

IMPEDANCE CHARACTERISTICS OF POLYFURAN FILMS*

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Abstract Electrochemical impedance spectroscopy (EIS) was first used for the characterization of polyfuran (PFu) films that had been formed electrochemically on an Au electrode. The polyfuran was measured in high oxidation state, intermediate oxidation state and reduction state, respectively. As the oxidation level is increased, the ionic conductivity of PFu/BF₄⁻ increases. And impedance studies on PFu show that the anion BF₄⁻ appears to be mobile with a high diffusion coefficient of approximately 10⁻⁸ cm² • s⁻¹.

Keywords Polyfuran, Electrochemical impedance spectroscopy, Capacitance

INTRODUCTION

It is well known that electrochemically synthesized conjugated polymers can be switched between the doped (conducting) and undoped (insulating) states. The process involves electron and ion transport within the film. The charge transport processes, inside the conjugated polymer bulk and across the conjugated polymer's interfaces, are important in many applications^[1].

Electrochemical impedance spectroscopy (EIS) has proved to be a quite useful tool for studying the charge transport inside the polymer and the charge transfer at the metal/polymer and polymer/solution interfaces^[2–5]. It is easy to obtain information about the interface resistance and capacity. Compared with conventional electrochemical techniques, it has one advantage. Cyclic voltammetry and other techniques involve large potential perturbations that might induce a non-homogeneous state of electroactive polymers. However the system is only infinitesimally perturbed with respect to the steady state under investigation of EIS^[6]. In principle, information could be obtained from EIS about the mobility and concentrations of different charge carriers in the oxidized form of the conducting polymer film^[7].

Many conducting polymers have been studied by EIS: polypyrrole^[8], polythiophene^[9, 10], polyaniline^[11, 12] and polyacetylene^[13, 14]. However polyfuran (PFu), because of the great difficulty encountered in its synthesis, is rarely characterized. Recently, we have successfully prepared polyfuran in a binary solvent system containing boron trifluoride-ethyl ether (BFEE) and additional ethyl ether (EE)^[15]. In this paper, the impedance characterization of polyfuran was performed.

EXPERIMENTAL

Materials

Furan (Fluka, 99%) was distilled twice under a nitrogen atmosphere before use. Acetonitrile was distilled over CaH₂ under a nitrogen atmosphere. BFEE was freshly distilled before use. Ethyl ether was dried and distilled in the presence of sodium. Tetrabutylammonium tetrafluoroborate (TBABF₄) was dried under vacuum.

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Electropolymerization and EIS Measurements

Electrochemical polymerization and measurements were performed in a one-compartment, three-electrode electrochemical cell. The working electrode was a gold disc of 3 mm in diameter embedded in polytetrafluoroethylene. The reference electrode was an Ag/AgCl (0.1 mol/L KCl) electrode and the counter electrode was a stainless steel electrode. All dc potentials (E_{dc}) are referred to this reference electrode. The cell solution was initially purged with argon, and all experiments were performed under an argon atmosphere. All electrochemical polymerizations were performed using an EG&G M273 potentiostat and the impedance spectroscopy equipment was an EG&G M5210 frequency response analyzer.

Prior to polymerization, the Au working electrode was polished with 0.3 μm alumina, rinsed with water and cleaned ultrasonically. Polyfuran was deposited on the Au electrode by galvanostatic electrochemical polymerization from a binary solvent system containing 0.1 mol/L furan. All the polymer film samples were synthesized at a current density of 1 mA/cm^2 to form films having a thickness of *ca.* 1.6 μm .

The Au/PFu electrodes in monomer-free acetonitrile (0.04 mol/L TBABF₄) were studied by EIS at different E_{dc} . The Au/PFu electrodes were equilibrated for 10 min at each E_{dc} before EIS was performed. The frequency range was 10 kHz to 10 mHz, wide enough to cover the processes of interest, and the perturbation voltage amplitude was equal to 10 mV.

