and what are its effects on the electrochemical behavior of lithium and on the performance of primary and secondary cells?

This paper is devoted to giving some answers to these questions.

Results and discussion

Active metal nonaqueous systems can be divided into three groups [10]: Type A — SEI-free, aqueous-like, active metal nonaqueous systems; Type B — Metal/solvent blue solutions, or solvated electron systems; Type C — the SEI battery systems.

Type A systems are, for example, the aluminum plating baths [7]. The electrode surface is clean and is in intimate contact with the solution. Thus, there is a direct exchange of electrons between the electrode and the ions in the solution. This type of system yields, under proper conditions, a compact, smooth, and dense metallic coating with 100% current efficiency, thus serving as an electroplating bath.

No alkali metal nonaqueous solution system has been definitely proved to belong to this group.

It is well known that alkali metals dissolve in several purified solvents such as ammonia, amines, and ethers to form blue solutions of solvated electrons [11, 12]. The alkali metal corrodes to a point where its potential equals that of the solvated-electron electrode. From this equilibrium, Makishima's equation was derived [13]:

$$E_M^0 - E_e^{-0} = \frac{RT}{F} \ln a_{M^+} a_{e^-}. \quad (1)$$

In ammonia, the difference between E_M^0 and E_e^{-0} is a few hundred mV. (In ammonia at -40°C $E_{\text{Li}}^0 = -2.1$ V and $E_e^{-0} = 1.86$ V vs. SHE [15].) Therefore the equilibrium concentration of e_{solv} is in the range of several mM, depending on the concentration of M^+ . Laitinen and Wyman [14] concluded that all metals should dissolve in ammonia to an extent governed by Makishima's equation. This conclusion can be extended to other inert solvents which are very slowly reduced by alkali metals.

Another important feature of metal/ammonia solutions is that in their electrolysis with the use of inert electrodes, the solvated electrons are oxidized on the anode and dissolve into the solution at the cathode, while no alkali metal deposits on the cathode [15].

The question we would like to answer now is, whether these two types of active metal nonaqueous systems can be used for lithium primary or secondary battery applications.

Type A — the aqueous-like system would be preferred. However, no such alkali metal system has been discovered. The reason for this is Makishima's equation. In sufficiently inert and purified solvents, according to thermodynamic considerations, it is expected that the alkali metals would dissolve to form a blue solution of solvated electrons [16].

It is clear that type B systems (the blue solutions) cannot be used for battery applications, as the solvated electrons and the alkali atoms would reduce the cathodic material [10]. In addition, it would be impossible to charge these batteries, as the plating of lithium is a very inefficient process, if possible at all.

The main conclusion resulting from this discussion is that the only type of system that can be applied in primary and secondary batteries is the Solid Electrolyte Interphase (SEI) electrode system which, in fact, is the system characteristic of today's commercial primary lithium batteries.

At the beginning of the century, it was found that the plating of lithium from organic solvents in the presence of water is associated with the formation of a passivating layer on the deposit [1]. Until 1970 this film was treated as an undesirable and interfering layer which should be avoided [7, 10]. In 1970, Dey concluded [4] that the apparent stability of lithium in PC is due to a lithium anode film, probably composed of Li_2CO_3 , which protects the metal from further attack. Dey also suggested that this film conducts lithium cations. In 1975, in a study of the electrochemistry of magnesium in thionyl chloride solutions, we came to similar conclusions which were presented at the 26th ISE Meeting in Vienna [17]. It was concluded that the magnesium electrode is covered by a passivating layer which is an electronic insulator but ionic conductor. The rate-determining step (RDS) for the deposition-dissolution process is the migration of magnesium cations through the PL. It was further proposed that this passivating-layer model should also be applied in the case of all alkali metal nonaqueous battery systems [17]. In 1977 Moshtev and coworkers [18] and Avigal and Peled [19], concluded that the rate-determining step for lithium deposition in thionyl chloride solutions is the migration of lithium in the passivating layer. Rauh and Brummer [20] reported that several additives such as water, nitromethane, and SO_2 enhance the lithium cycling efficiency in propylene carbonate (PC). They suggested that these additives form lithium cation conductive films. The loss of cycling efficiency on open circuit has been attributed to the formation of an insoluble insulating film on the lithium cation conducting film.

