Surface films of lithium: an overview of electrochemical studies

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Abstract

There is considerable ambiguity in the literature about the importance of lithium surface film on the electrochemical reaction at the lithium/electrolyte interface. Some studies attribute the measured interfacial properties to the surface film on lithium alone and other studies consider the measured properties due entirely to electron-transfer reaction; while a few studies provide due recognition to both the surface film as well as the charge-transfer reaction. Literature on DC polarization and AC impedance spectroscopic studies of Li/non-aqueous liquid and solid polymer electrolyte interface is reviewed. Our electrochemical impedance spectroscopic studies of lithium/solid polymer electrolyte interface are analyzed using simple equivalent circuit models. The models include both the surface film properties as well as the electron-transfer reaction. The experimental results and reviewed literature support that both the surface film on lithium and the electron-transfer reaction are equally important interfacial phenomena, and should be considered simultaneously during an investigation. © 1998 Elsevier Science S.A.

1. Introduction

Lithium metal is extremely attractive as a negative electrode material in electrochemical power sources (i.e., batteries). The importance of Li originates from its low atomic weight (viz., 6.94), high negative electrode potential (viz., -3.03 V) and high specific capacity (viz., 3.86 Ah g^{-1}). These favourable factors, which are possessed by no other metal, are responsible for the development of so called 'lithium batteries'. These batteries are able to meet the increasing demand for high energy, light weight and compact electrical power sources for a wide range of applications where portability is often the prime requisite. Unlike the other battery systems which employ an aqueous electrolyte, a lithium battery requires a non-aqueous electrolyte medium due to the high reactivity of Li with water. Even in non-aqueous electrolytes, the solvents of interest for lithium batteries are the dipolar–aprotic solvents, which ensure the absence of labile or active hydrogen atoms [1].

It is known that passivity of metals and alloys is an essential and significant phenomenon responsible for their stability and utility in almost all applications. Most structural metals are viable in an engineering sense because of the existence of a surface oxide film, the thickness of which may be no more than a few nanometers [2]. The film isolates and protects the metal from rapid reactivity with it's environment. For example, aluminium has a free energy of reaction with oxygen as high as that of a fossil fuel but is stable for a variety of structural applications. The continued integrity of the structure is due entirely to the aluminium oxide that exists on the surface. Lithium metal with its passive surface layer is in no way different from the rest of the metals. However, in aqueous and oxygen environments which are highly reactive, the thin passive film on the surface of Li does not protect the metal. A rapid reaction takes place resulting in a total disintegration of the metal. However, in organic aprotic media lithium metal is protected by its surface film.

The importance of the passive layer on lithium and its role on the performance of the lithium as a negative electrode in electrochemical power sources has been under discussion for a long time. While Peled [3], Peled and Gabano [4] and Dey [5] emphasized the need of a passive film on Li for proper functioning of primary lithium cells, Brummer [6] and Newman [7] believed that a passivated anode could offer only a limited cycle life of secondary cells. According to the latter authors, the lithium anode must be free from a passive layer and it should be kineti-

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cally stable in the electrolyte in order to obtain a deep-discharge and high cycle life lithium secondary battery. There is innumerable published literature on various aspects of the passive layer on lithium. Literature on electrochemical behaviour of lithium with associated passive film are also large in quantity. A survey of the recent literature on electrochemical measurements of Li/electrolyte interface reveals the existence of a controversy in understanding this system. While some authors attribute the experimental results entirely to the passive film, others ignore the presence of the passive film and explain the results based on electron-transfer reaction. There are only a few papers that consider both the electron-transfer reaction and the passive film present on lithium. The purpose of this article is to overview the existing literature on this controversy and to present the results of the authors' investigations of lithium in solid polymer electrolyte medium.

2. Overview of literature

Peled [4] had reviewed the electrochemical considerations at the lithium/electrolyte interface. Until the early 1970s, it was generally believed that lithium was kinetically stable in many organic solvents. Although some passivating film was assumed to cover at least part of the surface, it was generally accepted that the rate determining step (r.d.s) of the deposition–dissolution process of lithium was the electron-transfer between the metallic electrode and lithium ion in the solution.

$$Li^+ + e^- = Li \tag{1}$$

Only after the investigations of Dey [5] in 1970, it was found that lithium is covered by a film of lithium carbonate when it is in contact with propylene carbonate. This work emphasized the importance of the passive film and its influence on the electrochemical process. Studying the kinetics of lithium in thionyl chloride [5], it was concluded that the r.d.s. for the deposition–dissolution process of lithium was the migration of lithium cations through the passivating layer.

