

On the stability of lithium during ageing of Li/PEO₈LiClO₄/Li cells

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Abstract

Symmetrical cells consisting of a thin film of PEO₈LiClO₄ solid-polymer electrolyte sandwiched between two lithium electrodes have been subjected to galvanostatic polarization and concomitant voltage changes measured at several intervals of ageing at ambient temperature. The interfacial resistance is found to increase gradually over about 150 days of ageing. The exponential increase of cell voltage is interpreted in the light of the diffusion-limited lithium-ion transport across the passive surface film on lithium.

Keywords: Lithium; Solid-polymer electrolytes; Passive films; Diffusion

1. Introduction

In recent years, lithium metal has been studied extensively as a negative-electrode material to develop high energy density, rechargeable, solid-state, lithium batteries. These batteries employ a thin solid-polymer film as the electrolyte and efforts are being expended to develop an appropriate solid-polymer electrolyte (SPE) that possesses high Li⁺ ion conductivity in addition to properties such as chemical and electrochemical stability, compatibility towards electrode materials, and providing efficient contact with electrodes to sustain electron-transfer reactions at the electrode/electrolyte interface. Although there have been several studies [1–3] on the physicochemical characterization of SPEs since the inception of polyethylene oxide (PEO) [4,5], electrochemical investigations on lithium metal in conjunction with an SPE are rather scarce [6].

The electrochemical behaviour of lithium in liquid electrolytes has been studied widely [7], and it is found that lithium is thermodynamically unstable, even in organic solvents. It is believed that lithium metal is covered by a passive surface film that protects the metal. The film consists of insoluble products of the reaction of the metal with the solution. The successful development of primary lithium batteries is due to the existence of this passive layer as it allows the anodic oxidation of lithium while protecting the latter from corrosion during open-circuit conditions. By contrast, dendritic growth of deposited lithium and decreasing reaction kinetics on cycling that are associated with the passive layer have ham-

pered the development of secondary lithium batteries. Thus, examination of the properties and electrochemical behaviour of the passive surface layer on lithium have become seminal for the development of rechargeable lithium batteries.

It has been reported [8] that the resistance of the passive film is proportional to its thickness. The formation of the passive film and its influence on the electrochemical reaction at the lithium electrode in propylene carbonate electrolyte have been studied [9] by applying a current pulse and interruption technique. A galvanostatic pulse method has been employed [10–12] for the non-destructive evaluation of the resistance and the capacitance of passive films. In other work [13], passivation of lithium has been compared in different electrolyte solutions by cycling semi-practical cells. These studies with impedance spectroscopy suggested that the film resistance increased during extended cycling when propylene carbonate was used as solvent. There are several other investigations of the passive layer on lithium; some of the recent have used X-ray photoelectron [14] and Auger electron [15] spectroscopies.

The formation and growth of the passive film on lithium in SPE media have been examined by using impedance spectroscopy [16–19]. The film is reported to be formed by an electrochemical reaction between lithium and PEO electrolyte [16]. The interfacial resistance is shown to increase gradually during about four days after the cells have been assembled. The kinetics of the electrochemical deposition and stripping of lithium in PEO electrolyte medium is influenced by the formation of the passive film [18,19]. It is demon-

strated that the development of the passive layer occurs faster in amorphous polymer electrolytes (e.g., polypropylene oxide) than in partially crystalline PEO electrolyte [17].

In this communication, the nature of the passive film on lithium is studied using a galvanostatic voltage transient method over about 150 days of ageing in $\text{PEO}_8\text{LiClO}_4$ SPE.

2. Experimental

Poly(ethylene oxide) (mol. wt. 4×10^6 , Aldrich) was used as received. Lithium perchlorate (Koch-Light) was dried at 100°C under reduced pressure before use. For making films of SPE, the required quantity of PEO was dissolved in acetonitrile (AR grade). A stoichiometric amount of LiClO_4 (required to maintain the O:Li ratio at 8:1) was dissolved in a small quantity of acetonitrile separately. After ensuring complete dissolution of PEO, the two solutions were mixed and stirred for several hours. Thin films of SPE were prepared by spreading the solution on Teflon-covered glass plates and evaporating the solvent. The SPE films on glass plates were dried at 80°C under reduced pressure for about 12 h and then transferred into an argon-filled dry box.

