ANION BEHAVIOUR IN A POLYACETYLENE CATHODE FOR A SECONDARY LITHIUM BATTERY

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Summary

The impedance of polyacetylene has been measured in electrolyte solutions of $LiClO_4$, $LiPF_6$ or $LiBF_4$ in propylene carbonate (PC). In the high frequency range, an impedance corresponding to a charge-transfer reaction has been observed in each electrolyte. The charge-transfer resistance has been estimated from the impedance measurement and has the lowest value in PC–$LiClO_4$.

Introduction

Polyacetylene is the simplest linear conjugated polymer that can be oxidized and reduced with electron acceptors and donors, and these reactions are accompanied by a rapid increase in conductivity, *i.e.*, by as much as 12 orders of magnitude at room temperature. It has also been demonstrated that these "doping" procedures can be achieved electrochemically [1]. In such procedures, the level of doping, which determines the conductivity of polyacetylene, can be controlled reversibly by the applied potential via both the incorporation or elimination of counter anions or cations and by the electron transfer between polyacetylene and the external circuit. This means that polyacetylene can be used as either a cathode [2, 3] or an anode [4] in rechargeable batteries. The merit of using polyacetylene as the cathode-active material in non-aqueous lithium secondary batteries has been studied by Kaneto. Although polyacetylene may possess some advantages as a battery active material, it has not yet reached practicality. Polyacetylene readily reacts with water and oxygen resulting in the loss of its unique performance [5, 6]. Furthermore, its coulombic efficiency, $Q(out)/Q(in)$, decreases during storage [3]. These considerations notwithstanding, it remains an object of continued investigation.

In this study, the reaction mechanism of polyacetylene when acting as a rechargeable cathode in secondary lithium batteries has been investigated by a.c. impedance measurements at several potentials in three different electrolytes. It is found that the charge-transfer reaction resistance of the dopant anions at the interface between electrolyte and fibril surface can be

determined by this means and that information can be obtained on the effect of the dopant anion species (*e.g.*, ClO_4^-, BF_4^-, PF_6^-) on the charge/discharge performance.

Experimental

Electrolytes were prepared by drying $LiClO_4$ (Wako Pure Chemical), $LiBF_4$ or $LiPF_6$ (Morita Chemical) at the appropriate temperature for more than 24 h and then individually dissolving these compounds in distilled propylene carbonate (PC). The preparation was undertaken in an argon-filled dry box just prior to experiment. Electrolytes of 1.0 M, 0.5 M and 0.1 M $LiClO_4$ in PC, 1.0 M $LiBF_4$ in PC, and 1.0 M $LiPF_6$ in PC were employed in this study. The counter and reference electrodes were both constructed from lithium metal with a Ni wire electrical lead. The working electrodes comprised polyacetylene films on platinum foil substrates with an area of 0.785 cm². Since the potentials of the lithium reference electrodes vary with the concentration and the kinds of electrolyte salts used, the potentials were measured against the redox potential of the ferrocene/ferrocinium couple using cyclic voltammetry (Table 1).

TABLE 1

Electrode potential of Li/Li^+ in various electrolytes with respect to Fc/Fc^+

Electrolyte	Li/Li^+ (*vs.* Fc/Fc^+)
1.0 M $LiClO_4$/PC	-3.274; -3.265*
0.5 M $LiClO_4$/PC	-3.285
0.1 M $LiClO_4$/PC	-3.360
1.0 M $LiBF_4$/PC	-3.278
1.0 M $LiPF_6$/PC	-3.248

*M. L'Her and J. Courtot-Coupez, *Bull. Soc. Chim. Fr.*, (1972) 3645.

The polyacetylene samples were prepared by compaction of trans-form polyacetylene powder. The samples had a dark brown appearance, a thickness of 0.3 mm, and a density of 0.3 g cm^{-3}. In order to investigate the potential dependence of the polyacetylene electrode reaction in various kinds of electrolytes, a.c. impedance measurements were applied to the polyacetylene sample in the following way: at first, polyacetylene was charged at a constant voltage; the charging potential was determined by cyclic voltammetry. Figure 1 shows a cyclic voltammogram for 1.0 M $LiClO_4$ in PC between 2.5 V and 4.2 V (*versus* Li/Li^+) at 0.8 mV s^{-1}. Similar cyclic voltammograms were obtained in the other electrolytes such as 1.0 M $LiBF_4$/PC and 1.0 M $LiPF_6$/PC. As the anodic current began to increase at 3.8 V, it was decided to charge the electrodes at 3.8 V for more than 24 h in order to accomplish homogeneous charging. Polyacetylene
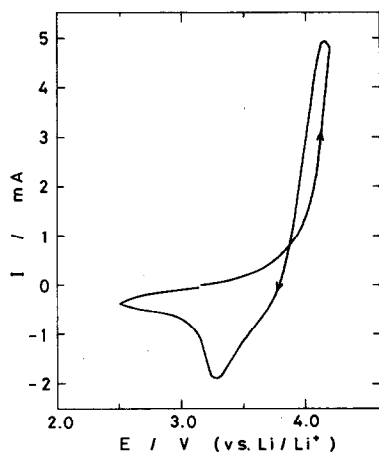
Fig. 1. Cyclic voltammogram of polyacetylene in 1.0 M LiClO$_4$/PC.