2.1. Direct current polarization studies

Sequeira and Hooper [8] in 1983 studied the kinetics of Eq. (1) in $PEO_x LiCF_3SO_3$ polymer electrolyte media. They employed DC techniques involving both micro (linear) polarization and macro (logarithmic) polarization measurements of two electrode cell assemblies consisting of Li and Ni electrodes separated by the polymer electrolyte film. The classical Butler–Volmer equation for a single-step and a single-electron process (Eq. (2)) was applied:

$$i = i_0 \left(e^{-\alpha F\eta / RT} - e^{(1-\alpha)F\eta / RT} \right) \tag{2}$$

where η is electrode overpotential corresponding to current density i, α is energy transfer coefficient and i_0 is

exchange current density. At low overpotentials, Eq. (2) was reduced to Eq. (3).

$$i = i_0 F\eta / RT \tag{3}$$

or

$$i_0 = RT / FR_{ct} \tag{4}$$

where $R_{ct} = (d\eta / di)$ and is known as charge-transfer resistance. The exchange current density of Eq. (1) was evaluated at several temperatures in $PEO_x LiCF_3SO_3$ polymer electrolyte. The micropolarization curves were reported linear up to ± 75 mV and they were free from hysteresis. Based on these results, it was concluded that the Li electrode behaved reversibly at low voltage excitations. However, at larger voltage excursions (up to ± 300 mV) the anodic and cathodic curves were not found to coincide and hence it was suggested that a relaxation effect occurred in the cell which was accompanied by the development of a high concentration overpotential. Although these studies and conclusions are very important contributions, some of their results were left unexplained. For e.g., negative values for the energy transfer coefficient (α in Eq. (2)) were reported based on the exchange current density vs. concentration of lithium salt in the polymer medium. However, an examination of the macropolarization data suggests that α has a positive value. In addition, an important factor not considered in this publication is the passive film on the Li metal. Because of this reason, Fautex [9] attributed the charge-transfer resistance reported in Ref. [8] to the resistance of the passive film. The results of Ref. [9] are briefly discussed in Section 2.2.

Recently, we have reported [10] measurements of the exchange current densities of Eq. (1) by using galvanostatic linear polarization of Li/SPE/Li symmetrical cells. With this type of investigations, one can avoid placing a reference electrode in the thin (100–200 μm) SPE film. Exchange current density and specific conductivity of the SPE were evaluated using symmetrical cells. The polarization data were within ± 10 mV. The interesting aspect of the measurements was that the fluctuations in measured voltages of the symmetrical cells were within ± 0.02 mV. Usually the potentials of passivated metals in aqueous electrolytes (corrosion systems) fluctuate at the tens of mV level during open-circuit as well as galvanostatic polarization measurements. If the lithium surface film in our investigations [10] was controlling the Li/SPE interface, high stability of electrode potentials at ± 0.02 mV could not have been achieved. The exchange current density (0.55 mA cm^{-2}) for Eq. (1) in $PEO_8 LiBF_4$ at 80°C was based on the assumption that the reaction proceeds uniformly throughout the area of the Li electrode, which is free from surface film. However, the surface film was taken into account as blocking a fraction of the Li surface thus resulting in a decreased electrochemically active surface area. Based on the results of this investigation, the actual exchange current density is greater than the measured value.

Cogley and Butler [11] evaluated true exchange current for lithium amalgam in LiCl–dimethyl sulfoxide electrolyte and obtained a value of 3 mA cm^{-2}. Scarr [12] employed an interrupted current method and a pulse method for obtaining current-potential data to evaluate the kinetic parameters of Eq. (1) in propylene carbonate containing several concentrations of LiClO$_4$. By constructing Allen–Hickling plots, the exchange current density and cathodic energy transfer coefficient were evaluated. Typically, for 1 M LiClO$_4$, these two parameters were 0.64 mA cm^{-2} and 0.63 respectively at room temperature. As the Allen–Hickling plots were linear, it was concluded that electron-transfer of Eq. (1) was the rate determining step. However, the plot showed two linear parts which was attributed to the effect of surface film on lithium metal. By comparing the data of interrupted current experiments and pulsed current experiments, the existence of a surface film was demonstrated and that the solid lithium electrode was active enough to compare favourably with other primary battery electrodes. The formation of surface film might reduce apparent activity of the metal. The discharge performance of a battery employing a lithium anode was expected to improve under continuous drain conditions while the film might prove beneficial during idle periods.