RESULTS AND DISCUSSION

Idealized EIS

The idealized impedance response of conducting polymer is that illustrated in Fig. 1, showing the different frequency-limited regions of the ac impedance response^[7, 16, 17]. At the highest frequency the impedance is measured from the tip of the reference electrode to the metal surface. Therefore the ohmic resistance of the polymer film and the impedance of the electrolyte between working and reference electrode should be considered. However, in the conducting state, the polymer film resistance is negligible compared to the electrolyte resistance. So the region identifies the bulk properties of the electrolyte and the intercept with the real axis (Z') provides the value of the electrolyte resistance, R_s . In the medium-frequency region, a charge transfer semicircle is expected (charge transfer resistance R_f in parallel with double-layer capacitance C_{dl}). The vertex of the semicircle gives the characteristic relaxation frequency (ω_{max}). After the charge transfer semicircle there is a 45° Warburg-type line controlled by the diffusion of the counterions into the polymer electrode. In the diffusion control region the ionic resistance R_L of the polymer film could be obtained by extrapolation. At the limit of low frequencies, the polymer-coated electrode behaves like a simple capacitor and the complex plane impedance response becomes almost vertical. The associated capacitance C_L , called "redox capacitance" or "limiting capacitance", is determined by the limiting resistance R_L and the anion diffusion coefficient D .

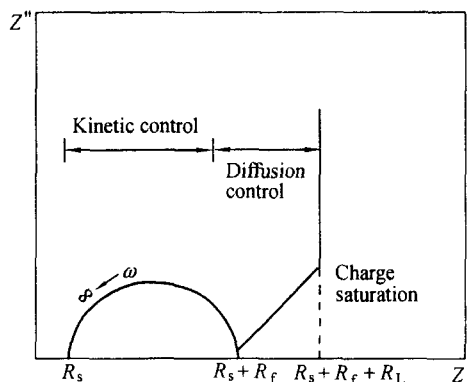


Fig. 1 The idealized impedance response of conducting polymer

General Characteristic of Impedance Response of Polyfuran

In our work, measurements were taken of the system metal electrode/polyfuran/electrolyte solution. The degree of oxidation of the polymer was varied by changing the dc potential between the metal electrode and the electrolyte solution. The transport of electrons across the metal/polymer interface and of ions across the polymer/electrolyte and the charge percolation inside the polymer bulk should be considered. Figure 2 shows a typical impedance plane plot of the results for an oxidized ($E_{dc} = 0.65$ V) polyfuran film. It is easy to distinguish the kinetic control region, the diffusion control region and the charge saturation region. Though the semicircle in the medium-frequency region is depressed due to non-uniformity of the field at a rough electrode surface, the intercept may still be evaluated by a numerical fitting program. In the low-frequency region, a nearly vertical line appears and the resistance R can be obtained by extrapolation of the line to $Z' = 0$. Because the real impedance response is not completely consistent with the idealized response, R_L could not reflect the real ionic resistance of the film. The more reasonable ionic resistance R_{ion} should equal to $3(R - R_s)^{[1]}$. The relevant impedance data for the PFu/BF₄⁻ electrode were determined by a fitting program and are reported in Table 1.

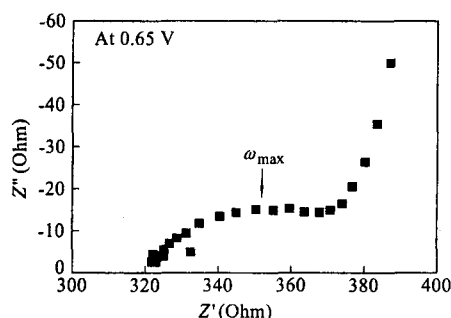


Fig. 2 Impedance response of PFu-coated electrode at 0.65 V in TBABF₄ MeCN solution.