was discharged soon after charging by changing the potential in steps of 50 or 100 mV in the negative direction. Constant-voltage discharge was continued until the polyacetylene reached equilibrium, defined as the time when the current had decreased below 1 μA per 1 mg of polyacetylene at each applied potential. After the attainment of equilibrium at each of the several potentials, a.c. impedance measurements were performed in the frequency range 2×10^{-2} Hz to 2×10^3 Hz. A white noise signal of +5 mV amplitude (random noise generator WG-721A (NF)) was applied to the cell and the response signal from a Hokuto Denko HA-301 potentio-galvanostat was analyzed by an Iwasaki Tsushinki SM-2100A F.F.T. signal analyzer using the averaging technique.

Results and discussion

Figure 2 is a complex plane plot (Cole–Cole plot) of the impedances measured at 3.50 V, 3.40 V and 3.25 V over the frequency range of *ca.*
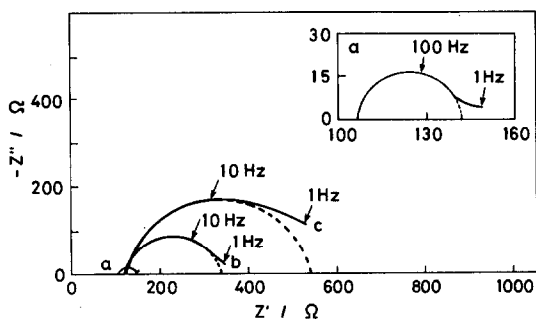

Fig. 2. Cole–Cole plots of polyacetylene obtained at different electrode potentials in 0.5 M LiClO$_4$/PC. (a) 3.50 V; (b) 3.40 V; (c) 3.25 V (*vs.* Li/Li$^+$).
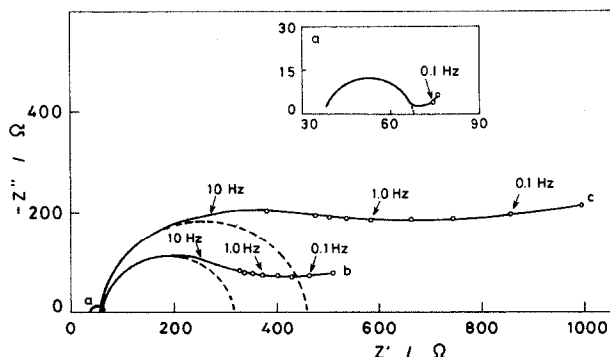
Fig. 3. Cole–Cole plots of polyacetylene obtained at different electrode potentials in 1.0 M LiClO$_4$/PC. (a) 3.50 V; (b) 3.40 V; (c) 3.20 V (*vs.* Li/Li$^+$).

1 Hz - 2 kHz in 0.5 M LiClO$_4$/PC. The impedance loci measured at each potential can be approximated by the dashed line semi-circles shown in the Figure, so that the electrode reaction of polyacetylene seems to be described by a simple Randles-type equivalent circuit model. Figure 3 shows Cole–Cole plots of impedances measured at 3.40 V, 3.30 V and 3.15 V (*versus* Li/Li$^+$) over the frequency range 2 × 10^{-2} Hz - 2 × 10^3 Hz in 1.0 M LiClO$_4$/ PC. As in Fig. 2, the impedance loci in the high-frequency region can be approximated by semi-circles. However, at low frequencies, the impedance loci deviate markedly both from semi-circles and from the straight lines of unit slope expected for diffusion processes. Consequently, the electrode reaction of polyacetylene cannot be described by a simple Randles-type equivalent circuit model in the low-frequency region.