A detailed model for the passivating layer which covers alkali and alkaline-earth metals in nonaqueous battery systems was presented in 1977 [7]. This was called the SEI (Solid Electrolyte Interphase) model. According to this model, the alkali and alkaline-earth metals in nonaqueous battery systems are covered by a solid electrolyte interphase under OCV, plating and stripping conditions. This film results from the precipitation of corrosion products of the anode.

In the same year, Dey concluded [4] that the success of all commercially promising liquid electrolyte-Li batteries rests on the passivating layer of the lithium anode.

The deposition-dissolution process of SEI electrodes involves three consecutive steps [7]: (a) an electron-transfer reaction at the metal/solid electrolyte interface; (b) migration of cations from one interface to the other for the case $t_+ = 1$ (or migration of anions for the case $t_x^- = 1$); (c) ion transfer at the solid electrolyte/solution interface. This simple presentation is valid only for measurements made near OCV conditions as in the case of a.c. or pulse-galvanostatic measurements. In these cases, the net charge passed through the electrodes does not change the morphology of the SEI or the concentration of the mobile lattice defects.

The dissolution-deposition process in a real case is more complicated. Under prolonged dissolution, a process of breakdown and repair of the SEI takes place. The mechanical breakdown of the SEI is caused by a preferential dissolution of the anode, for example, near the grain boundaries of the SEI, and by stresses in the SEI due to uneven retreat of the anode. The new anode surface exposed to the electrolyte, immediately reacts with the electrolyte to form a thin, new protective layer which slows further local corrosion. The minimum thickness of the SEI is determined by the tunneling range of the electrons in the SEI and by a mechanism of dielectric breakdown of the SEI. This was found to take place under an electric field of about 10^7 V cm⁻¹ [21]. Thus, it can be eliminated when the SEI thickness is several tens of Angstroms.

During prolonged deposition, two mechanisms of partial short circuits through the SEI may take place. The first [7] results from tunneling or dissolution of electrons at the M/SE interface. That part of the SEI which is close to the M/SE interface becomes a temporary electronic conductor. Therefore metallic lithium starts to deposit inside the SEI. However, when the plating current is interrupted, these temporary internal short circuits disappear, leaving isolated metallic lithium in the bulk of the SEI. These masses of electrically isolated lithium are not available for anodic dissolution.

Another possible mechanism for internal short circuits in the SEI is preferential deposition of lithium at sites where the ionic conductivity is highest, for example, in the area close to grain boundaries of the SEI [10, 33]. This may lead to the growth of thin lithium dendrites which eventually reach the SE/solution interface. At this point the solvent is reduced and this causes thickening of the SEI above the lithium dendrites. When the new film is sufficiently thick to block the electronic current, the deposition of metal-

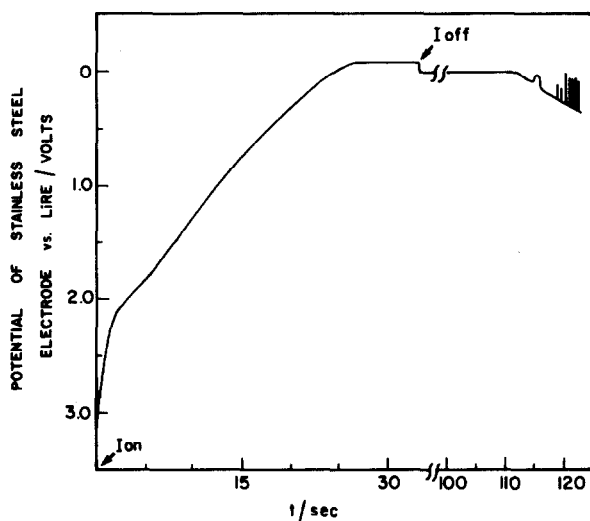


Fig. 1. Potential/time plot during electrodeposition of lithium on stainless steel electrode from 1M LiAlCl_4 -TC solution at a c.d. of 1 mA cm^{-2} (from ref. 22).

lic lithium is renewed. This deposition mechanism leads to a deposit which consists of many islands of lithium surrounded by a passivating layer and connected to each other and to the current collector by thin dendrites. On wet standing, or under anodic dissolution, these thin lithium connectors dissolve first, leaving isolated lithium masses with no electrical connection to the current collector.

The deposition of alkali [22] or alkaline-earth [6, 17] metal on an inert electrode starts only after a sufficiently thick SEI is formed on the inert cathode.