Table 1. Impedance data for polyfuran in high and intermediate oxidation state

Potential (V)	R_s (Ω)	ω_{max} (Hz)	R_f (Ω)	C_{dl} (μF) ^a	R (Ω)	R_{ion} (Ω) ^b	σ_{ion} ($S \cdot cm^{-1}$) ^c
0.65	320	158.5	80.5	78.0	386	198	1.2×10^{-5}
0.40	435	215.2	262	15.1	626	573	4.1×10^{-6}

^a $C_{dl} = 1/(\omega_{max}R_f)$; ^b $R_{ion} = 3(R - R_s)^{[1]}$; ^c $\sigma_{ion} = d/(R_{ion}A)$ (d : the thickness of the film; A : the area of the film)

The charge transfer resistance of the PFu/BF₄⁻ electrode in the MeCN-TBABF₄ solution was found to be $R_f = 80.5 \Omega$. The double-layer capacitance was calculated to be $1098 \mu F/cm^2$ according to Ref. [16]. This value is much higher than the typical values of electrode/electrolyte double-layer capacitance reported by Bockris and Reddy^[18]. The result is related to the highly disordered surfaces of polymer films produced by electropolymerization and agrees with that of the polypyrrole reported by Scrosati *et al.*^[16].

The impedance responses of the highly oxidized forms of PFu can be interpreted using a simple transmission line model. When E_{dc} is reduced to 0.4 V, the polymer is in the intermediate oxidation state. The impedance plot, as shown in Fig. 3, is more complex than that in highly oxidized form. But some data could be obtained by a numerical fitting program, as also shown in Table 1.

Comparing the data in Table 1, there appear some differences. The lightly oxidized form of the polymer (at 0.4 V) has a lower ionic conductivity than the highly oxidized form (at 0.65 V). Because the oxidation of polymer is progressive, when the electrode potential moves towards more positive potential, an increase of the counterion concentration in the solution which is trapped in the polymer appears concomitantly. At the same time, the double-layer capacitance C_{dl} decreases with the decrease of electrode potential. As mentioned above, C_{dl} is related to the real electrode/electrolyte contact area. The decrease of C_{dl} means the reduction of real contact area. When the polymer is in fully oxidized state, the polymer chains are positively charged and repulse each

other, so the free volume of the polymer increases. The polymer film is in an open porous state and the real surface area increases in favor of the intercalation of the doping anion. When the polymer is in the neutral state, the doping anion concentration in the bulk polymer is negligible and the polymer chains have no charges. The conformational relaxation will lead to the compact arrangement of the PFu chains and reduces the porosity of the polymer film and real surface area. Polypyrrole (PPy) was researched by Otero and co-workers^[19, 20] and they found that when the potential of PPy was reduced somewhat, the intercalation of the doping anion became difficult. Our result is in accord with theirs.

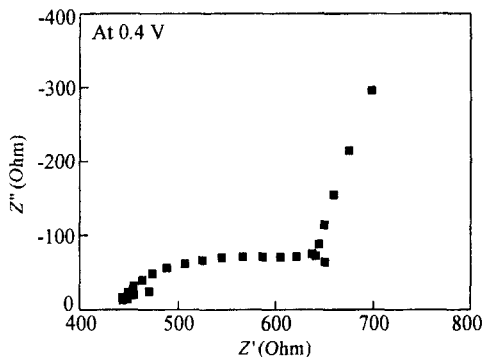


Fig. 3 Impedance response of PFu-coated electrode at 0.4 V in TBABF₄⁻ MeCN solution

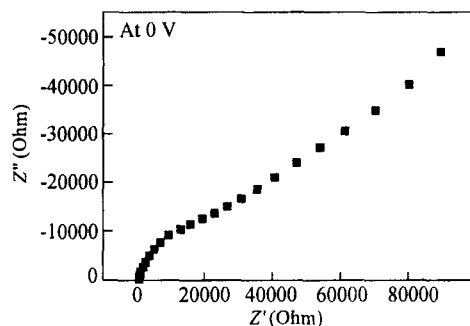


Fig. 4 Impedance response of PFu-coated electrode at 0 V in TBABF₄⁻ MeCN solution.

The impedance plot of PFu is reported in Fig. 4 for its neutral state. It is entirely different from the impedance plots in the high and intermediate oxidation state and is difficult to distinguish the kinetic control region, the diffusion control region and the charge saturation region. This is expected because there are no intercalations of the doping anions in the neutral conducting polymer. Mostany *et al.* reported their work on the impedance of neutral PPy and obtained the charge transfer resistance. But this is related to the difficulty of complete reduction of PPy^[21].