Li/SPE/Li symmetrical cells were assembled in Teflon holders. The latter were provided with stainless-steel leads that were in contact with lithium foils. The area of each lithium electrode was 1.0 cm^2 and the polymer electrolyte thickness was 100 to 200 μm . The assembly was contained in a stainless-steel cylindrical container with a lid and isolated lead terminals. The lithium electrode leads were soldered to the lid terminals, and the lid was welded to the container by argon welding.

The electrochemical measurements were carried out at a cell temperature of $80 \pm 1^\circ\text{C}$. The cell was polarized by passing a constant current. This was applied with a galvanostatic circuit that consisted of a regulated d.c. power source, a high resistance (500 k Ω) and a galvanometer. The cell voltage was measured by means of a digital voltmeter ($\pm 0.1\text{ mV}$ resolution) and/or an x-y recorder (Rikadenki).

A constant current (10 to 50 μA) was passed through the cell and changes in voltage were measured over 15 to 30 min. After completing the measurements by passing a given current, the circuit was opened and the cell was allowed to relax for about 1 h under open-circuit conditions followed by passing the same magnitude of current in the reverse direction. The cell was allowed to stand at open circuit for a few hours before changing the magnitude of current. This procedure ensured that equilibrium conditions were established in the cell before starting an experiment and that the data were reproducible. For studying the ageing effect, the cells were stored at ambient temperature, while the electrochemical measurements at several intervals of ageing were performed at $80 \pm 1^\circ\text{C}$. The measured voltage versus time data were fed to a computer and the slopes at different times were calculated by using a curve-fitting procedure.

3. Results and discussion

In a symmetrical cell, the two lithium electrodes with their inherent surface films are separated by the SPE. As the two electrodes of the cell are identical, the open-circuit voltage of the cell is 0 V. At the instant of passing a galvanostatic current (I), there is a sudden rise in cell voltage followed by an exponential increase. A typical plot of the cell voltage transient is shown in Fig. 1. To explain the exponential increase in cell voltage, the following possibilities can be considered.

The equivalent circuit of the symmetrical cell is given in Fig. 2. It consists of several resistive and capacitive components, as defined in the legend. The exponential increase in cell voltage may be considered to be due to charging of the double-layer capacitance of the lithium electrode, C_{dl} . This possibility, however, is unlikely because the value of C_{dl} between lithium and its surface film is as low as $1\text{--}2\ \mu\text{F cm}^{-2}$ [6]. The charge-transfer resistance (R_{ct}) due to the electrode

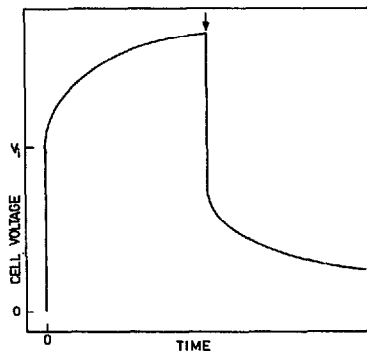


Fig. 1. Schematic diagram of cell voltage as a function of time when a d.c. current is passed through an $\text{Li}/\text{PEO}_8\text{LiClO}_4/\text{Li}$ cell. V_0 is the initial voltage jump. Arrow indicates the time when the current is terminated.

