

Impedance Spectroscopy of N-Substituted Oligo-Oxyethylene Polypyrrole Films

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ABSTRACT: The electrochemical properties of neutral (dedoped) and oxidized (doped) poly(1,11-bis(1,1-pyrrole)-3,6,9-trioxaundecane) (poly-I) film electrodes were investigated using cyclic voltammetry and electrochemical impedance spectroscopy (EIS) techniques. Poly-I was deposited on glassy carbon electrode (GCE) from acetonitrile solution containing $5.0 \times 10^{-3} M$ 1,11-bis(1,1-pyrrole)-3,6,9-trioxaundecane (I) and 0.1M LiClO₄ supporting electrolyte. Doped poly-I exhibits a single semicircle in its complex-capacitance

plots, indicating a single dominant ion transport process, together with high capacitance values. These features make this polymer film a candidate for an energy storage material. Also, poly-I can be a candidate as a sensory material for the detection of Ag⁺ based on impedance parameters. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2373–2378, 2008

Key words: electrochemistry; electrochemical impedance spectroscopy; sensor; polypyrrole; polyether

INTRODUCTION

Because of the large range potential applications of conducting polymers, in light emitting diodes, electrochromic devices, solar cells, electrochemical supercapacitor, and field transistors,^{1–5} the interest in them is still growing. One important property, especially in electrochromic device applications, is the switching time which depends both on the electron and ion transport within the polymer film.^{6–8} Electrochemical impedance spectroscopy (EIS) is a powerful ac technique, which can be used to obtain many useful information for the conducting polymer films including charge transfer, ion diffusion, interface resistance, and capacitance. Also, EIS can be used to detect the small changes in the properties of the materials when adsorption/or insertion of species occurs.^{9–11}

Conducting polymers functionalized with crown ethers and polyether chains exhibit complexing properties toward alkaline and alkaline-earth metal cations, that is why, they have attracted great interest. In recent years, there are few studies on N-substituted dipyrrolyl linked with flexible spacers (Scheme 1).^{12,13} It is reported that black conducting polymer films can be obtained via anodic oxidation of such monomers.

The complexing properties of such polymers, after undoping by tetraalkylammonium hydroxide, have been investigated and a strong affinity toward Co²⁺, Cs⁺, and K⁺ were obtained. Also, it was reported that electroactive poly-I has complexing properties toward Ag⁺.¹²

In the present work, EIS was used for the electrochemical characterization of poly-I. The usage of poly-I as a sensory material was also tested for the detection of metallic cations such as Ag⁺.

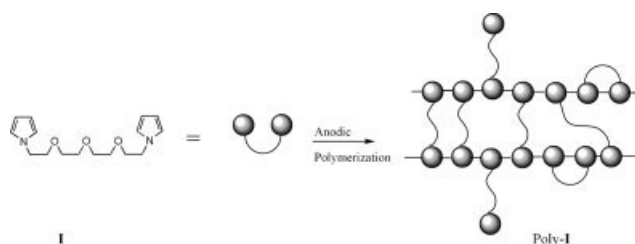
EXPERIMENTAL

Monomer I was synthesized according to a general procedure already described.¹² LiClO₄ (Aldrich), AgNO₃ (Merck), and acetonitrile (Merck) were used without further purification.

Electrochemical polymerization and measurements were performed using a one-compartment, three-electrode electrochemical cell. The cell solution was initially purged with nitrogen and then all experiments were performed under nitrogen atmosphere at room temperature. The polymer films were coated on glassy carbon electrode (GCE) (0.03 cm²) during constant potential electrolysis at 1.0 V from a reaction medium containing $5.0 \times 10^{-3} M$ I and 0.1M LiClO₄ in acetonitrile. A platinum wire was used as a counter electrode and Ag/AgCl in 3M NaCl(aq.) solution as a reference. All dc potentials (E_{dc}) are referred to this reference electrode. After polymerization the films were rinsed with acetonitrile and transferred into another cell containing monomer-free electrolytic solution. All electrochemical mea-

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Scheme 1 Electrochemical polymerization of I.

measurements were performed using Gamry PCI4/300 potentiostat galvanostat.

Before polymerization, GCE was polished with 0.3 μm alumina, rinsed with acetonitrile, and cleaned ultrasonically. To obtain different film thicknesses polymerization was performed in the range 1–25 mC. The thickness, d , of the films was calculated using the relationship between the thickness and the deposition charge during the anodic polymerization.⁸ FTIR spectra of the monomer and the polymer film were performed with a Bruker Vertex 70 Spectrophotometer.