Redox Capacitance of Polyfuran

The redox capacitance or limiting capacitance C_L of PFu can be calculated from the charge saturation region. Figure 5(A–C) shows the complex capacitance plots at 0.65 V, 0.4 V and 0 V, respectively. Complex capacitance plot (Fig. 5A) shows one semicircle, indicating a single dominant ion transport process^[1, 22]. The capacitance of a unit area of surface can be obtained by extrapolating of the curve to $\omega = 0$. So the limiting capacitance C_L is 2.658 mF and the capacitance of a unit area is 37 mF/cm², which is approximately close to the capacitance of PPy^[1]. This implies that PFu like other conducting polymers has the potential to become an energy-storage material or an electrode material^[23, 24]. As shown in Fig. 5(B), some aberrance takes place in the complex capacitance plot. The redox capacitance is reduced to 1.4 mF. This is because an increase of the oxidation level promotes a greater influx of counterions into the bulk polymer. These counterions are necessary to keep the film electroneutral as the positive charges on the polymer molecules increase. So a decrease of redox capacitance is expected when the potential is decreased. However, in neutral PFu the complex capacitance plot does not show one semicircle, which is different from PPy. Pickup *et al.* observed that the complex capacitance plots showed one semicircle even though the potential reached -0.8 V. This is related to the instability of undoped PPy and the difficulty of reduction of PPy^[1]. But in our case PFu is easy to reduce.

From the results of the redox capacitance C_L and the ionic resistance R_L , the anion diffusion coefficient of PFu is estimated to be $1.8 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ ^[16]. In conventional conducting polymer the diffusion coefficient of the doping ion is less than $10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$. Diffusion coefficient of $2.8 \times 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1}$ for ClO₄⁻ in PPy/ClO₄⁻ and $3.7 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ for Na⁺ in PPy/poly(styrenesulfonate) (PSS) were obtained. This is due to the strong electronic interaction between the doping ions and the PPy chain^[1].

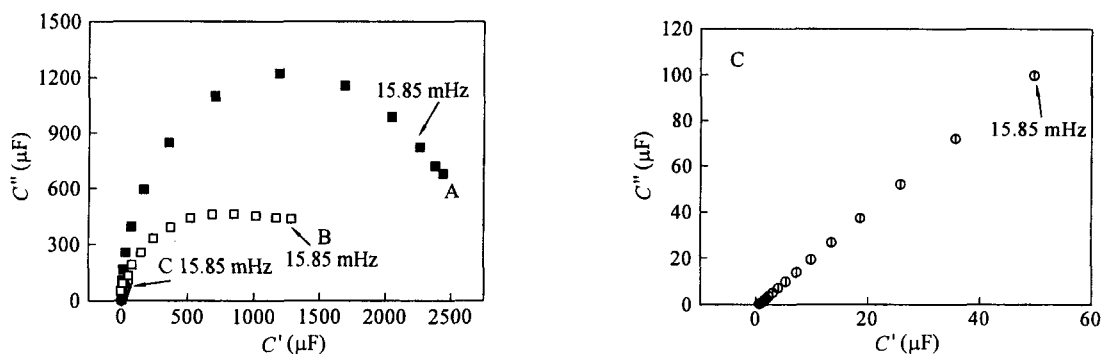


Fig. 5 Complex capacitance plots at different electrode potentials (A) 0.65 V, (B) 0.4 V, (C) 0 V for PFu/BF₄⁻

CONCLUSIONS

The impedance spectra of electropolymerized PFu films on gold electrode were analyzed. The impedance spectra were influenced by electrode potential. Because the polymer in the oxidized state would behave as a highly porous electrode, the ionic conductivity is higher than that in the intermediate oxidation state and the neutral state. At the same time the redox capacitance in the highly oxidized state is higher than that in other conditions. Because of the weak electronic interaction between the doping ions and the PFu chain, the diffusion coefficient of doping ions has a relatively high value.

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