Figure 1 shows a potential/time plot for deposition of lithium on SS from TC solution [22]. The thickness of the PL needed for the initiation of lithium deposition was calculated by two independent methods; one from the reduction charge passed prior to lithium deposition, and the other from the differential electrode capacitance. The minimum SEI thickness was about 100 \AA and the overall thickness of the PL was about 400 \AA . Twenty mC cm^{-2} of charge passed prior to the starting of Li deposition [22].

The clear difference between the mechanism of lithium deposition on an SEI electrode and that of lithium deposition on an inert electrode is shown in Fig. 2. It can be seen that the deposition of lithium from TC solution on a calcium electrode starts immediately after the electrode has been charged to about $5 \mu\text{C cm}^{-2}$. This charge is just what is needed to charge the interfacial electrode capacitor. Furthermore, deposition of an amount of lithium equivalent to about 3% of a monolayer of lithium on calcium is enough to stabilize its potential at zero volts vs. the lithium reference electrode [22].

Another characteristic phenomenon of the dissolution process is the fluctuation of the electrode potential (spikes) during either anodic dissolu-

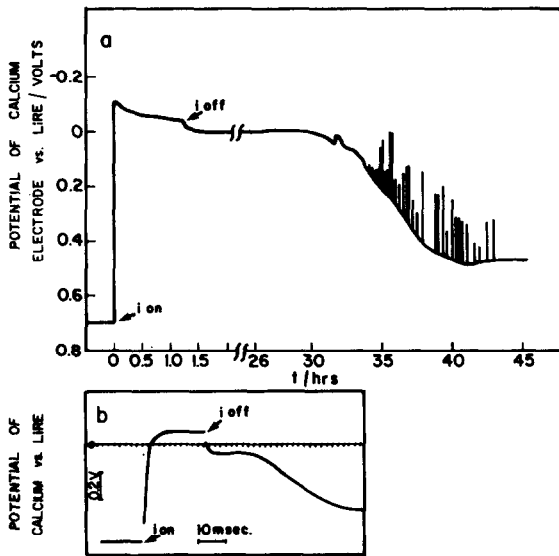


Fig. 2. Potential/time plot during electrodeposition of lithium on calcium electrode from 1M LiAlCl_4 -TC solution at a c.d. of 1 mA cm^{-2} . (a) Long electrodeposition; (b) oscilloscope transient of 20 ms cathodic galvanostatic pulse (from ref. 22).

TABLE 1

The thickness of the SEI of some active metals in nonaqueous battery systems during OCV, plating and stripping*

Metal	Electrolyte	SEI apparent thickness (\AA)			References
		OCV**	Plating	Stripping	
Li	THF-LiClO ₄	100+	36	360	Yamin and Peled (1981)
Li	THF-Li ₂ S ₈	30+	40	38	Peled and Yamin (1980)
Li	SOCl ₂ -LiAlCl ₄	20+	50 - 100		Peled and Yamin (1978)
Li	SOCl ₂ -B ₁₀ Cl ₁₀ ²⁻	200			Meitav and Peled (1982) Moshtev <i>et al.</i> (1981) (Schlaikjer <i>et al.</i> 1979)
Li	PC-LiClO ₄	25+			Geronov <i>et al.</i> (1980)
Ca	SOCl ₂ -Ca(AlCl ₄) ₂	50 - 100		30 - 150	Meitav and Peled (1982) sub.
Mg	SOCl ₂ -Mg(AlCl ₄) ₂	25+	ca. 25	ca. 25	Peled and Straze (1977)
Ca	SO ₂ Cl ₂ -Ca(AlCl ₄) ₂	20 - 40			Meitav and Peled (1981)
Li alloys	TC-SOCl ₂	25 - 50			Tulman <i>et al.</i> (1981) Peled <i>et al.</i> (1978)

*From ref. 10.

**For freshly immersed electrodes.

tion or corrosion of lithium from calcium or SS electrodes. This seems to be due to the formation of temporary metallic connections between the islands of lithium metal in the SEI and the substrate metal [22].

The thickness of the SEI of some anodes in NA battery systems is shown in Table 1. It is important to notice that the SEI exists even during

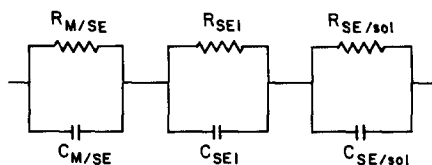


Fig. 3. An equivalent circuit for an SEI electrode.