Some interesting papers appeared in 1994 on microelectrode studies of Eq. (1). Verbrugge and Koch [13] employed linear sweep and cyclic voltammetry. The experimental data were analyzed in view of the Butler–Volmer equation (Eq. (2)). An exchange current density of about 0.5 mA cm^{-2} and a symmetry factor of 0.5 were reported for 1 M LiClO$_4$ in propylene carbonate. Although the authors pointed out that the linearity of current voltage relation might be due to the ohmic nature of surface film, it appears that the measured exchange current densities were not corrected for the contribution of the film. The exchange current density and symmetry factor for Eq. (1) were measured at several temperatures and the enthalpy of activation was evaluated to be 11.9 kcal mol^{-1}.

Xu and Farrington [14] employed nickel microelectrodes and investigated the kinetics of Eq. (1) in polymer electrolytes by using potential sweep and potential step experiments. Using the linear approximation of Butler–Volmer equation (Eq. (2)), an exchange current density of 2 mA cm^{-2} and a charge-transfer coefficient of 0.5 were reported at 50°C. Tafel plots were shown to be linear up to about 300 mV of overpotentials. From Arrhenius plots of exchange current densities, the energy of activation of Eq. (1) was evaluated to be about 0.72 eV. Although the authors briefly discuss the instability of lithium deposited on nickel microelectrode in various electrolytes due to surface film formation, the influence of surface film on kinetic parameters was not discussed.

Pletcher et al. [15] studied kinetics of nucleation and growth of lithium electrodeposition on a nickel microdisc electrode, as well as the kinetics of Eq. (1) in propylene carbonate based electrolytes. From current-time transients,

it was concluded that a lithium phase was formed on nickel by a mechanism involving progressive nucleation and three-dimensional growth under electron transfer control. From current-potential measurements, the exchange-current density was reported as 3 mA cm^{-2} and energy transfer coefficient as 0.45. It was shown that the current-potential characteristics for lithium deposition and dissolution were fully explained by electron-transfer reaction obeying Butler–Volmer kinetics at the microelectrode. The mass-transport limitation in the electrolyte occurred at higher overpotentials. Eq. (1) was treated simply as a redox couple. They further emphasized that there was no need to invoke surface films to understand the behaviour of Eq. (1). It was stated that the surface film was present on lithium but it did not control the rate determining step. Similar to our results [10], it was reported that the surface films were porous and the electrolyte could move through the sites where Eq. (1) is rapid.

Recently, Christie and Vincent [16] studied kinetics and mechanism for the electrodeposition of lithium using propylene carbonate and poly(methylmethacrylate) gelled electrolytes at a nickel microelectrode. They employed chronoamperometric, cyclic voltammetric and chronopotentiometric methods. Exchange current densities ranging from 0.01 mA cm^{-2} to 2.4 mA cm^{-2} were reported for several electrolytes. From chronoamperometry measurements, it was shown that three-dimensional nucleation and growth models were followed by all the systems. Although passivation behavior of freshly deposited lithium was investigated by a double potential step method, it appears that the influence of the surface film on exchange current was not taken into account in this work.

Rahner et al. [17] characterized the lithium electrode in propylene carbonate-based electrolytes by using DC polarization and AC impedance techniques. The resistance evaluated from DC polarization measurements was attributed to the resistance of the surface passive layer of lithium. However, the AC impedance results were analyzed separating the charge-transfer resistance and surface film resistance.

2.2. AC impedance studies

The studies on lithium in PEO$_x$LiCF$_3$SO$_3$ polymer electrolyte by Fautex [9] were based on an electrochemical impedance spectroscopic technique. Symmetrical cells—Li/SPE/Li were constructed and subjected to impedance studies at several temperatures between ambient temperature and 105°C. At lower temperatures, the Nyquist plot of the impedance data consisted of two semicircles. The high frequency semicircle was attributed to bulk resistance of the SPE film and low frequency semicircle to the interfacial resistance at the Li/SPE interface. Even though the interfacial resistance arises due to the surface film on lithium metal, as well as the electrochemical reaction, the author considered it only due to the surface film on Li.

Arrhenius plots of interfacial resistance were constructed and energy of activation was calculated in several concentrations of a lithium salt. At low concentrations, the activation energy obtained was 0.65 eV and at high concentrations it was 0.78 eV. These values were close to the value reported in the literature for films formed on metallic lithium, thus supporting the view of Fautex [9]. Furthermore, he considered the charge-transfer resistance reported by Sequeria and Hooper [8] as the resistance of the surface film and calculated the values of activation energy. As these values were also similar in magnitude to what he obtained from AC impedance measurements, Fautex [9] argued that the micropolarization data reported in [8] was not for the charge-transfer resistance of Eq. (1) but for the resistance of the surface film on lithium metal.