EIS was performed at various E_{dc} values in the range -0.2 to 0.8 V. Poly-I electrodes were equilibrated for at least 2 min at each E_{dc} before EIS was performed. Impedance measurements were performed in the frequency range of 10^5 – 10^{-2} Hz with an ac modulation of amplitude ± 10 mV. Before and after EIS, the electrochemical properties of the polymer film were checked using cyclic voltammetry.

RESULTS AND DISCUSSION

Cyclic voltammetry

A cyclic voltammogram for a poly-I electrode in the LiClO_4 -acetonitrile solution is shown in Figure 1(a,b). Polymer film has a well-defined and reversible doping process. Electrochemical behavior of the polymer film was studied as a function of scan rate and it is found that the peak currents for the film increase linearly with increasing scan rate, indicating nondiffusional redox processes, and well-adhered electroactive polymer film to the working electrode surface [Fig. 1(c)].

The FTIR spectroscopy analysis shows that the structure of the polymer film is consistent with that of the monomer. The peaks at 2965 and 2866 and 1092 cm^{-1} can be attributed to the methylene and etheric groups, respectively, remained unaltered upon polymerization. Also, the disappearance of the band at 3099 cm^{-1} , assigned to the α -hydrogen of the pyrrole ring, confirms mainly a 2,5-coupling. In addition, the peak at 623 cm^{-1} in the polymer spectrum indicates the presence of ClO_4^- dopant ion.

The degree of oxidation can be calculated easily using the following equation for different polymerization charges;

$$Q_{\text{ox}} = \frac{xQ_p}{4+x}$$

In this relationship, Q_p is the charge density required for the formation and deposition of the oxidized polymer from monomer solution and Q_{ox} is