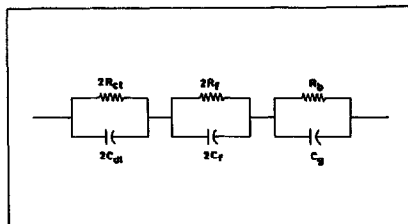


Fig. 2. Equivalent circuit of an $\text{Li}/\text{PEO}_8\text{LiClO}_4/\text{Li}$ symmetrical cell. R_{ct} , R_f and R_b are charge-transfer resistances at the Li/passive layer, resistance of passive layer and resistance of SPE, respectively. C_{dl} , C_f and C_p are double-layer capacitance at the Li/passive layer interface, capacitance of passive layer and capacitance of polymer film, respectively. R_c of the two lithium electrodes are added and shown as $2R_c$, so also R_{ct} and C_f .

reaction is of the order of $50 \Omega \text{ cm}^2$, which is calculated from the exchange current of the reaction (0.5 mA cm^{-2}) [6]. The time constant for this resistor/capacitor pair is $100 \mu\text{s}$. Therefore, the charging of the double-layer capacitor is completed in a very short time and the variation of cell voltage at longer times is not due to this process. Similarly, the charging of C_f and C_d are also completed in a very short time as these parameters also have low values [20]. An appropriate explanation for the voltage behaviour (Fig. 1) based on a slow diffusion of Li^+ ions in the surface film of lithium metal can be offered as discussed below.

Since the capacitors C_{dl} , C_f and C_d attain complete charge in less than a second, the initial voltage rise (V_i) is attributed to the voltage drop across $[2(R_{ct} + R_f) + R_b]$. Therefore

$$2(R_{ct} + R_f) + R_b = V_i / I \quad (1)$$

or

$$2R_i + R_b = V_i / I \quad (2)$$

where $R_i (= R_{ct} + R_f)$ is the interfacial resistance associated with the electron-transfer reaction and the surface film. If the resistance of the SPE film (R_b) is known, then the interfacial resistance (R_i) can be evaluated by using Eq. (2).

The voltage transients of a symmetrical cell at different currents are shown in Fig. 3. The curves are reproduced by reversing the direction of current. The cell voltage at 15 s after the current was allowed to pass was taken as V_i . The plots of V_i versus I for several intervals of ageing are shown in Fig. 4. The plots are fairly linear. The slope (dV_i/dI)

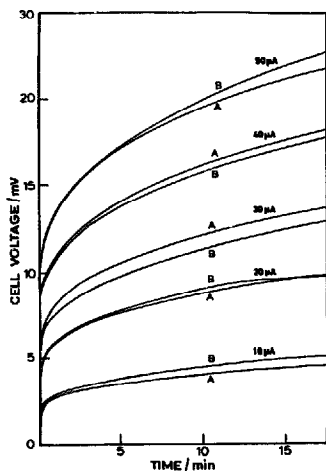


Fig. 3. Voltage transients of a Li/PEO₃LiClO₄/Li symmetrical cell at different currents. (A) and (B) refer to forward and reverse directions of current, respectively. Experiment is carried out 46 days after the cell was assembled. Cell temperature: 80 °C, electrode area: 1.0 cm², and polymer electrolyte thickness: 100 μm.

provides the sum of the interfacial resistance and the resistance due to SPE, i.e. $2R_i + R_b$, in accordance with Eq. (2). Using the specific conductivity of PEO₃LiClO₄, viz. $5 \times 10^{-4} \text{ S cm}^{-1}$ [6], the resistance R_b of the film with 100 μm thickness and 1 cm² area of cross-section is found to be 20Ω at 80 °C. Thus, R_i was calculated using Eq. (2). Assuming R_b to be invariant on ageing, the time evolution of R_i is shown in Fig. 5. The interfacial resistance of lithium in PEO₃LiClO₄ SPE increases with time after the cell is assembled. This increase is essentially attributed to the increase in the resistance of the surface film on lithium. It is believed that the surface film is composed of two types of layers [7]. The immediate layer on the lithium surface is known as the primary passive film and is beneficial to the stability of the metal. When current flows through the electrode, the primary film allows the diffusion of Li^+ ions without hindering the electrochemical reaction. The secondary passive layer, which overlays the primary layer, is likely to hinder the passage of Li^+ ions. The increase in R_i (Fig. 5) is attributed to the secondary film due to the increase in its thickness, or the increase in the surface coverage, or the change in its chemical

