Ionic processes in solid-electrolyte passivating films on lithium

Abstract The electrochemical behaviour of a Li electrode in solutions of LiAlCl$_4$ in thionyl chloride, LiBF$_4$ in $\gamma$-butyrolactone and LiClO$_4$ in the mixed solvent propylene carbonate (PC) + dimethoxyethane (DME) in the process of cell storage has been investigated by the methods of electrode impedance spectroscopy and pulse voltammetry. Analogous studies have been carried out in PC + DME solution with the Li electrode coated with a specially formed protecting film of Li$_2$CO$_3$. The results have been compared with those obtained earlier for other lithium electrochemical systems. The general regularities of the Li electrode electrochemical kinetics attributed to the process of Li$^+$ ion transport through a passivating film coating a lithium surface have been discussed.

Key words Lithium electrode · Passivating film · Ionic transport · Impedance spectroscopy · Pulse voltammetry

Introduction

The stability of a lithium electrode exposed to a non-aqueous electrolyte solution is well known to be provided by a solid passivating film (PF) formed spontaneously on its surface and presenting a thin continuous layer of insoluble products of metal interaction with the solution components [1–7]. Such a PF is an ionic conductor or solid electrolyte and determines to a great extent the lithium electrode electrochemical behaviour in the electrolyte concentrated solutions, since the kinetics of anodic and cathodic processes are limited by the ion transport in the film [2–7]. A PF is generally recognized to have a complex structure consisting of a dense part in the vicinity of the metal and a porous part exposed to the solution; it is the porousless layer that provides the electrode stability and exerts the greatest resistance to electric current passing.

For describing the structure and electric properties of such a PF, a number of models have been proposed, among which the pioneering ones were the solid electrolyte interphase (SEI) by Peled [2–4] and the polymer electrolyte interphase (PEI) by Thevenin and Garreau [8–10]. The model in most common use is SEI, according to which the passivating films on lithium are considered as a solid electrolyte layer with unipolar cationic conductivity forming immediately after the metal's contact with the environment [2–7]. The initial PF thickness consists of a few nanometres and is capable of enlarging during storage. The limiting stage of the electrochemical reaction is supposed to be the cations’ migration through the SEI, and the contributions of metal|film and film|solution interfaces are negligible [3, 4]. The presence of different organic and inorganic compounds in a PF provides its complicated structure that may be conceived as a compositional or multi-layered construction. Proposed later, therefore, were the models of a non-uniform PF combining the SEI and PEI models [11]. Recently, Peled et al. suggested the advanced SEI model, taking into consideration the SEI conductivity via intergrain boundaries [12].

We have also developed a model of ionic processes in solid-electrolyte passivating films on lithium and in similar systems, which is based essentially on the SEI model, but, however, in contrast to the latter, takes into account both the existence of a space-charge region in the solid-electrolyte film at the metal interface and finite duration of ionic carrier transport through the PF [13–18]. The space-charge region occurrence in the solid-electrolyte film at the metal interface is allowed for owing to the appropriate capacitance involvement in the electrode equivalent circuit [17, 18]. A small finite duration of ion transport across a PF comparable to
Maxwell dielectric relaxation time leads, at high overpotentials, to the disturbance of electroneutrality in the bulk of the film and to the appearance of space-charge limited currents (SCLCs) [13–16].

A good quantitative agreement of the model theoretical equations with experiment was demonstrated earlier, exemplified by several systems with nonaqueous electrolytes and electrodes made from pure lithium [13, 16, 17], Li-Sn-Cd alloys [15, 18], as well as by a Li electrode incorporated into Li/I2 current sources [14].

It was of interest to elucidate whether the regularities found are common for lithium electrochemical systems. For this purpose, in the present work the electrochemical behaviour of a lithium electrode in electrolytes based on thionyl chloride (TC), γ-butyrolactone (BL) and propylene carbonate (PC) + diethoxyethane (DME) in the course of the electrode storage in electrolyte solution has been explored by electrochemical impedance spectroscopy and pulse galvanostatic methods. The analogous investigations have been carried out using the Li electrode coated with a previously formed protecting film of Li2CO3 in the electrolyte based on PC + DME. The validity of the model we proposed earlier for describing the results of these studies has been assessed.

**Experimental**

The electrochemical measurements were conducted in hermetically sealed glass three-electrode cells containing a few millilitres of electrolyte. The electrodes were made of metallic lithium (99.9%, Mayak, Russia) with four impurities specified as Na, 40 ppm; K, less than 30 ppm; Ca, 75 ppm; Mg, 20 ppm; Al, 30 ppm; N, 30 ppm; Mn, less than 10 ppm. The working electrode was a faced disk electrode obtained by pressing lithium in a glass holder. The electrode surface was formed by cutting off surplus metal before its exposure to the electrolyte solution. The counter electrode was shaped like a cylinder with 12 cm² area of internal surface and was manufactured by pressing lithium foil onto a nickel support. The reference electrode was made from lithium wire. All the operations concerned with electrode fabrication, filling with electrolyte solution, assembling and sealing the cells were performed in a glove box.

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In all cases the values of polarization measured during forward and backward scanning of the polarization curve were found to coincide. Thus, the charge applied to the electrode in the course of the pulse measurements was sufficiently small and the PF remained undamaged.

**Results and discussion**

**Impedance spectroscopy**

Figure 1 shows, in the complex plane, typical impedance Z spectra for the systems under question, registered as a result of their storage under open-circuit conditions. All the spectra are qualitatively similar to each other, as well as to the Li electrode impedance spectra in different organic and inorganic electrolyte systems, the data on which are presented in fairly ample literature dealing with this subject (see, e.g., [8–12, 19–25]). Such spectra are commonly regular or somewhat distorted semicircles with the centre below the real axis. During the process of electrode storage in the electrolyte, spectral characteristic changes are observed, in particular, the semicircle radius enlargement and the frequency diminution in the spectral maximum $\omega_{\text{max}}$ ($\omega = 2\pi f$ is angular frequency, $f$ is frequency in Hz). The high-frequency intercept value on the real axis determined by spectrum extrapolation is assigned to the resistance $R_{\text{el}}$ of the electrolyte solution layer, that is supported by its proportional dependence upon the specific solution conductivity. In the low-frequency region, deviations from an arc are not uncommon. It should be noted that the authors who