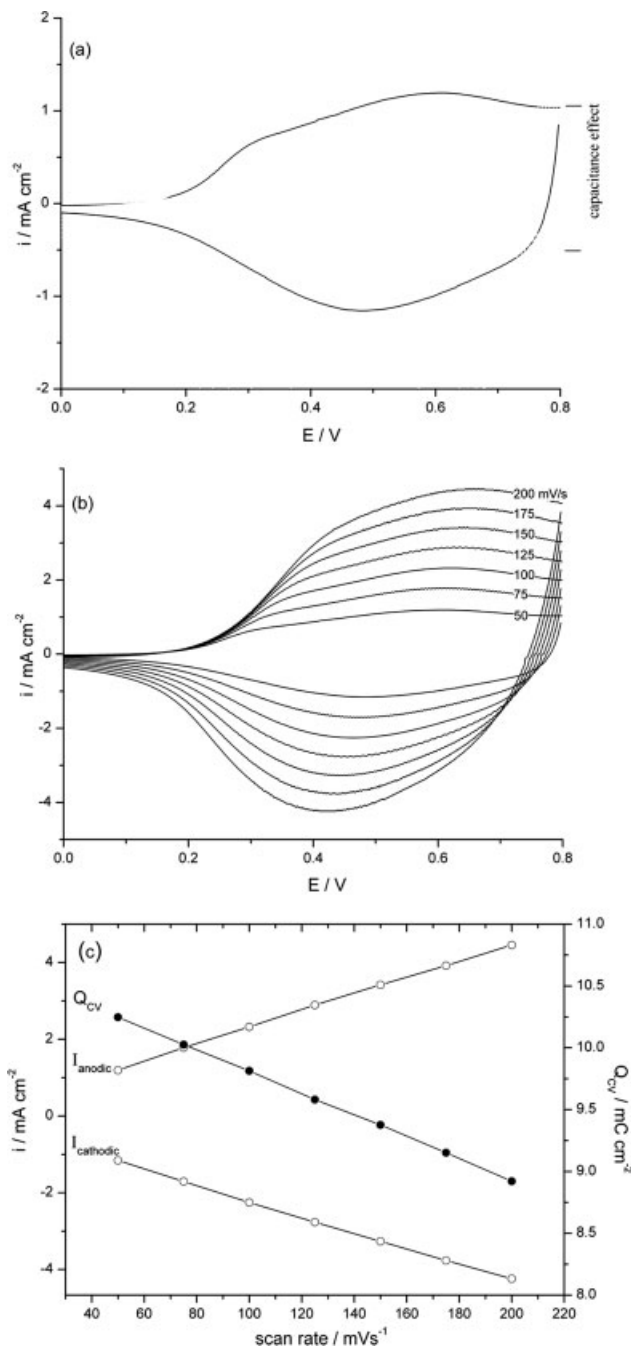


Figure 1 Cyclic voltammogram of poly-I at a scan rate of 50 mV s^{-1} . (b) Scan rate dependence of poly-I. (c) Variation of anodic (I_{anodic}), cathodic (I_{cathodic}) peak currents, and charge (Q_{CV}) as a function of scan rate. Electrolyte solution is $0.1\text{M LiClO}_4/\text{acetonitrile}$ and polymerization charge = 5 mC .

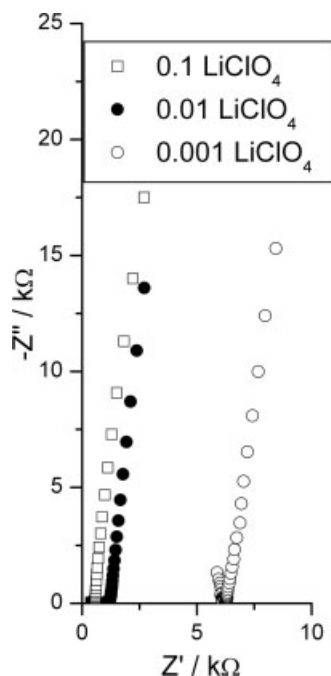


Figure 2 Nyquist plots of the poly-I (5 mC) at 0.6 V in acetonitrile containing different concentrations of supporting electrolyte.

the charge density corresponding to $4 + x$ electrons per monomer, where x is the number of electrons per monomer required for switching.¹⁴ Therefore, x can be estimated from the slope of Q_{ox} versus Q_p plot and x value of 0.25 is obtained, indicating about one charge per four repeat units.

The charge (Q_{CV}) was obtained by integration of the cyclic voltammograms [Fig. 1(a)] in the potential range -0.2 to 0.8 V:

$$Q_{CV} = \frac{(Q_a - Q_c)}{2}$$

where Q_a and Q_c are the anodic and cathodic charges, respectively. The Q_{CV} obtained from cyclic voltammogram was found to increase from 8.92 to 10.25 mC cm⁻² while decreasing the scan rate from 200 to 50 mV s⁻¹ in Figure 1(b). Since the linear relationship between the redox currents of the polymer film and scan rates [Figure 1(c)] excludes the charge transport limitations, this decrease in Q_{CV} might be due to either the presence of a slow faradaic redox reaction occurring in parallel with doping of poly-I or reversibility of the system.¹⁵

Since the voltammetric response shows a capacitive effect [Fig. 1(a)] beyond doping peak, the voltammetric capacitance C_{CV} of the polymer film can be obtained from the cyclic voltammograms based on the following equation:

$$C_{CV} = \frac{i}{v}$$

where v is the voltage scan rate and i is the current. At a scan rate of 50 mV s⁻¹, a C_{CV} value of 22.3 mF

cm⁻² was obtained. The origin of such large capacitance in polymer electrodes may be explained on the basis of charge saturation effect, which takes place at the end of the doping process.^{16,17}

Electrochemical impedance spectroscopy

Typical impedance spectra of the polymer electrode in 0.1 , 0.01 , and 0.001 M LiClO₄ in acetonitrile are shown in Figure 2. As shown in Figure 2, the high frequency intersection with Z' axis depends strongly on the electrolyte concentration and it confirms that this behavior is determined mainly by the solution resistance and not by the ohmic resistance of the polymer film.^{15,18}

The low frequency capacitance C_L , a type of the frequency dependence of charging processes, of poly-I can be calculated from the charge saturation region observed at low frequency. The complex capacitance plots of poly-I shown in Figure 3(a) consist of single semicircles, which is explained by Ren and