Similar to the view of Fautex [9], in recent reports, Aurbach et al. [18] and Zaban et al. [19] considered that the lithium/electrolyte interface is essentially governed by the surface film on Li. These authors extensively investigated the interface in several liquid non-aqueous electrolytes and proposed a five-layer model for the surface film. Their studies were based on AC impedance measurements. The Nyquist plot of the Li/non-aqueous electrolyte consisted of a depressed semicircle coupled with a Warburg type straight line. The experimental data were evaluated by modeling a Voigt type equivalent circuit analog in which five R/C elements were taken into account. Each R and C parallel combination was attributed to each layer of the surface passive film. The authors argued that the five-layer model was justified because of the growth of thick surface film when Li metal was continuously in contact with the electrolyte medium. The resistance values of the different layers reported as a function of salt concentration in propylene carbonate, 1,3-dioxolane and tetrahydrofuran are worth examining. At low concentrations, the resistance values of the individual layers are at their highest, and they decrease with an increase in salt concentrations. Besides the explanation given in Ref. [19], the dependence of resistance values on salt concentration can also be explained in a different way if the resistance is attributed to the kinetics of Eq. (1) at the interface. From kinetic principles of simple electrochemical reactions, the exchange current density is related to the concentration of the electrochemically active species as [20]:

$$i_0 = FK^0 C^{(1-\alpha)} \qquad (5)$$

where K^0 is a constant and α is energy transfer coefficient. Eq. (5) can be rewritten as Eq. (6).

$$\ln i_0 = \ln(FK^0) + (1-\alpha)\ln C \qquad (6)$$

On differentiation, we get

$$d\ln i_0 / d\ln C = (1-\alpha) \qquad (7)$$

Thus, a plot of $\ln i_0$ vs. $\ln C$ is linear with a slope of $(1-\alpha)$. The value of α ranges from 0 to 1. As Eq. (1) is generally considered to be reversible, the value of α is
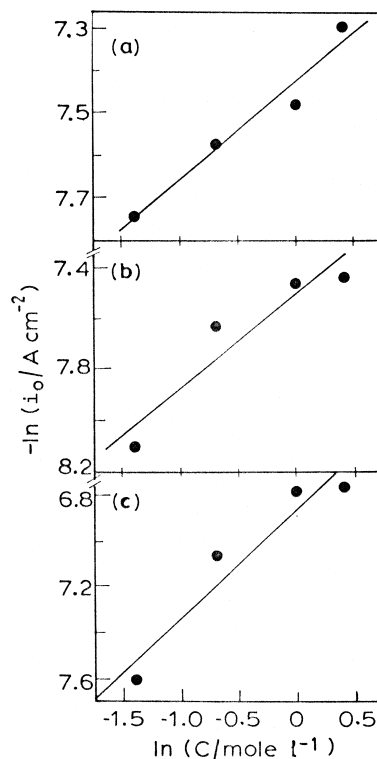

Fig. 1. Exchange current density (i_0) against concentration of LiClO$_4$ in (a) propylene carbonate, (b) dioxolane and (c) tetrahydrofuran. i_0 values are calculated from resistance values given in Fig. 5 of Ref. [19].

expected to be about 0.5. The resistance values of the layers of passive film on Li in PC, DN and THF electrolytes containing LiCF$_3$SO$_3$ salt are obtained from Fig. 5 of Ref. [19]. By assuming the resistance of the film (obtained by summing resistance of individual layers) to be charge-transfer resistance of Eq. (1), the exchange-current densities are calculated for each concentration using Eq. (4). The plots of $\ln i_0$ vs. $\ln C$ (Fig. 1) are found to be reasonably linear. Slopes ($= 1 - \alpha$) of linear fits are obtained (Eq. (7)) as 0.23, 0.36 and 0.48 for PC, DN and THF electrolytes respectively. Thus, the values of energy-transfer coefficient α in the three electrolytes are 0.77, 0.64 and 0.52 respectively. This analysis suggests that the resistances reported in Ref. [19] are probably charge-transfer resistances.