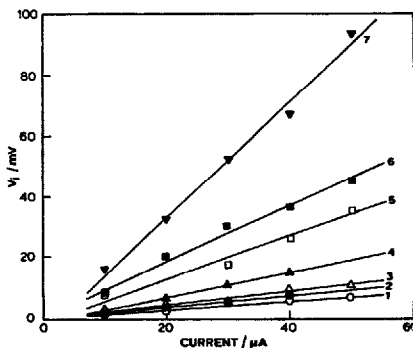


Fig. 4. The initial voltage jump, V_i , as a function of current flowing through the symmetrical cell when the ageing time was (1) 6, (2) 46, (3) 57, (4) 76, (5) 105, (6) 135 and (7) 165 days. Cell temperature: 80 °C, electrode area: 1.0 cm², and polymer electrolyte thickness: 100 μm.

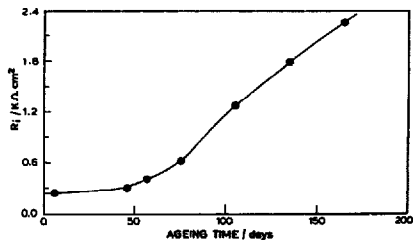


Fig. 5. Time evolution of the interfacial resistance (R_i) of lithium in PEO₃LiClO₄ electrolyte at 80 °C.

composition. The factors that may influence the passive film include: (i) corrosion of lithium during open-circuit conditions of the cell; (ii) residual water present in SPE film; (iii) frequent heating of the cell to 80 °C during experiments, and (iv) cycling of the cell by passing currents in the range 10 to 50 μ A. The dependence of the R_i of lithium in SPE on ageing time (Fig. 5) is similar to that reported from a.c. impedance measurements [21].

The exponential increase in cell voltage due to current flow (Fig. 3) can be attributed to slow diffusion of Li^+ ions in the surface passive film as discussed below.

The generally accepted electron-transfer reaction at a lithium electrode is



The equilibrium voltage (V_e) of the cell is given by

$$V_e = E_e^c - E_e^a \quad (4)$$

where E_e^c and E_e^a are the equilibrium potentials of the positive (cathode) and negative (anode) electrodes, respectively. $V_e = 0$, as the cell under consideration is Li/SPE/Li. When current flows through the cell, the forward reaction occurs at a lithium cathode while the reverse reaction occurs at an anode. Lithium ions produced at the anode Li/surface-film interface travel through the anode surface film, the solid-polymer electrolyte and the cathode surface film before reaching the cathode Li/surface-film interface. Reduction of Li^+ ions occurs at the cathode Li/surface-film interface and result in surface deposition. The transport of Li^+ ions in the surface film is considered to be slower than the remaining steps. Hence, the concentration of Li^+ ions at the cathode/film interface is smaller than that in SPE and, simultaneously, it is higher at the anode Li/film interface. The concentration gradients in the SPE are neglected.

The cell voltage (V), in the region of voltage increase is given by

$$V = E_i^c - E_i^a + 2IR_i + IR_b \quad (5)$$

The cell overvoltage, $\Delta V_i (= V_i - V_e)$ is thus

$$\Delta V_i = V_i = |\eta_i^c| + |\eta_i^a| + 2IR_i + IR_b \quad (6)$$

The variation of V_i is due to variations in overpotentials $\eta_i^c (= E_i^c - E_e)$ and $\eta_i^a (= E_e - E_i^a)$ with time, which in turn depend on the variation of the concentration of Li^+ ions at the electrode/surface-film interface. Using the Nernst equation

$$|\eta_i^c| = (RT/F) \ln[C_e/C_i^c] \quad (7)$$

and

$$|\eta_i^a| = (RT/F) \ln[C_i^a/C_e] \quad (8)$$

where C_e is the concentration of Li^+ ions in SPE. Eqs. (7) and (8) are justified considering the fact that the reaction (3) is fast and reversible with an exchange current of about 10 mA cm^{-2} . Therefore, the electrode reactions do not occur under charge-transfer control when currents are small in mag-

nitude as in the present study. At any instant t , the concentration decrease ($\ln C_e - \ln C_i^c$) at the cathode/film interface is equal in magnitude to the concentration increase ($\ln C_i^a - \ln C_e$) at the anode/film interface. Therefore

$$|\eta_i^c| = |\eta_i^a| = \eta_i \quad (9)$$

Eqs. (6) and (9) yield

$$V_i = 2\eta_i + 2IR_i + IR_b \quad (10)$$

On differentiation, Eq. (10) becomes

$$dV_i/dt = 2(d\eta_i/dt) \quad (11)$$

The time-dependence of the concentration of Li^+ ions at the cathode/film interface may be obtained by differentiating Eq. (7) with respect to time (t) as given below.