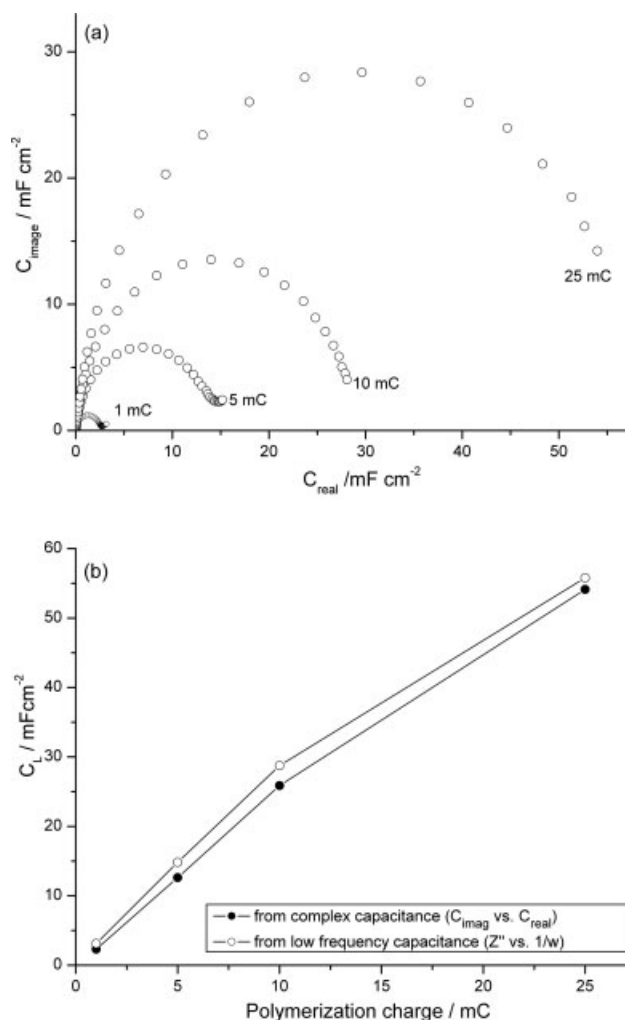


Figure 3 (a) Complex capacitance plots for poly-I films having different polymerization charges. (b) Plots of low-frequency capacitances from impedance spectroscopy versus polymerization charge at 0.4 V.

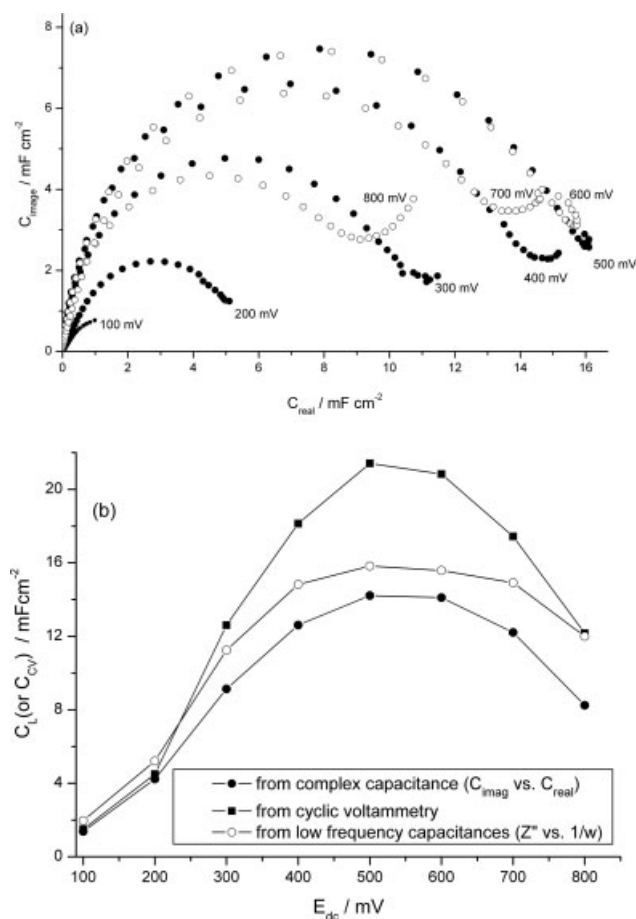


Figure 4 (a) Complex capacitance plots for poly-I (5 mC) films at various electrode potentials. (b) Variation of capacitance values as a function of electrode potentials in 0.1M LiClO₄/acetonitrile.