Thevenin and Muller [21] critically examined several models viz., solid–electrolyte interface (SEI) model, polymer–electrolyte interface (PEI) model, solid–polymer layer (SPL) model and compact–stratified layer (CSL) model, to fit experimental electrochemical impedance results of lithium electrodes in organic electrolytes. The electron transfer process (Eq. (1)) was taken into consideration both in the PEI and SPL models, whereas the impedance behaviour was attributed to the surface film in SEI and CSL models. The authors stated that all the information about any of the models could be derived in principle by fitting the calculated impedance spectrum to the measured data.

Based on the assumptions made regarding the values of the permittivity and conductivity, CSL and SPL models were reported to be useful for understanding the main properties of the Li/lithium perchlorate in propylene carbonate interface. It is noteworthy that the SPL model takes into account of the surface film as well as Eq. (1) at the interface.

2.3. Open circuit potential studies

Odziemkowski and Irish [22] developed an in situ cutting technique to expose bare lithium metal in various organic electrolytes. On cutting the Li electrode while in contact with the electrolyte, a potential change due to removal of surface film was observed. The magnitude of the potential change, however, was in the range of 5–25 mV which is considerably lower than a similar situation involving metals such as Ni, Fe or Al in aqueous electrolytes [23]. The interfaces of these metals are essentially governed by their respective surface films where the corrosion potentials of these metals differ from the reversible potentials by hundreds of mV. Thus, even though Li metal is covered with a surface film, the electrochemistry of the Li/non-aqueous electrolyte interface is not controlled by the film to a significant extent.

2.4. Charge–discharge studies

In recent investigations Montesperelli et al. [24] subjected semipractical Li–LiV$_3$O$_8$ cells containing different organic liquid electrolytes to extensive charge–discharge cycles and studied the impedance behaviour of the cells at periodic intervals. These investigations were conducted aiming at an analysis of performance decline and failure of secondary lithium cells. The Nyquist plot of impedance data of a cell was shown to contain three semicircles. The high frequency semi circle was considered to be due to the surface film resistance (R_f) and its capacitance (C_f); the middle frequency semicircle due to charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}); and low frequency semicircle due to diffusional impedance (Z_d). The SEI model of the surface film on Li was discarded, as it is generally represented by a single semicircle. The authors were inclined to believe that the PEI model was a rough approach to real film structure. Therefore, they assumed the formation of a relatively compact polymeric membrane due to solvent decomposition, and inorganic compounds due to salt decomposition were imbedded in the polymeric membrane. From the high frequency semicircle, the resistance (R_f) of the surface film (or polymeric membrane) was obtained using an appropriate equivalent circuit model, and time evolution of R_f was shown to be approximately exponential. This was attributed to a decrease in specific conductivity of the surface film due to compositional changes during cell storage and/or to an increase in its thickness on aging. The thickness of the surface film was found to increase from 30 Å to about 200 Å in 15 days of aging of the cells. From values of R_{ct}, the exchange current densities i_0 were calculated using Eq. (4) and they were found to vary from 0.1 to 0.5 mA/cm^2. On subjecting the cells to charge–discharge cycles, it was found that R_{ct} increased from about 1 Ω cm^2 to about 30 Ω cm^2 in 450 cycles. A lithium electrode cycling efficiency of 73% was obtained after 466 cycles. The decline in performance of the cells over a large number of cycles was attributed to dendritic deposits of lithium.

From the above overview, it is clear that there is considerable ambiguity about the significance of the sur-
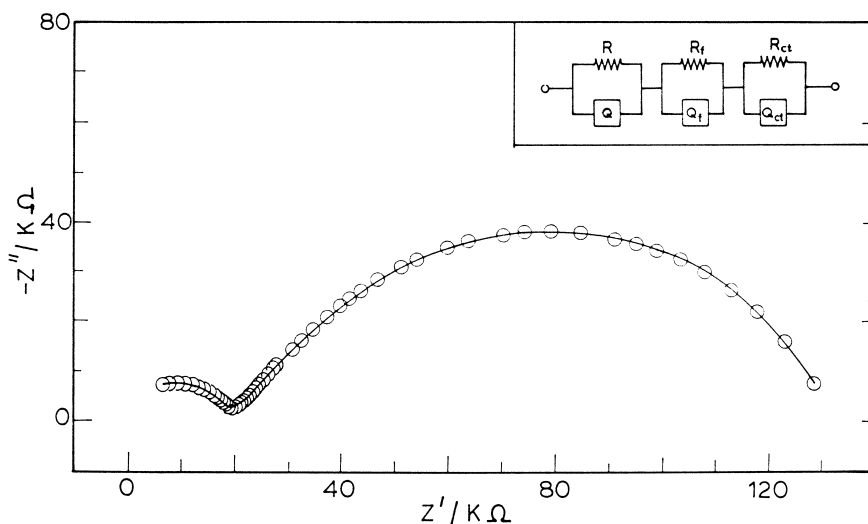