Eq. (7) is re-written as

$$C_i^c/C_e = \exp(-\eta_i^c F/RT) \quad (12)$$

On differentiation Eq. (12) yields

$$(1/C_e)(dC_i^c/dt) = -\exp(-\eta_i^c F/RT)(F/RT)(d\eta_i^c/dt) \quad (13)$$

or

$$dC_i^c/dt = -(FC_e/RT)(d\eta_i^c/dt) \exp(-\eta_i^c F/RT) \quad (14)$$

As the concentration C_i^c is governed by the diffusion of Li^+ ions in the surface film when a constant current (I) flows through the cell, C_i^c can be evaluated by solving Fick's law of diffusion. By analogy with diffusion of an electroactive ion in a diffusion layer of an electrode/electrolyte interface [22]

$$C_i^c = C_e - 2It^{1/2}K/FAD^{1/2}\pi^{1/2} \quad (15)$$

where K is a constant related to the thickness of the surface film on lithium and other symbols have their usual meanings.

Differentiation of Eq. (15) gives

$$dC_i^c/dt = -IK/FAD^{1/2}\pi^{1/2}t^{1/2} \quad (16)$$

From Eqs. (14) and (16)

$$d\eta_i^c/dt = (IRTK/F^2AC_eD^{1/2}\pi^{1/2}t^{1/2}) \exp(\eta_i^c F/RT) \quad (17)$$

Similarly, it can be shown that

$$d\eta_i^a/dt = (IRTK/F^2AC_eD^{1/2}\pi^{1/2}t^{1/2}) \exp(\eta_i^a F/RT) \quad (18)$$

Therefore, generalizing Eqs. (17) and (18) for either cathode or anode

$$d\eta_i/dt = (IRTK/F^2AC_eD^{1/2}\pi^{1/2}t^{1/2}) \exp(\eta_i F/RT) \quad (19)$$

From Eqs. (11) and (19)

$$dV_i/dt = (2IRTK/F^2AC_eD^{1/2}\pi^{1/2}t^{1/2}) \exp(\eta_i F/RT) \quad (20)$$

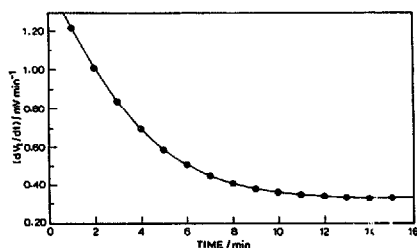


Fig. 6. Variation of (dV/dt) with time of measurement at $50 \mu\text{A}$. Experiment was carried out 6 days after cell assembly. Cell temperature: 80°C , electrode area: 1.0 cm^2 , and polymer electrolyte thickness: $100 \mu\text{m}$.

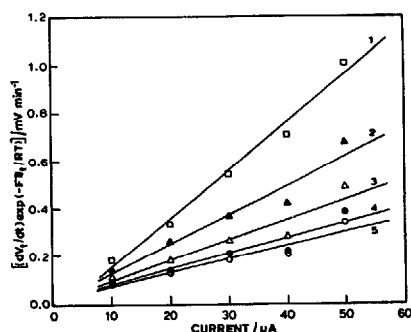


Fig. 7. The product $[(dV/dt) \exp(-\eta_a F/RT)]$ as a function of current when measured at (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 min during polarization. Experiment is carried out 46 days after the cell was assembled. Cell temperature: 80°C , electrode area: 1.0 cm^2 , and polymer electrolyte thickness: $100 \mu\text{m}$.