Pickup as involving a single dominant ion transport process.⁸ Also, the capacitances increase linearly with the polymerization charge of the poly-I film, as shown in Figure 3(b). The capacitance of a unit area is 33.84 mF cm⁻² at 0.4 V (polymerization charge = 0.48 C cm⁻²), which is approximately close to the capacitance of polypyrrole/ClO₄⁻ possessing ~35 mC cm⁻² at -0.2 V (polymerization charge = 0.48 C cm⁻²).⁸ This implies that poly-I like other conducting polymers has the potential to become an energy storage material or electrode material. The redox capacitance is increased from 1.37 mF cm⁻² at 100 mV to 14.22 mF cm⁻² at 500 mV in Figure 4(a) (polymerization charge = 5 mC). During the p-doping (oxidation) process the positive charges formed in the polymer chain and their number increases with the applied potential. On the other hand, the number of counterions also increases to keep the film electro-neutral. Therefore, an increase in redox capacitance is expected when the potential is increased. However, in neutral poly-I at potentials <100 mV the complex capacitance plots do not show any semi-

circle (not shown in the text) because of the high resistance value during polymer reduction. This behavior is different from polypyrrole/ClO₄⁻, where the complex capacitance plots showed one semi-circle even though the potential reached -0.8 V.⁸ This is related to the instability of undoped polypyrrole because of the difficulty of reduction; on the other hand, it is easy to reduce poly-I at potentials <100 mV.¹⁹

At low frequencies the real impedance could not reach a constant value, attributed to polymer coated electrodes and low frequency capacitance can be found using a plot of Z'' versus 1/ω, which should be linear with the slope of 1/C_L. Low frequency capacitances and complex capacitances are shown in Figure 4(b). The results were also compared with the capacitances calculated from cyclic voltammogram. As can be seen from Figure 4(b), capacitances from impedance measurements and cyclic voltammetry exhibit considerable differences at higher potentials. A possible reason is that cyclic voltammetry gives the total current containing the faradaic and nonfaradaic process and also conformational changes during doping/dedoping process affect the impedance spectroscopy and cyclic voltammetry results in different ways.⁸

The impedance data at -0.2 V forms a large arc in Figure 5(a), attributed to a parallel RC circuit with a resistance of 873 kΩ and a constant phase element (CPE) of 7.3 × 10⁻⁶ (S × sⁿ). The magnitude of this capacitance was produced by charge accumulation at the polymer-solution interface. Although, in reality n_{CPE} should be equal to 1, lower n_{CPE} < 1 value is related to the roughness of the polymer film surface on the working electrode.

The high frequency real axis intercept of the impedance data represents the sum of the resistances of the electrolyte solution (R_s) and the polymer film (R_E). Using a bare GCE, R_s was determined as 180.3 Ω and the polymer film resistance was found as 962.7 Ω.

Scheme 2 shows a modified Randles equivalent circuit to describe the experimental observations in the study. Therefore, the electrochemical processes occurred in the polymer film can be easily defined using this equivalent circuit, where R_S is the resistance of the electrolyte between the working and reference electrodes, R_{film} is the sum of the electronic (R_E) and ionic (R_I) resistances of the film, R_{ct} is the charge transfer, CPE is the double layer capacitance between polymer and solution interface, Z_W is the Warburg diffusion impedance element, and C_L is the capacitance of the polymer film.

Nyquist plots for an oxidized poly-I at different potentials in acetonitrile containing 0.1 M LiClO₄ are shown in Figure 5(b). At potentials higher than 0.1 V, the polymer film is partially p-doped and exhibits an