Fig. 2. Nyquist plot of electrochemical impedance spectrum of Li/PEO$_8$LiClO$_4$/Li cell at ambient temperature, with experimental ($-$) and simulated data (o). Equivalent circuit is shown in the inset. R, R_f and R_{ct} are resistance of the SPE film, resistance of surface film and charge transfer resistance respectively; Q, Q_f and Q_{ct} are corresponding constant phase elements. The values of evaluated parameters are as follows: $R = 1.845 \times 10^4$ Ω; $R_f = 3.339 \times 10^4$ Ω, $R_{ct} = 8.128 \times 10^4$ Ω, $Q = 1.087 \times 10^{-9}$ ($n = -0.838$), $Q_f = 4.781 \times 10^{-6}$ ($n = 0.507$), $Q_{ct} = 1.242 \times 10^{-6}$ ($n = 0.845$).

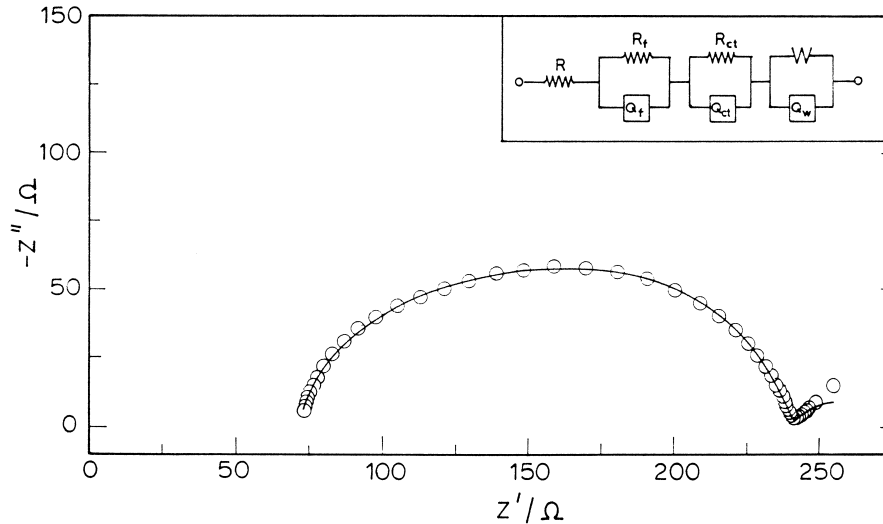Fig. 3. Nyquist plot of electrochemical impedance spectrum of Li/PEO$_8$LiClO$_4$/Li cell at 80°C, with experimental ($-$) and simulated data (o). W in the equivalent circuit refers to warburg impedance and Q_w is the corresponding constant phase element, other symbols are as given in the legend of Fig. 2. The values of evaluated parameters are as follows: $R = 72.4$ Ω, $R_f = 39.457$ Ω, $R_{ct} = 128.04$ Ω, $W = 5.9647 \times 10^{-2}$ Ω^{-1}, $Q_f = 4.740 \times 10^{-7}$ ($n = 1.0$), $Q_{ct} = 3.083 \times 10^{-6}$ ($n = 0.862$), $Q_w = 2.083 \times 10^{-4}$ ($n = 1.0$).

face film on Li both in non-aqueous and solid polymer electrolytes. While some reports credit Eq. (1) with controlling the interface and ignoring the surface film on lithium, other reports conclude that the interface is entirely controlled by the surface film. There are, however, a few reports which take into account the surface film while studying the kinetics of Eq. (1) as a charge-transfer con-

trolled process at the Li/electrolyte interface. We strongly support the third category.

