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PASSIVATING FILMS ON LITHIUM ELECTRODES. AN APPROACH BY MEANS OF ELECTRODE IMPEDANCE SPECTROSCOPY

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Summary

A study has been made of the models proposed in the literature to account for the properties of the passivating films formed in lithium primary and secondary batteries. The electrode impedance spectra characteristic of the Solid Electrolyte Interphase and the Polymer Electrolyte Interphase are analysed.

Introduction

The passivation process of lithium in nonaqueous electrolytes, which is generally considered as mainly responsible for the difficulties encountered in cycling this alkali metal, remains not well understood. Considerable efforts have been undertaken in a number of directions on that subject which have resulted in a better determination of the morphological and kinetic properties of the passivated lithium electrodes. Significant results have been obtained in recent years by means of electrode impedance spectroscopy. This method, particularly convenient in separating the elementary processes induced by the presence of a passivating film on the lithium electrode, is a powerful means for their characterization and, consequently, in rationally discussing the models proposed in the literature. The purpose of this paper is to review the present state of the art concerning the study of the lithium passivation process in lithium primary and secondary batteries by means of electrode impedance spectroscopy.

Two models have been proposed to account for the properties of the passivating films which appear as lithium ion conductors and electronic insulators: the Solid Electrolyte Interphase and the Polymer Electrolyte Interphase models. These models both consider that the passivating films act as interphases between the electrode and the electrolyte and are, respectively, constituted either by mineral or organic compounds resulting from the chemical degradation of the electrolyte towards lithium. An analysis of the literature generally shows that the passivating films formed in certain

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organic electrolytes can have a more complex structure due to a mixture of mineral and organic compounds. Hence, the above definitions given for the models are only useful when trying to classify the passivating films.

The Solid Electrolyte Interphase (SEI)

This type of passivating film, clearly observed in the case of the liquid cathode primary batteries [1, 2] leads, at the equilibrium potential, to a characteristic electrode impedance spectrum. Figure 1 shows that the high frequency loop increases and the low frequency loop decreases with storage time. The steady state spectrum consists of a single capacitive semi-circle with a very high polarization resistance compared with the electrolyte resistance. Observation of the passivating film by means of scanning electron microscopy demonstrates that it is well represented by a polycrystalline layer the composition of which has been determined by means of X-ray analysis. This is the case with lithium chloride in thionyl chloride inorganic electrolytes and lithium dithionite in sulfur oxide organic electrolytes [3].

The crystallization of a lithium salt on the lithium electrode leads to consideration of the classical system of a solid electrolyte on a non-blocking electrode (Fig. 2(a)). Assuming that the ionic conduction in the solid electrolyte is governed by the basic equation:

$$i = kc \exp(bV)$$

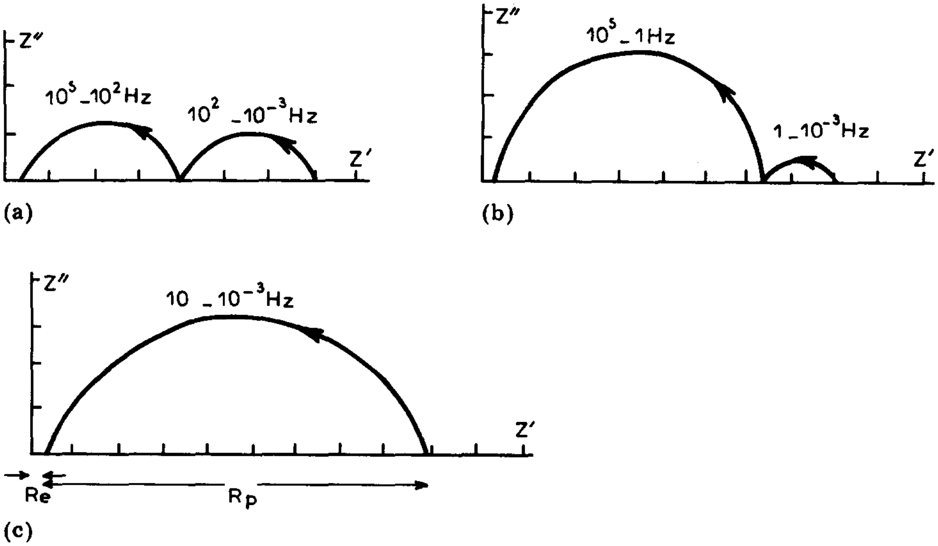

Fig. 1. Evolution at the equilibrium potential of the electrode impedance spectrum as a function of the storage time in liquid cathode primary batteries. Arbitrary units. (a) One day; (b) one week; (c) one month.

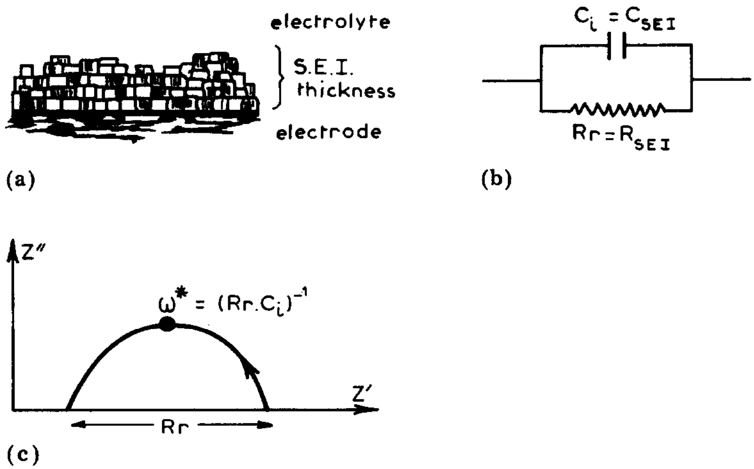

Fig. 2. SEI model. (a) Schematic view; (b) equivalent circuit; (c) electrode impedance spectrum.

where c is the charge carrier concentration and V the applied potential, the equivalent circuit and the characteristic complex plane spectrum are given in Fig. 2. At the equilibrium potential, the reaction resistance R_r is equal to the bulk resistance of the SEI. The radial frequency ω^* at the maximum of the semi-circle is related to the reaction resistance and the interfacial capacitance, C_i, which is equal to the geometric capacitance of the SEI:

$$R_r = R_{SEI} = \frac{d}{\sigma A}$$

$$C_i = C_{SEI} = \frac{\epsilon A}{d}$$

For this situation, when the dielectric constant, ϵ, of the solid electrolyte is known, the SEI model permits the evaluation of the thickness, d, and the conductivity, σ, of the passivating film considered as a cylindrical resistor and a parallel plate capacitor on the surface area, A, of the electrode:

$$d = \epsilon A R_r \omega^*$$

$$\sigma = \epsilon \omega^*$$

The Solid Electrolyte Interphase, which has apparently a simple chemical composition, can have a complex structure due to the formation of compact and/or porous films [1]. The study of the passivated lithium electrode under an anodic polarization demonstrates a dual behavior of the SEI linked to the voltage delay effect [4]. The voltage delay, which is easily detected when considering a galvanostatic transient curve, is associated with a steady state, bell-shaped polarization curve. As shown in Fig. 3(a), an inductive loop appears on the electrode impedance spectrum having a