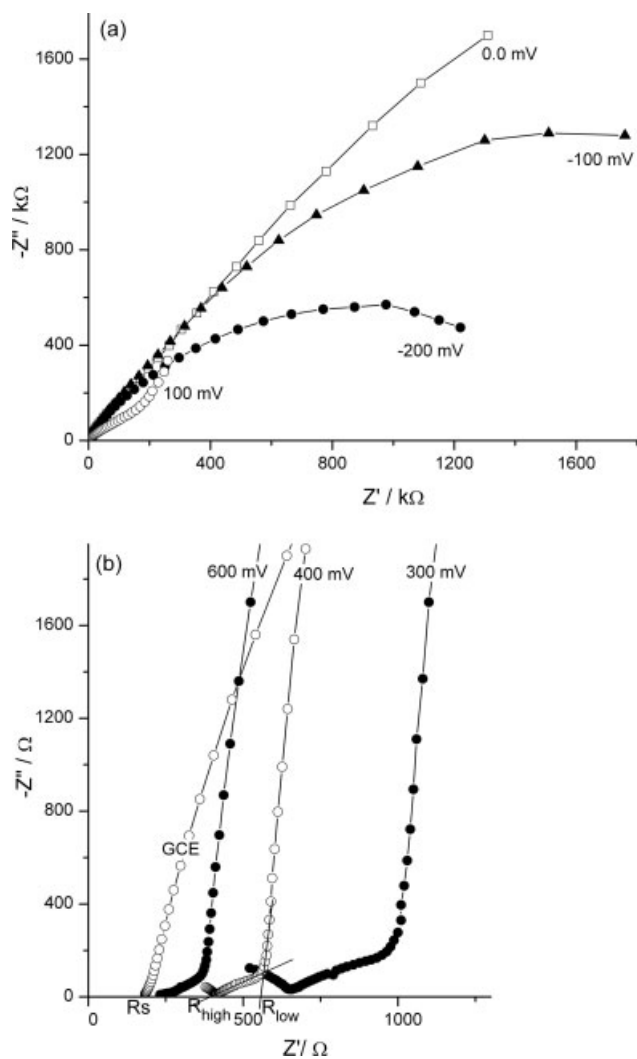


Figure 5 (a) and (b) Nyquist plots of poly-I (5 mC) at various electrode potentials in 0.1M LiClO₄/acetonitrile. A bare GCE is carried out at open circuit potential.

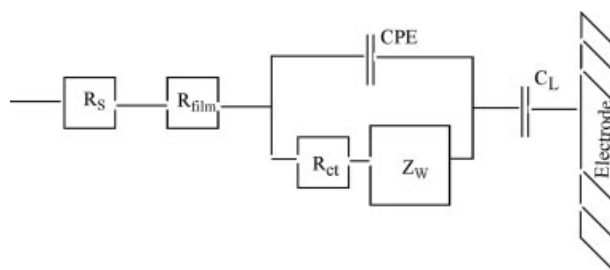
electrochemical response. This redox involves transport of both ions and electrons within the film. By using these plots R_E and R_I of the polymer film can be estimated from the high and low-frequency limiting resistances (R_{high} and R_{low}).^{20,21} The electronic and ionic resistances of the oxidized polymer films can be obtained using the following relationships;

$$\frac{1}{R_{high} - R_S} = \frac{1}{R_E} + \frac{1}{R_I} \quad \text{and} \quad 3(R_{low} - R_S) = R_E + R_I$$

Oxidation process promotes the movement of counterions into the polymer film in order to keep the polymer film electroneutral. Thus, an increase in the oxidation level leads to an increase in the ionic conductivity with the increasing applied potentials.

The ionic conductivity of the film σ_{ion} is given by

$$\sigma_{ion} = \frac{d}{R_I A}$$



Scheme 2 Equivalent circuit of poly-I electrode.

where A is the geometric area of the electrode and d is the film thickness. The ionic conductivity of poly-I, shown in Figure 6(a), increases with increasing potential as the amount of incorporated ClO₄⁻ is increased. Since the ClO₄⁻ concentration in the polymer is proportional to its oxidation level, there is a linear relationship between ionic conductivity and the voltammetric charge. Ren and Pickup reported

