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Applied Surface Science 92 (1996) 447–451

applied surface science

An electrochemical impedance spectroscopy study of thin polymeric films

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Received 12 December 1994; accepted for publication 1 June 1995

Abstract

The limiting parameter for the application of various thin film organic conductors is their conductivity value. Because of strong interfacial effects, which cause nonohmic voltage drops, impedance spectroscopy is one of the best methods of measuring their conductivity. This technique was used with both blocking and in a three electrode cell for in situ measurements of synthetic metals. Results allow calculation of the conductivity and also permit a study of the properties of the phase boundary between the electrode and the electrolyte.

1. Introduction

Thin films of organic conductors have already been applied to a few electrochemical devices such as fuel cells, lithium batteries and electrochromic windows. In the last two cases both electronically conductive materials (synthetic metals, SMs) and ionically conductive materials (polymeric electrolytes, SPEs) or liquid electrolytes are used. The limiting value of ionic conductivity of the thin film used for these applications is equal to 10^{-4} S/cm. The observed values of long-time current densities of lithium batteries are about one order of magnitude lower than the values predicted on the basis of the ohmic drop in the electrolyte layer. This phenomenon can be explained by the formation of a passivation layer at the interface between the polymeric electrolyte and the lithium anode. Similar problems are observed with interfaces between thin films of electronically conductive materials (polyaniline polypyrrole, etc.) and electrolytes. These materials are often used as cathodes for lithium batteries and counterelectrodes in electrochromic windows.

2. Experimental

Thin films of solid polymeric electrolytes were obtained by the solvent-casting technique from an acetonitrile solution. The solvint was then removed in vacuum and finally the film was annealed for about 20 days to allow time for recrystallization. The resulting films were sandwitched between two stainless steel electrodes to measure their impedance. For some films (those used in lithium batteries) measurements were also carried in symmetric Li/polymer/Li and cathode foil/polymer/cathode foil cells. The cathode foil was prepared by hot pressing a mixture

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SSDI 0169-4332(95)00274-X