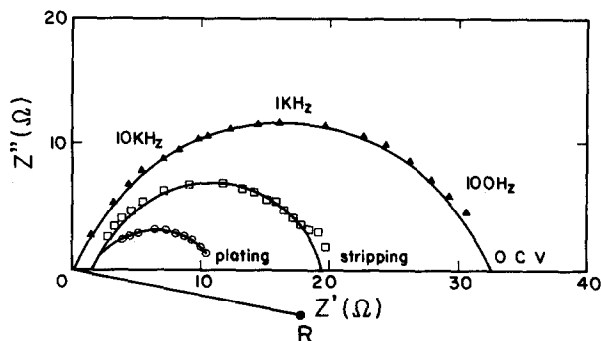


Fig. 4. An a.c. impedance spectra (Cole-Cole plot) for the lithium electrode in LiI-2-Me-THF solution (from ref. 25).

plating or anodic dissolution. In some cases (Li-THF), its thickness decreases during plating, while in others it does not change. Anodic dissolution causes thickening of the SEI in the case of the Li-THF system while in other cases it does not change the thickness of the SEI. When the initial thickness of the SEI is high, *e.g.*, 1000 Å, anodic dissolution always decreases it by the breakdown and repair mechanism.

SEI electrodes, which are generally anionic conductors, exhibit a much more complicated deposition-dissolution mechanism [7, 23, 24, 22, 21]. The Faradaic yield for deposition is close to zero and the deposition process is associated with very high overpotentials of the order of tens of volts. These electrodes are Mg and Ca in TC.

Figure 3 shows the equivalent circuit for an SEI electrode. SEI electrodes can be represented by a series combination of three parallel RC circuits. The first one represents the M/SE interface, the second the SEI, and the third represents the SE/solution interface. In principle, any one of the three consecutive steps in the dissolution-deposition process can be the rate-determining step. However, as the ionic conductivity of solid electrolytes is rather low at room temperature, it is expected that the RDS will be ionic transport through the SEI. Many studies near OCV conditions confirm this [7, 10].

Moreover, in some cases, even during deposition or dissolution of lithium, although the SEI is very thin, the RDS is still ionic migration. This can be seen in Fig. 4. The impedance spectrum taken under OCV, continuous deposition, and continuous dissolution of lithium in 1M LiI-2-Me-THF solution consists of a single semi-circle [25]. The equivalent circuit which be-

TABLE 2

The composition and resistivity of SEI electrode systems*

Metal	Solvent system	Electrolyte	SEI composition	SEI resistivity (Ω cm)
Li	SOCl ₂	LiAlCl ₄	LiCl	10 ⁷ - 10 ⁸
Li	PC	LiClO ₄	Li ₂ CO ₃	0.5 - 2.5 × 10 ⁸
Li	THF	Li ₂ S _{8,4}	Li ₂ S	1 - 4 × 10 ⁷
Li	Dioxolane	LiClO ₄	**	10 ⁷ - 10 ⁸
Li	THF	LiClO ₄	**	10 ⁸
Li	2-Me-THF	LiI	**	1 - 3 × 10 ⁷
Li	SO ₂ + AN	LiBr	Li ₂ S ₂ O ₄	10 ⁹
Mg	SOCl ₂	Mg(AlCl ₄) ₂	MgCl ₂	10 ⁹ - 10 ¹⁰
Ca	SOCl ₂	Ca(AlCl ₄) ₂	CaCl ₂	10 ⁸ - 10 ¹⁰
Ca	SO ₂ Cl ₂	Ca(AlCl ₄) ₂	CaCl ₂	10 ¹⁰

*From ref. 10.

**Insoluble reduction products of the electrolyte or Li₂O.

longs to such a spectrum is a parallel RC circuit. The fact that the center of the semi-circle is located below the Z' axis indicates that we have many parallel RC combinations with similar values [25].

With the assumption that the RDS is ionic migration through the SEI, eqn. (2) shows the current/voltage relation for migration of ions in SE [26].

$$i = 4Fzanv \exp(-W/RT) \sinh(azFE/RT). \quad (2)$$

For high-field conditions ($azFn > RTL$) a Tafel-like equation is obtained where the Tafel slope depends linearly on the SEI thickness, eqn. (3).

$$b = \frac{2.3RTL}{azF}. \quad (3)$$

For low-field conditions Ohm's law is obtained and the electrode reaction resistance depends linearly on L .