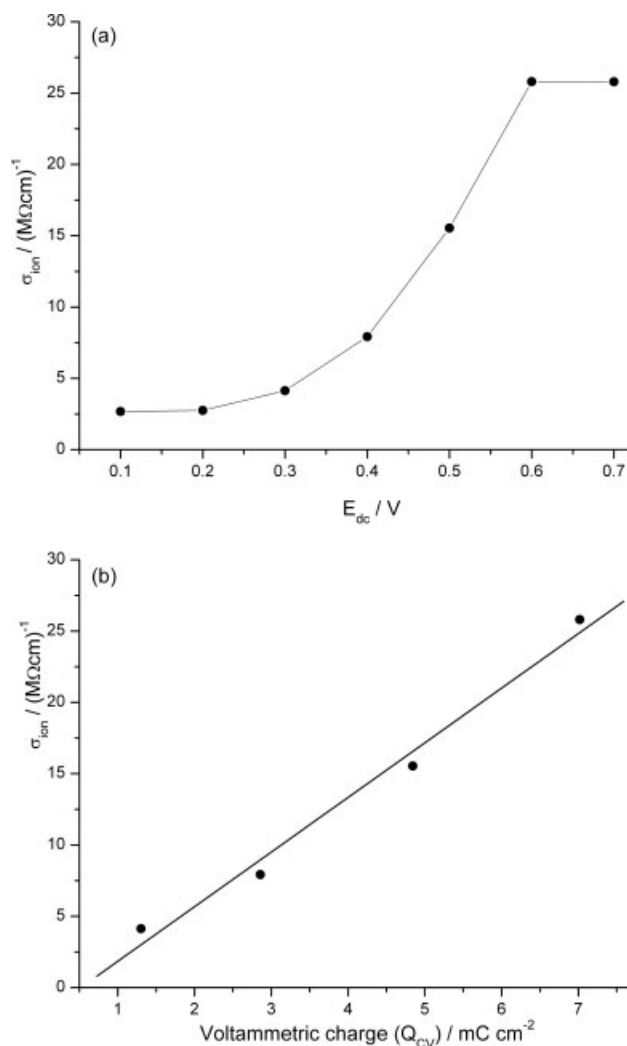


Figure 6 (a) Plot of ionic conductivities versus electrode potentials and (b) Ionic conductivities versus voltammetric charges in 0.1M LiClO₄/acetonitrile.

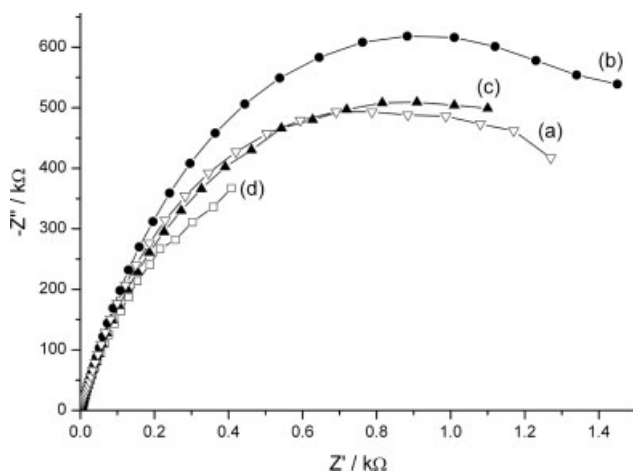


Figure 7 Nyquist plots for (a) dedoped poly-I with hydrazine and dedoped poly-I treated with (b) 1 ppm, (c) 10 ppm, and (d) 100 ppm AgNO_3 in 0.1M LiClO_4 /acetonitrile at open circuit potential for 30 min.

that the diffusion coefficient (D_{ion}) of the counterion can be estimated from the slope of the conductivity versus charge plot [Fig. 6(b)] by using the Nernst-Einstein relationship;

$$D_{\text{ion}} = \frac{\sigma_{\text{ion}} RT}{F^2 C_{\text{ion}}}$$

where C_{ion} , the counterion concentration, is proportional to the voltammetric charge. Diffusion coefficient of $1.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for ClO_4^- in poly-I is about two times smaller than that of $2.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for ClO_4^- in polypyrrole/ ClO_4^- .⁸ Also, the diffusion coefficient ($1.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) estimated from the slope of R_I versus $1/C_L$ plot ($D_{\text{ion}} = \frac{d^2}{3R_I C_L}$) is very close to the previous one. This suggests that the low mobility of ClO_4^- is due to an electronic interaction with poly-I having the crosslinked structure. Also, our studies exhibit that there is no cation binding capability of the polymer toward Li^+ .

EIS is a useful technique to detect the small changes in the materials parameters when adsorption/or insertion of species occurs. Therefore, this technique can be used to determine metallic cations such as Ag^+ when poly-I was used as a sensory material. Figure 7 shows the Nyquist plot for the silver-poly-I-modified electrode. It appears clearly that the R_{ct} increases when the poly-I-modified electrode is exposed to Ag^+ . On the other hand, with the increasing amount of Ag^+ , a decrease in the R_{ct} was observed, indicating a more conductive modified electrode because of the presence of silver on the electrode surface. In short, changing the concentra-

tion of Ag^+ can affect the element of the circuit such as R_{ct} and C_{dl} and, therefore, a trend can be obtained between circuit elements and the concentration of Ag^+ . This system is under further study in order to develop an electrochemical method for determination of cations.

CONCLUSION

Electrochemically synthesized N-substituted polythetereal polybispyrrole (poly-I) film has good stability and reversible redox process. The corresponding polymer film was used to detect Ag^+ ions using EIS measurements, which makes the polymer film a good candidate in many practical use such as for the recovery of metals and ion sensor. EIS studies also showed a fast charge transfer between film and electrolyte interface as well as a single dominant ion transport process. Furthermore, because of the relatively high capacitance value, poly-I can be used as an energy storage material.

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