Electrical Capacitance of Polypyrrole-Perchlorate and Polypyrrole-Naflon Film Electrodes

Jaewoong Um[#] and Woon-kie Paik*

Department of Chemistry, Sogang University, Seoul 121-742, Korea
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Electrical capacitance at the interface between electrolyte solution and conducting polypyrrole film electrode was measured by a simple electrochemical method. The polymer films were electropolymerized in the presence of perchlorate (PPy-ClO_4) or Nafion (PPy-Nafion) anions as the dopant ions. Both polymers exhibited large double layer capacitances which were slightly potential dependent within the potential range where the polymers are conductive. The capacitance increased in proportion to the polymer thickness. The specific capacitance were about 10 F g^{-1} and 44 F g^{-1} for PPy-Nafion and PPy-ClO_4, respectively.

Introduction

Much attention has been drawn in recent years to large double layer capacitance exhibited by film electrodes of conducting polymers at the polymer-electrolyte interface.[1~4] The large non-faradaic capacitance is due to the polymer film's porosity and appears as large background currents in the cyclic voltammograms in both anodic and cathodic directions. The large capacitance has technical importance because of increased charge storage capacitance in the polymer batteries and also because of the possibility of realization of industrial supercapacitors.[3,5,6] The exact electrical response of a conducting polymer electrode in various potential ranges depends on the associated anions. The association of the anions with the polymer is usually labile and the anions may be dissociated from the polymer at cathodic potentials or may be exchanged with ions in the electrolyte solutions in contact.[7,8] Some polyelectrolyte anions and large polyanions are stable in their association with the polymer and are not expelled from the polymer matrix, hence the nature of the conducting polymers formed with such polyelectrolyte anions may remain unchanged in electrolyte solutions after repeated electrical excursions as in the application of their capacitance.[9] Study on the capacitance of polymers with such stably associated anions is also hoped to shed light on the role of diffusional motion of ions in the polymer.

Apart from the oxidation and reduction behavior of the polymer backbone, which gives rise to the current waves in the cyclic voltammograms, the double layer capacitance dominates the impedance properties of the polymer in the oxidized (conducting) state. Hence, only the imaginary part of the complex impedance shows a strong frequency-dependence at the anodic potentials, resulting in near vertical lines in the complex-plane impedance plot of Z_{imag} vs. Z_{real}.[4] This capacitive character of the polymer electrode renders its measurement rather simple, and measurement of the capacitance employing simple electrochemical methods is possible.

In the present study the double layer capacitance of film electrodes of polypyrrole doped with small anions and polymer anions were measured at various electrode potentials by simple electrochemical methods. The specific capacitance, a figure of merit for capacitors, was estimated for each type of the electrodes.

Experimental

Nafion-associated polypyrrole (PPy-Nafion) film was electrochemically synthesized by anodic polymerization from an aqueous solution of 0.1 M pyrrole which also contained 0.2% acidic Nafion[1] as the sole electrolyte. Pyrrole was purified before use by distillation. Water used as the solvent was purified to the resistivity values higher than 10 M ohm-cm. The pyrrole solutions were deaerated by bubbling purified nitrogen for about 30 min before introducing the Nafion solution, and were shielded from oxygen contamination during the polymerization by passing nitrogen over the solution. The solutions could not be deaerated by bubbling an inert gas once Nafion was introduced because of extensive foaming. A three-electrode two-compartment glass cell was used for the electrochemical synthesis and voltammetric experiments, which were controlled by a potentiostat and a potential programmer (EG & G). The reference electrode used was a saturated calomel electrode (SCE) which was placed in a tube with the Luggin capillary connected at the bottom. All the potentials reported in this paper are referred to SCE. A piece of Pt foil or Pt wire was used as the electrode on which the polymerization and voltammetric experiments were performed. Platinum was also used as the counter electrode. The PPy-Nafion film and the PPy-ClO_4 film used for comparison experiments were synthesized either by cyclic potential scans with the anodic limits at 0.70 V or by applying constant potential of 0.70 V. The films tested for the electrochemical properties were mostly polymerized at 0.70 V. All the experiments were conducted at room temperature.

Results and Discussions

The cyclic voltammograms (CV) during the polymerization in the presence of Nafion was similar to those obtained with

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*Author responsible for correspondence.
[#]Present Address: Yukong Research Laboratory, Yusung-ku, Taejon 305-370, Korea

[1]Nafion is a perfluorinated sulfonic acid polymer of E. I. du Pont de Nemours and Company. The solution was diluted from 5% EW1100 Nafion solution in isopropanol (85%)-water solvent supplied by Solution Technology, Inc., Mendenhall, Pennsylvania.
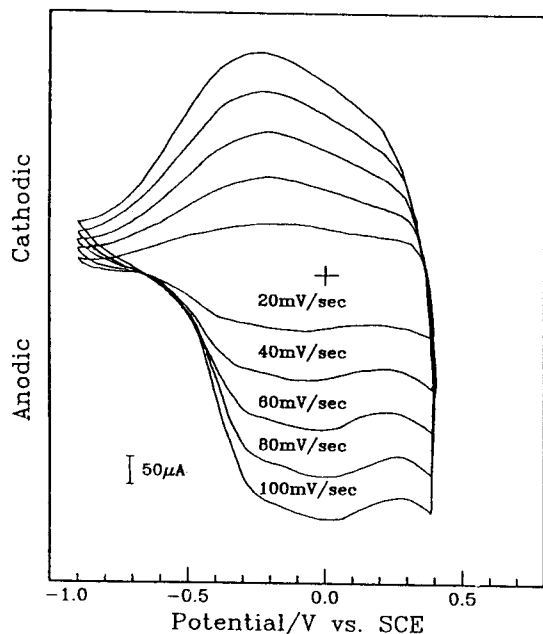
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Figure 1. Cyclic voltammogram of PPy-Nafion (geometric area 0.157 cm²) obtained at different scan rates in 0.1 M LiClO₄ aqueous solution.