Table 2 presents the SEI resistivity for a number of SEI electrodes together with the SEI composition.

Several factors affect the SEI resistivity. It was generally found [10] for Li/PC, Li/TC, Mg/TC, Ca/TC, and Li/polysulfide systems, that the SEI resistivity increases with its thickness.

It was found that the resistivity of the SEI of Li in the Li/TC system decreases with increase in the electrolyte concentration [28, 29]. However, this effect diminishes as the thickness of the SEI increases. This was explained by the doping of the SE/solution interface by Al³⁺ which results in an increase in the concentration of cationic vacancies near the SE/solution interface.

Table 3 shows the effect of dissolution and plating of lithium in 1M LiClO₄-THF solution on the SEI resistivity. During plating the resistivity

TABLE 3

The ionic resistance, the thickness and the resistivity of the SEI of lithium in 1M LiClO₄-THF solution, during plating and during stripping (From ref. 25.)

	OCV	Stripping	Plating
Reaction resistance ($\Omega \text{ cm}^2$)	110	23.5	12.6
SEI thickness (\AA)	180	360	36
SEI resistivity ($10^{-7} \Omega \text{ cm}$)	6.1	0.65	3.5

TABLE 4

The apparent thickness and resistivity of the SEI on a stainless steel electrode upon electrolysis and under OCV in 1M LiAlCl₄-TC solution (Meitav and Peled, 1982)

State of the electrode	Capacitance ($\mu\text{F cm}^2$)	Apparent thickness (\AA)	SEI resistivity ($\Omega \text{ cm} \times 10^{-7}$)
OCV, prior Li deposition	30	—	—
During Li deposition (0.5 mA cm^{-2})			
After 10 min of deposition	1.0	100	1.3
After 30 min of deposition	1.7	60	1.5
After 40 min of deposition	1.8	50	1.4
Li coated, under OCV			
5 min under OCV	1.5	65	2.6
20 min under OCV	1.3	75	3.0
50 min under OCV	1.2	80	4.0

decreases by a factor of two in comparison with its OCV value, while dissolution decreases the resistivity by one order of magnitude.

Similar results were obtained for the Li/TC system as can be seen in Table 4. During lithium plating, the resistivity reaches its lowest value. On OCV it increases slowly to its steady-state value of $10^8 \Omega \text{ cm}$. It can be further seen that the apparent thickness of the SEI decreases during plating, and increases on OCV.

It was generally found that the SEI resistivity during plating and dissolution of lithium is about the same as that of a freshly immersed electrode which is covered by a thin SEI (less than 100 \AA in thickness). It was suggested that under the above-mentioned conditions, the SEI is continuously renewed by the breakdown and repair mechanism [10, 21, 22]. As a result, it consists of small crystals having a higher degree of disorder and therefore a high concentration of mobile lattice defects [20 - 22, 28, 29]. A thick SEI consists of large and more ordered crystals and with less contribution of the grain boundaries to the ionic conduction.

Figure 5 shows the Tafel behavior of an Mg electrode in TC solution. It was found that the Tafel slope is a linear function of the SEI thickness [24]. Moreover, the thickness of the SEI, which was calculated from interfacial capacitance and from the Tafel slope, was the same.

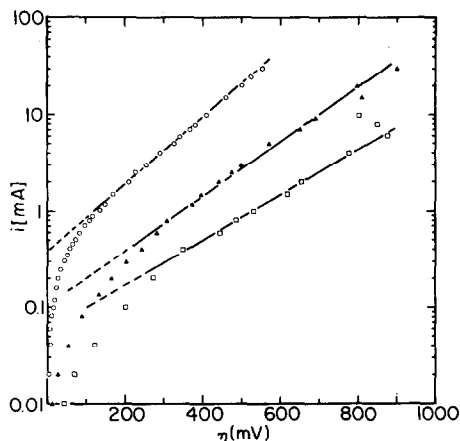


Fig. 5. Tafel plots of a magnesium electrode immersed for 1 (○); 20 (△); and 40 (□) h in 0.6M $\text{Mg}(\text{AlCl}_4)_2$ -TC solution (from ref. 24).

TABLE 5.

Comparison between experimental and theoretical Tafel slopes (1M LiClO_4 -PC solution.)