    In general, the impedance of an electrode reaction consists of a charge-transfer reaction in the high-frequency region and a diffusion-limited reaction in the low-frequency region. In this study, it is assumed that the resistance estimated from the diameter of the high-frequency semi-circle corresponds to the charge-transfer reaction resistance at the interface between the polyacetylene fibril and the electrolyte. The anion doping and undoping reactions of polyacetylene shown in eqn. (1) are regarded as the reversible redox reaction between dopant anion A$^-$ and dopant A shown in eqn. (2) [15].

$$(CH)_x + A^- \underset{\text{undoping}}{\overset{\text{doping}}{\rightleftharpoons}} [(CH)_x A] + e^- \qquad (1)$$

$$R \rightleftharpoons O + e^- \qquad (2)$$

This is consistent with the fact that electrochemical doping proceeds via the neutralization of the charge that appears on the conjugated chain by incorporating the counter ion. Therefore, the charge-transfer reaction resistance (θ) of the polyacetylene electrode system is written in the form of eqn. (3), as well as the usual redox reaction system.

$$\theta = \frac{RT}{n^2 F^2 A K^0 C(O)^{*(1-a)} C(R)^{*a}} \tag{3}$$

In eqn. (3), $C(O)^*$ is the dopant concentration in the polyacetylene fibril and $C(R)^*$ is the dopant anion concentration in the bulk electrolyte. The parameter $C(O)^*$ represents the dopant level, and therefore determines the potential of the polyacetylene. Equation (3) shows that the charge-transfer reaction resistance is a function of both the potential of the polyacetylene and the concentration of the bulk electrolyte. The dependence of the resistance (estimated from the Cole–Cole plot) on both the electrode potential and the electrolyte concentration was examined.

Figure 4 shows the resistances measured in PC with 1.0 M, 0.5 M, and 0.1 M $LiClO_4$ at different electrode potentials. The electrode potential in Fig. 5 is referred to the lithium reference electrode in 1.0 M $LiClO_4$ in PC according to the data given in Table 1. The dependence of the charge-transfer resistance on the electrode potential (Fig. 4) was in general agreement with eqn. (3); the resistances estimated from the diameters of the semi-circles increased with decreasing concentration of each electrolyte, even at the same potential. This suggests that the above assumption is reasonable, $i.e.$, the resistances estimated from the diameters of the semi-circles provide a measure of the charge-transfer reaction resistances.

The effect of the dopant anion species on the charge and discharge reactions was also investigated by measuring the charge-transfer reaction resistance. The results of the a.c. impedance measured in PC with 1.0 M $LiClO_4$, 1.0 M $LiBF_4$, and 1.0 M $LiPF_6$ were very similar, so that the reaction mechanism of polyacetylene is the same in three electrolytes. Figure 5 shows the dependence of the charge-transfer reaction resistances on the electrode potential measured in PC with 1.0 M $LiClO_4$, 1.0 M $LiBF_4$, and 1.0 M $LiPF_6$. The results show that ClO_4^- gives the lowest transfer resistance
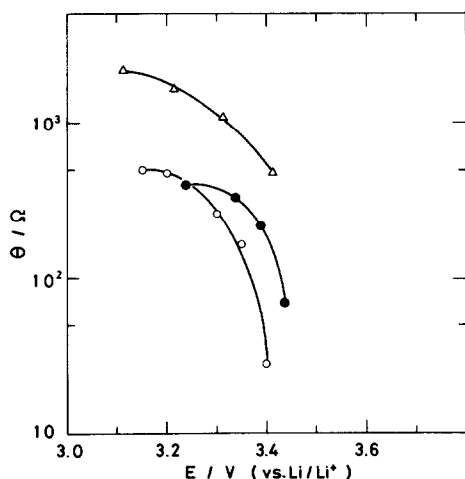

Fig. 4. Dependence of reaction resistance of polyacetylene on electrode potential. ○, 1.0 M $LiClO_4$/PC; ●, 0.5 M $LiClO_4$/PC; △, 0.1 M $LiClO_4$/PC.
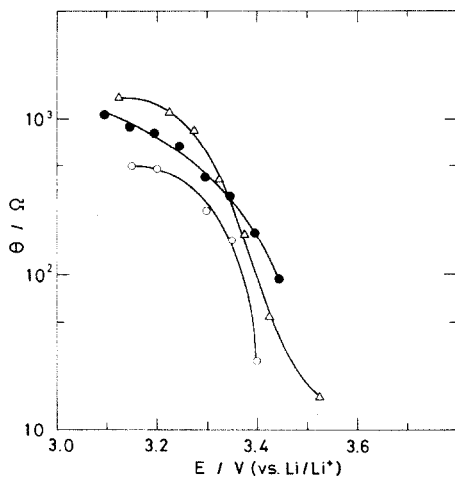
Fig. 5. Dependence of reaction resistance of polyacetylene on electrode potential. ○, 1.0 M LiClO$_4$/PC; ●, 1.0 M LiBF$_4$/PC; △, 1.0 M LiPF$_6$/PC.

and is therefore the best dopant anion among the three studied. Figure 5 also shows that the mechanism of the charge-transfer reaction is the same in the three electrolytes because of the same dependence of the charge-transfer reaction resistance on the electrode potential.

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