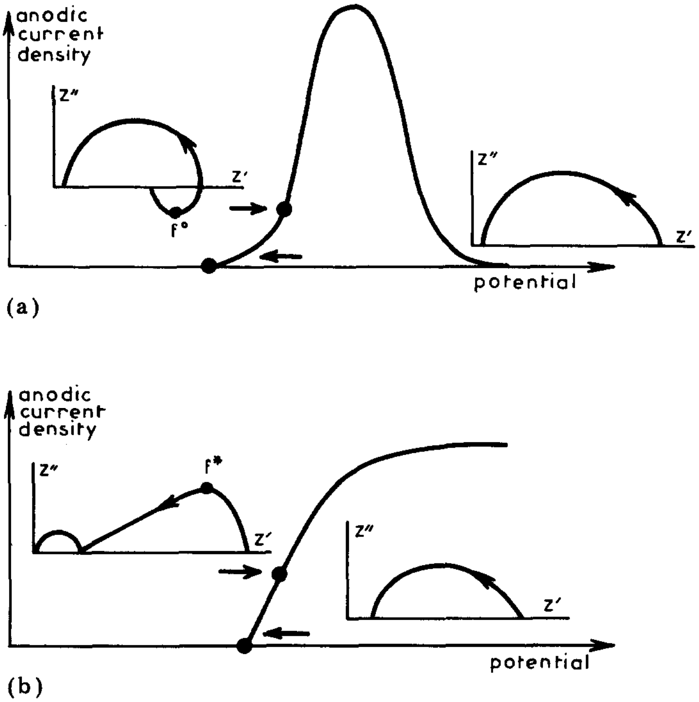

Fig. 3. Evolution of the electrode impedance spectrum as a function of the anodic polarization state in liquid cathode primary batteries. (a) With voltage delay effect; (b) without voltage delay effect.

characteristic frequency, f°, which is an increasing function of the current density. This feature expresses a slow increase of the ionic conductivity of the SEI under the anodic polarization. In the case of electrolytes where the lithium electrode does not exhibit the voltage delay effect, the steady state polarization curve presents a plateau. As shown in Fig. 3(b), a capacitive loop with a Warburg type portion appears on the electrode impedance spectrum and has a characteristic frequency f^* which is a decreasing function of the current density. This feature expresses a slow diffusion of the reacting species through the SEI, which appears to consist of primary compact and secondary porous films.

The Polymer Electrolyte Interphase (PEI)

This type of passivating film, observed in organic electrolyte secondary batteries [5, 6], leads, at the equilibrium potential, to a different electrode impedance spectrum. Figure 4 shows a large increase in the low frequency loop associated with a weak increase in the high frequency loop during the storage time. The steady state spectrum, of which the polarization resistance is of the same order as the electrolyte resistance, consists of two capacitive

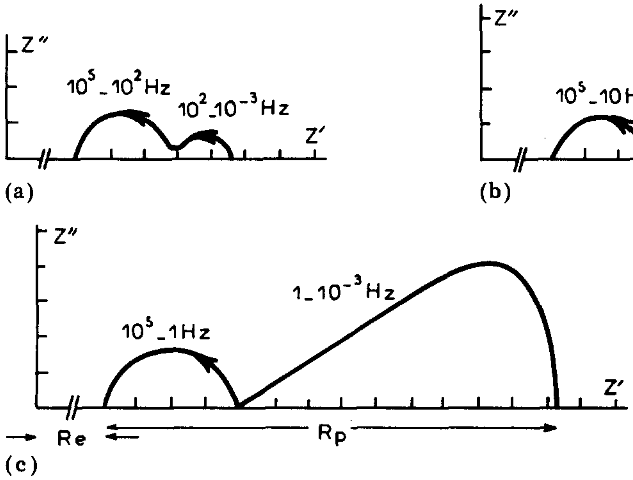

Fig. 4. Evolution at the equilibrium potential of the electrode impedance spectrum as a function of the storage time in organic electrolyte secondary batteries. Arbitrary units. (a) one hour; (b) one day; (c) one week.

loops, with a Warburg type portion in the low frequency range. Observation by means of scanning and transmission electron microscopy demonstrates that the passivating film is suitably represented by an organic membrane, the composition of which has been studied by means of infrared and mass spectroscopy. This type of passivating film consists, essentially, of polyethers in the case of dioxolane, tetrahydrofuran and derivative based electrolytes [7]. The polymeric membrane, formed in the propylene carbonate-based electrolytes [5], is also a matrix for the inclusion of lithium carbonate microcrystallites, which result from a side decomposition reaction of the electrolyte; moreover, the porosity of the membrane is demonstrated by the inclusion of the anhydrous solute microcrystallites when the solvent is eliminated under vacuum.