3. Results and discussion

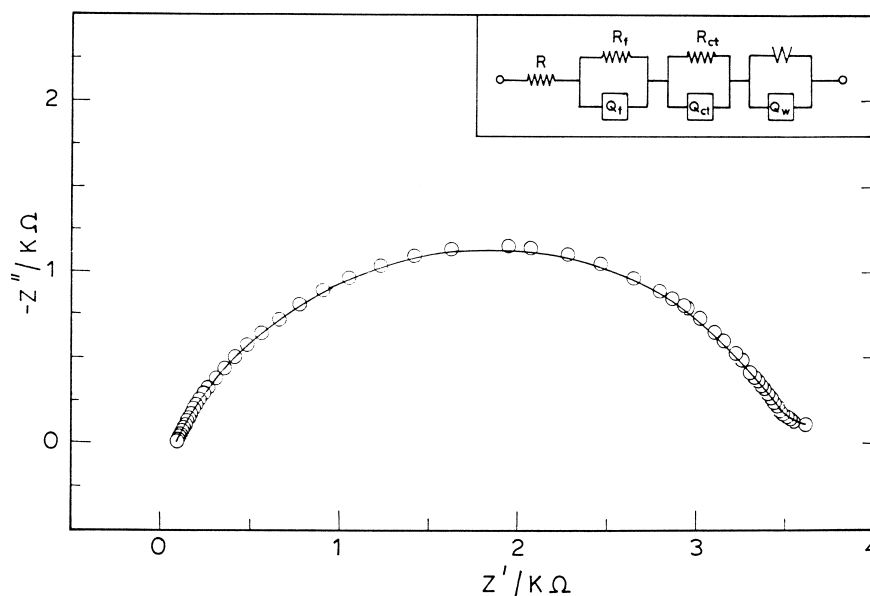In the present investigations, we have assembled several symmetrical Li/SPE/Li cells having varied the SPE com-

Fig. 4. Nyquist plot of electrochemical impedance spectrum of Li/PEO$_8$LiClO$_4$—propylene carbonate/Li cell at ambient temperature, with experimental ($-$) and simulated data (o). Symbols of the equivalent circuit are as given in the legends of Figs. 2 and 3. The values of evaluated parameters are as follows: $R = 89.319$ Ω, $R_f = 231.030$ Ω, $R_{ct} = 3.161 \times 10^3$ Ω, $W = 6.599 \times 10^{-3}$ Ω^{-1}, $Q_f = 8.02 \times 10^{-6}$ ($n = 0.813$), $Q_{ct} = 4.31 \times 10^{-6}$ ($n = 0.785$), $Q_w = 1.282 \times 10^{-3}$ ($n = 0.302$).
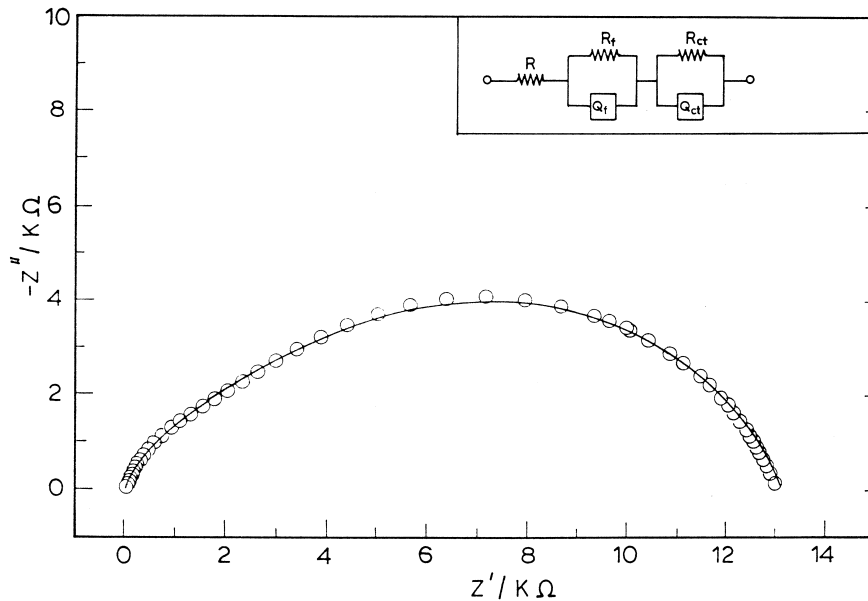
Fig. 5. Nyquist plot of electrochemical impedance spectrum of Li/PAN–PC–EC–LiClO$_4$/Li cell at ambient temperature, with experimental ($-$) and simulated data (o). Symbols of the equivalent circuit are as given in the legends of Figs. 2 and 3. The values of evaluated parameters are as follows: $R = 50.079$ Ω, $R_f = 1.590 \times 10^3$ Ω, $R_{ct} = 1.138 \times 10^4$ Ω, $Q_f = 5.784 \times 10^{-7}$ ($n = 0.864$), $Q_{ct} = 1.774 \times 10^{-6}$ ($n = 0.778$).

positions. Electrochemical impedance measurements have been made, and the cell parameters were evaluated by using Boukamp NLLS fit procedure [25] with a good degree of accuracy. Simple Voigt type of equivalent circuits were considered for fitting the data. Since the experimental impedance spectra contained depressed and overlapped semicircles in Nyquist plots, constant phase elements (Q) were taken in place of the capacitances [26].