Eq. (20) can be verified by the following

- (i) at any instant t , the product $[(dV/dt) \exp(-\eta_a F/RT)]$ should increase linearly with I , and
- (ii) for any constant current, the product $[(dV/dt) \exp(-\eta_a F/RT)]$ should increase linearly with $t^{-1/2}$.

The experimental data obtained with several current values in the $10\text{--}50 \mu\text{A}$ range and over several intervals during ageing of the symmetrical cells were analysed to verify the validity of Eq. (20). A typical plot of dV/dt versus t is shown in Fig. 6. As may be expected from V_i versus t data (Fig. 3), dV/dt decreases with time and finally becomes invariant within about 10 min. The values of overpotential (η_a) at each lithium electrode is calculated as $(V_i - V_1)/2$, and the product $[(dV/dt) \exp(-\eta_a F/RT)]$ versus I at several times are plotted. A typical plot for the data obtained 46 days after cell assembly is shown in Fig. 7. All the plots are linear. Similarly, $[(dV/dt) \exp(-\eta_a F/RT)]$ versus $t^{-1/2}$ plots shown in Fig. 8 are also linear. Thus, the data agree with Eq. (20) and confirm the exponential voltage increase of the symmetrical cell which is due to diffusion-limited mass transport in the passive film present on the lithium surface.

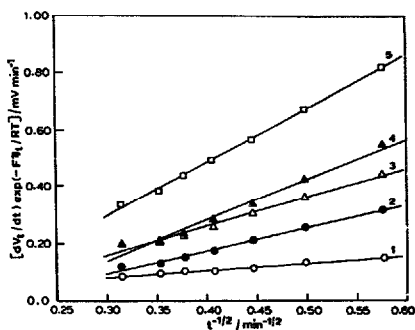


Fig. 8. The product $[(dV/dt) \exp(-\eta_a F/RT)]$ as a function of $t^{-1/2}$ when the current is (1) 10, (2) 20, (3) 30, (4) 40 and (5) $50 \mu\text{A}$. Experiment is carried out 46 days after the cell was assembled. Cell temperature: 80°C , electrode area: 1.0 cm^2 , and polymer electrolyte thickness: $100 \mu\text{m}$.

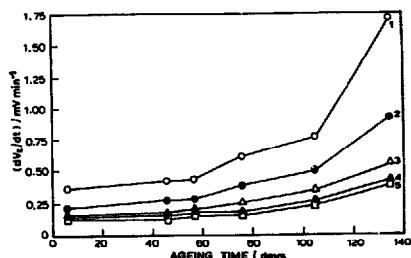


Fig. 9. The slope, (dV/dt) , as a function of ageing time when measured at (1) 2, (2) 4, (3) 6, (4) 8 and (5) 10 min during polarization. Cell temperature: 80°C , electrode area: 1.0 cm^2 , polymer electrolyte thickness: $100 \mu\text{m}$, and galvanostatic current: $20 \mu\text{A}$.

If diffusion-limited mass transport in SPE is considered to explain the exponential increase of cell voltage, the slope (dV/dt) is expected to be invariant with ageing. A plot of (dV/dt) versus ageing time is shown in Fig. 9 for $20 \mu\text{A}$ cell current at several t values of $V-t$ curves. The increase in (dV/dt) with ageing suggests that the process of voltage increase is associated with a passive layer on the lithium. This corroborates further the above discussion. It may, therefore, be concluded that the time-dependent voltage variation in symmetrical cells on passing a galvanostatic current is due to the diffusion-limited transport of Li^+ ions in the surface passive films on the lithium electrodes.

4. Conclusions

A direct-current method has been used to evaluate the stability of lithium in a PEO SPE. Experiments during 150 days of ageing suggest a gradual increase in the interfacial resistance of the lithium electrode in $\text{PEO}_3\text{LiClO}_4$ electrolyte.

The exponential increase of symmetrical cell voltage is analysed in terms of diffusion-limited Li^+ -ion transport in the passive layer on the lithium surface.

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