The formation of a macroreticular membrane swollen by the electrolyte leads to consideration of the classical concepts of the ionic diffusion layer (Fig. 5). The kinetic behavior of the lithium electrode is given by the following basic equations:

$$i = i_0\left\{\frac{c}{c^*}\exp\left(\frac{\alpha F\eta}{RT}\right) - \exp\left(-\frac{(1-\alpha)F\eta}{RT}\right)\right\}$$

$$i/F = 2D(\mathrm{c} - \mathrm{c}^*)/\delta$$

where c and c^* are, respectively, the ion concentrations on the electrode surface and in the bulk electrolyte, and D is the diffusion coefficient of the lithium ion through the thickness, δ, of the passivating film. The equivalent circuit and the complex plane spectrum are given in Fig. 5. On the passivated

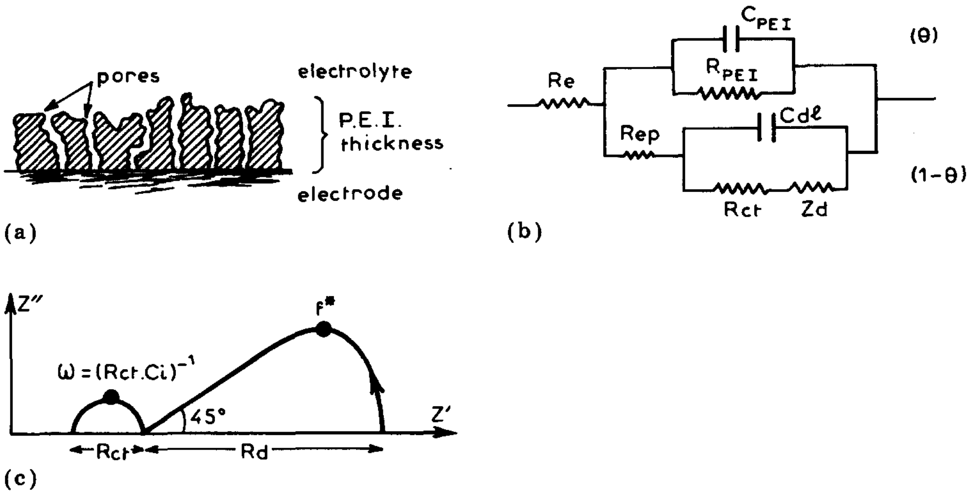

Fig. 5. PEI model. (a) Schematic view; (b) equivalent circuit; (c) electrode impedance spectrum.

area, θ, of the electrode surface, the circuit is represented by the geometric capacitance and the bulk resistance of the PEI. On the active area $(1-\theta)$, the circuit is represented by the electrolyte resistance in the pores of the membrane, the double layer capacitance, the charge transfer resistance, and the diffusion impedance. In the case of a thin passivating film, the diffusion impedance Z_d with its diffusion resistance R_d and characteristic frequency f^* are given by the equations below:

$$Z_\mathrm{d} = R_\mathrm{d}\,\frac{th(j2\pi f\delta^2/D)^{1/2}}{(j2\pi f\delta^2/D)^{1/2}}$$

$$R_\mathrm{d} = \delta RT/2Dc^*F^2 \qquad 2\pi f^* = \omega^* \# 0.4D/\delta^2$$