Y (Å)	b_{exp} (mV)	$b_{\text{theor.}} = 20 Y$ (mV)
25	460	500
37	670	740
65	1150	1300
103	1840	2060
130	2400	2600
138	2650	2760
162	3155	3240

Geronov, Schwagner and Muller (1980).

Similar results for the Li/PC system can be found in Table 5. Here, again, the calculation of the SEI thickness from electrode capacitance and from Tafel slope gives the same results [27].

It was generally found that the thickness of the SEI grows with time as a result of the slow corrosion of the metal [6, 7, 10]. The RDS of this process is always the cathodic reaction, which means the reduction of the electrolyte [6, 7, 17]. Two possible mechanisms for this process were proposed [7]. The first is galvanic corrosion. Under the assumptions [7] that the corrosion electronic current follows Ohm's law and that a constant fraction of the reduction product precipitates on the surface of the metal, a parabolic law for the growth rate of the SEI is obtained, eqn. (4)

$$L = \left(L_0^2 + \frac{2KV_0}{\rho(e)} t \right)^{1/2} \quad (4)$$

The second mechanism [7] involves diffusion of holes or electrons through the SEI as the RDS. This, too, leads to a parabolic law of growth, eqn. (5)

$$L = (L_0^2 + 2KFDC_0t)^{1/2} \quad (5)$$

One of the most important factors affecting the growth rate of the SEI is probably the mechanism of precipitation of the corrosion products. In cases where, for the most part, they precipitate directly on the surface of the anode to form a compact and hole-free SEI, it is expected that the corrosion of the anode will be markedly reduced and the growth rate of the SEI will be nearly parabolic. However, when most of the corrosion products dissolve in the solution and precipitate far from the surface of the anode to form a secondary porous layer, then the thickness of the SEI will grow very slowly and the corrosion current will be much higher than in the first case. It should be emphasized that the breakdown and repair mechanism holds true also for corrosion and not only for anodic dissolution. This is another factor which slows the thickening of the SEI during corrosion. It is clear that any impurities that can contaminate the SEI will increase its electronic conductivity and therefore will accelerate corrosion. It was found that iron [32] and copper [10] and even electrolyte concentration [28, 29] increases the growth rate of the SEI of Li in TC solutions.

When a lithium cell is loaded after prolonged storage at elevated temperature, its voltage immediately falls below its nominal operating voltage, and after some time it slowly recovers. This phenomenon is called "the voltage-delay problem". It is more severe in the Li/SOCl₂ system than it is for other lithium batteries. For each system, the transition minimum voltage (TMV) and the recovery time are a function of duration and temperature of storage, discharge current density and temperature, and the history of the cell. The most severe voltage delay will be encountered for cells stored at elevated temperatures and discharged at low temperatures and high current density. At room or elevated temperatures, for low-current-density applications, this phenomenon is not detectable.

It is clear that the voltage delay is caused by the passivating layer on the lithium anode (Dey and Schlaikjer [30], Dey [4]). Two different types of film can be identified [10]. The first is a thin and compact film. Figure 6(a) describes the voltage-time transient for such a case. There is a very fast depression of the working voltage due to the *IR* drop on the SEI, then the voltage recovers as a result of the breakdown and repair mechanism of the SEI previously described. This type of film is associated with relatively high TMV and a short recovery time (seconds or less). It is typical of fresh cells which have been stored at low or room temperatures for short times.

The second type of passivating film consists of a compact SEI on top of which a thick, mechanically strong, low-porosity secondary layer has developed. These two types of film are the extreme cases, while in reality many intermediate cases can be found. The voltage-time transient for this film is described by Fig. 6(b). The voltage falls sharply as a result of the *IR* drop on

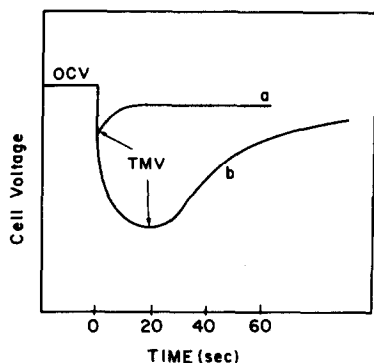


Fig. 6. The voltage delay for: (a) an anode covered by a thin SEI, with or without an open structured secondary layer; (b) an anode covered by an SEI on top of which a dense and thick secondary layer was formed (from ref. 10).