The fit procedure of Boukamp involves an initial estimation of approximate values of resistances and constant phase elements. These values are used to evaluate refined values by non-linear least square fit procedure. The experimental data and simulated data obtained from evaluated parameters agreed well and the χ^2 parameter was in the range of 10^{-4} to 10^{-5}. In Figs. 2–6, the experimental and simulated impedance data are shown for five different
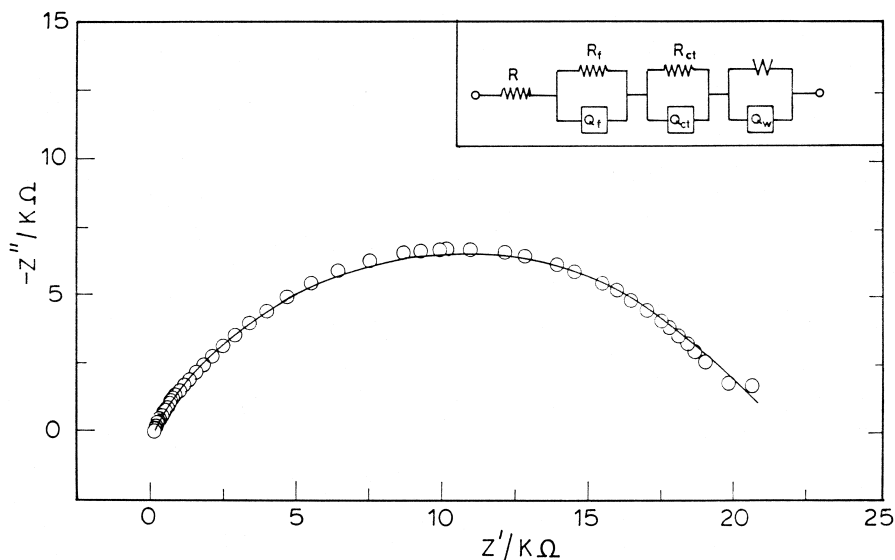

Fig. 6. Nyquist plot of electrochemical impedance spectrum of Li/PEO–PAN–PC–EC–LiClO$_4$/Li cell at ambient temperature, with experimental ($-$) and simulated data (o). Symbols of the equivalent circuit are as given in the legends of Figs. 2 and 3. The values of evaluated parameters are as follows: $R = 141.03$ Ω, $R_f = 1.008 \times 10^3$ Ω, $R_{ct} = 1.845 \times 10^4$ Ω, $W = 7.309 \times 10^{-4}$ Ω^{-1}, $Q_f = 2.283 \times 10^{-6}$ ($n = 0.855$), $Q_{ct} = 2.236 \times 10^{-6}$ ($n = 0.788$), $Q_w = 6.160 \times 10^{-6}$ ($n = 1.0$).

compositions of solid polymer electrolytes. The equivalent circuits employed in estimating of the parameter values are shown in the inset of the respective figure. It may be noted that the equivalent circuits are simple and the simulated impedance spectra from best fit values coincide with experimental impedance spectra fairly well. In analysis of all these experimental results, passive film resistance and charge-transfer resistance are evaluated independent of each other.

4. Conclusions

There is no ambiguity on the existence of surface film on lithium metal when present in a non-aqueous or a solid polymer electrolyte. However, the ambiguity, concerns the role of the surface film in the electrochemical reaction $(Li^+ + e^- = Li)$ that is expected at Li/electrolyte interface. The reviewed literature indicates three categories of reports. The first category of studies attributes the measured interfacial property entirely to the charge-transfer reaction, whereas the second category considers the measured property due entirely to the surface film. A few studies belonging to the third category provide proper recognition to both the surface film as well as the charge-transfer reaction. Substantial evidence in this present overview, shows that the third category view point is more appropriate in the case of Li/electrolyte interface. Apparently, the surface film causes a partial blocking effect for the electrochemical reaction. The surface coverage may be partial or the film itself may be highly porous for Eq. (1) to undergo between Li and Li^+. It appears that the term-passive film on Li is a misnomer, since such a passive-film usually protects the metal underneath from all aggressive conditions, e.g., film on an A1 surface. On lithium, however, the film acts bifunctional in the sense that it protects the metal under normal reactive conditions and also allows the electrochemical reaction to proceed between Li metal and Li^+ ion in the electrolyte. Hence it may be appropriate to term the film as surface film rather than passive film.

Acknowledgements

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