Assuming that the geometric capacitance of the PEI is negligable compared with the double layer capacitance, the ratio $(1-\theta)$ can be evaluated when considering the interfacial capacitance and a standard value of the double layer capacitance:

$$C_\mathrm{i} = C_\mathrm{dl}(1-\theta) + C_\mathrm{PEI}\theta$$

$$(1-\theta) \# C_\mathrm{i}/C_\mathrm{dl}$$

For this situation, the PEI model permits the evaluation of the thickness of the passivating film d, and the diffusion coefficient, D, of the lithium ion through this porous medium:

$$\delta \# \frac{0.2RT}{\omega^* c^* F^2 R_\mathrm{d}(1-\theta)}$$

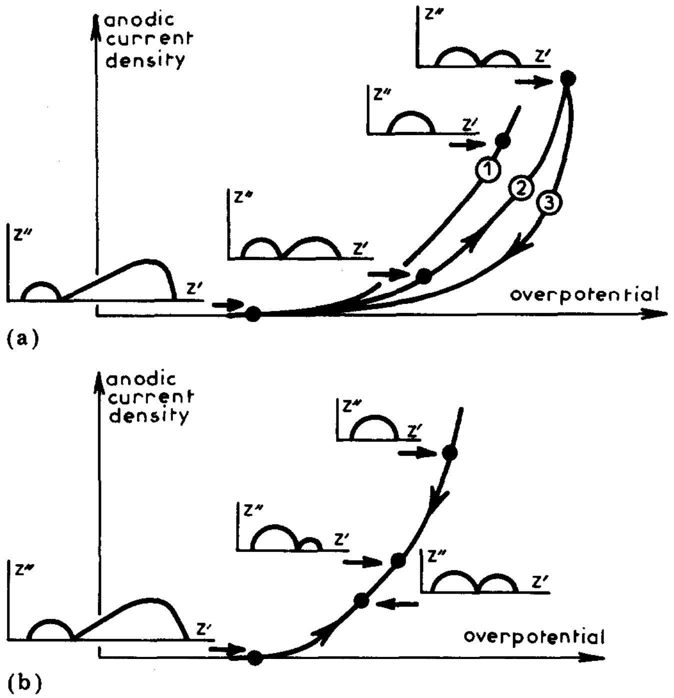

Fig. 6. Evolution of the electrode impedance spectrum as a function of the anodic polarization state in organic electrolyte secondary batteries. (a) With anodic passivation effect; (b) without anodic passivation effect.

$$D \# \frac{0.1R^2T^2}{\omega^* c^{*2} F^4 R_d{}^2 (1-\theta)^2}$$

The Polymer Electrolyte Interphase, which has been described as a macroreticular membrane swollen by the electrolyte, can have a more or less porous structure. Study of the passivated lithium electrode under an anodic polarization demonstrates a dual kinetic behavior of the PEI linked to the anodic passivation effect [8]. This effect is responsible for the hysteresis of the steady state polarization curve, as shown in Fig. 6(a). In fact, the dissolution of the underlying lithium is unable to depassivate the electrode. In that condition, the electrode impedance spectrum remains constituted by two capacitive loops at any anodic polarization point. The return to the equilibrium potential leads to a complex impedance plane spectrum the parameters of which demonstrate the formation of a thicker and more porous passivating film. In the case of organic electrolytes where the anodic polarization is able to depassivate the lithium electrode, the steady state polarization curve is reversible, as shown in Fig. 6(b). The electrode impedance spectrum becomes a single semicircle characteristic of a simple charge transfer process.

In this case, the exchange current density is correctly related to the ion concentration in the electrolyte. However, the low value of the interfacial capacitance suggests that the active area of the electrode surface remains considerably reduced.

Conclusion

Electrode impedance spectroscopy appears to be a powerful method to characterize two types of passivating films formed on the lithium electrode in primary and secondary batteries. The SEI and PEI models, which are based on the simple assumption that the passivating film consists of either mineral or organic compounds, are evidently a very rough approach to its actual composition. Nevertheless, analysis of the electrode impedance data provides the opportunity of developing practical and sensitive tests to characterize the lithium passivation state. Such a characterization seems to justify a more systematic search for new, adequate electrolytes for lithium primary and secondary batteries.

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