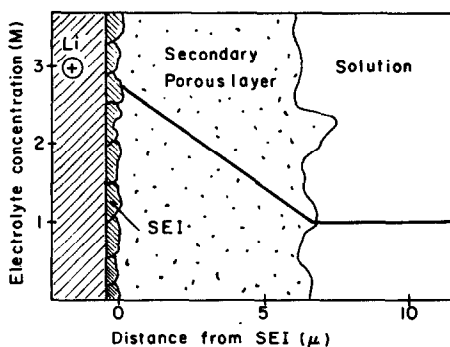


Fig. 7. A schematic description of the concentration profile in the pores of the secondary layer during the voltage delay phenomenon (from ref. 10).

the SEI, then more slowly to the TMV and later recovers very slowly. The slow decrease of the voltage to the TMV results from the IR drop in the solution occupying the pores of the secondary layer and from anodic concentration overpotential. The porous secondary layer can be looked upon as a membrane which slows the mass transport of ions to the SEI. During discharge (for a 1:1 electrolyte), $Q \cdot t/F$ equivalents of electrolyte are added to the porous layer [10]. As the electrolyte concentration builds up in the porous layer, diffusion of electrolyte from the SEI to the solution begins.

This results [10] in the formation of a concentration profile schematically described in Fig. 7. If the electrolyte concentration near the SEI/PL interface exceeds the maximum solubility of the electrolyte salt, it will precipitate in this region. This process may lead to heavy blocking of the electrode and the TMV will be close to zero volts. In less severe cases, the concentration build-up may cause a significant increase in the viscosity of the electrolyte inside the pores of the secondary layer. Therefore its diffusion out of the PL will be slowed and this will accelerate the build-up process. As the viscosity increases, solution conductivity decreases and the IR drop across the PL increases.

For example, the viscosity of LiAlCl_4 -TC solution at 20 °C is 0.8, 1.1 and 5 cp for 0.3, 1.0 and 3.5M concentrations, respectively. The viscosity of 3.5M LiAlCl_4 -TC solution is 20 cp at -30 °C and only 2.5 cp at 60 °C [10]. The porosity of the secondary layer has a marked effect on the voltage delay problem. As the porosity decreases, the volume of the electrolyte in the pores decreases and the concentration build-up process (during initiation of discharge) speeds up.

The recovery of the voltage from TMV has two causes: (a) the mechanical rupture of the PL [4]; (b) the heat developed in the PL during the voltage delay period helps in this rupture process and, in addition, decreases the viscosity of the solution in the pores of the secondary layer [10].

The voltage delay problem can be eliminated by changing both the solution and the PL variables [10]. It is necessary to reduce the growth rate of the PL and to change its morphology from a dense, nonporous, to an open, structural layer. This is done in the case of the Li-TC cell by adding SO₂ to the electrolyte [31]. Of course the purity of the electrolyte is of great importance to the growth rate of the PL (as was previously discussed). Iron, for example, enhanced the growth rate of the PL in the Li-TC cell [32]. In addition to the elimination of the thick and dense PL, the viscosity of the solution must be reduced. Dey's findings [4] that the voltage delay in Li-TC cells can be eliminated with the use of a lower concentration of electrolyte can be attributed to both the decrease in the thickness of the PL and to the decrease of the viscosity of the solution [10]. The fact that the voltage delay problem is much less severe in the Li-SO₂ cells than in the Li-TC cells may be attributed, at least in part, to the lower viscosity of the AN-SO₂ electrolyte.

List of symbols

a	Half-jump distance
a_{M^+}, a_{e^-}	Activity of alkali metal ion and activity of solvated electron, respectively, in saturated solution of alkali metal
b	Tafel slope
C_0	Concentration of electrons or holes at the SE near M/SE interface, or near the SE/sol interface, respectively
D	Diffusion coefficient of electrons or holes in the SEI
E	Electric field
E_M^0	Standard potential of the alkali metal electrode
$E_{e^-}^0$	Standard potential of the solvated electron electrode
F	Faraday's constant
i	Current density
K	A constant
L	Thickness of the SEI
L_0	Thickness of the SEI at $t = 0$
n	Concentration of lattice defects
R	Universal gas constant
t	Time
T	Temperature
V_0	Open circuit voltage
W	A barrier energy for jumping
z	The valance of the mobile ion
η	Overpotential
$\rho(e)$	Electronic resistivity of the SEI
ν	Vibration frequency of the ion in the crystal

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