Figure 2. CV's obtained from PPy-Nafion by cyclic linear potential scans within successively smaller potential ranges, from top to bottom. Scan rate $s=20$ mV s^{-1}.

other electrolytes. Polymerization of pyrrole in the presence of Nafion was, however, achieved at a much slower rate compared to the polymerization with perchlorate or other electrolytes. The currents were smaller in the CV, and the anodic wave was shifted toward more anodic potential. This is understandable because the equivalent concentration of the Nafion anion in the 2 wt% solution is very small due to the large molecular weight. The equivalent weight of EW1100 Nafion for each sulfonate group is 1100. In the initial few scans there were small oxidation waves near $-0.2 \sim -0.3$ V, which gradually disappeared. This was confirmed to be oxidation of isopropanol component of the solvent for Nafion by a separate CV with isopropanol solution.

The PPy-Nafion film obtained by electropolymerization at the constant potential of 0.70 V was washed with distilled water and transferred to a cell containing 0.1 M LiClO₄ aqueous solution. The CV's obtained at different scan rates in this solution are shown in Figure 1. From the figure it appears that the polymer has good conductivity as well as good electrochemical activity as was reported by Momma *et al.*[10] from their study of PPy-Nafion and PPy-ClO₄.

The general feature of the CV's did not change on repeated potential scans in the perchlorate as is shown in Figure 1. When the film was treated with cyclic potential scans in a K₄Fe(CN)₆ solution, aqueous or nonaqueous, and transferred back to the CLO₄⁻ solution, the CV same as Figure 1 was obtained again. This confirms that exchange of anions that can alter the nature of the polymer film does not occur. The polyelectrolyte anion of Nafion must have been tightly intertwound with the cationic polypyrrole backbone, and the charge compensation on reduction of the polymer must be achieved by migration of cations of the electrolyte solution into the polymer matrix. The conductivity of the dried polymer film was measured by the four probe method to be
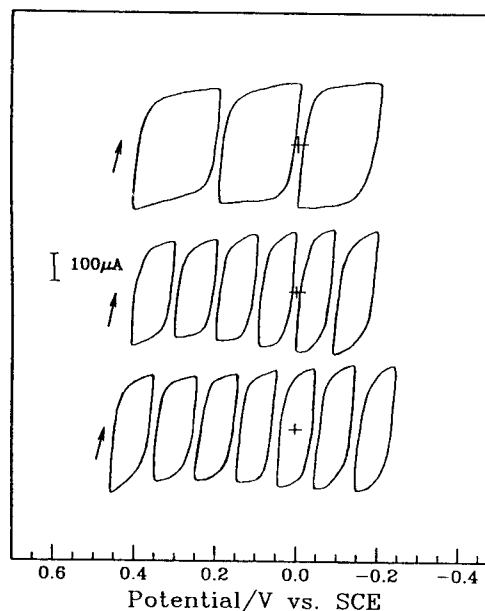
about 10 Scm⁻¹ when the potential of the electrode was maintained between -0.20-0.20 V before taking the polymer out of the polymerization cell. The conductivity decreased beyond both sides of this potential range, especially steeply on the cathodic side, becoming almost insulating at -0.40 V.

The relatively large currents in the CV's over a wide range of potential both in the anodic and the cathodic directions, which is proportional to the scan rate (Figure 1), are due to the large differential capacitance of the polymer electrode. The large capacitance is also responsible for the near-rectangular CV's shown in Figure 2. In the figure, CV's obtained from cyclic linear potential scans within successively smaller potential ranges are shown from top to bottom. The heights of the anodic and the cathodic currents are almost the same and almost independent of the potential within the potential range where the conductivity is good. A pure capacitance would give rectangular CV's with the height of the rectangle being equally divided into positive and negative currents; the current is proportional to the scan rate when the absolute potential scan rate is constant with only the sign alternating, *i.e.*,

$$I = \pm sC \qquad (1)$$

where s is the absolute potential scan rate $s=|dV/dt|$ and C is the capacitance. The distortion of the CV's from rectangular shape is caused by the resistive component of the impedance of the film as is shown by the CV's obtained from an equivalent circuit consisting of pure R and C components in series, Figure 3(b). The slight variations in the height of the rectangles represent the potential dependence of the differential double layer capacitance and the contribution from the oxidation-reduction activity of the polymer.

Assuming that a film electrode of PPy-Nafion or PPy-CLO₄ is equivalent to a series RC circuit as in Figure 3(b), the
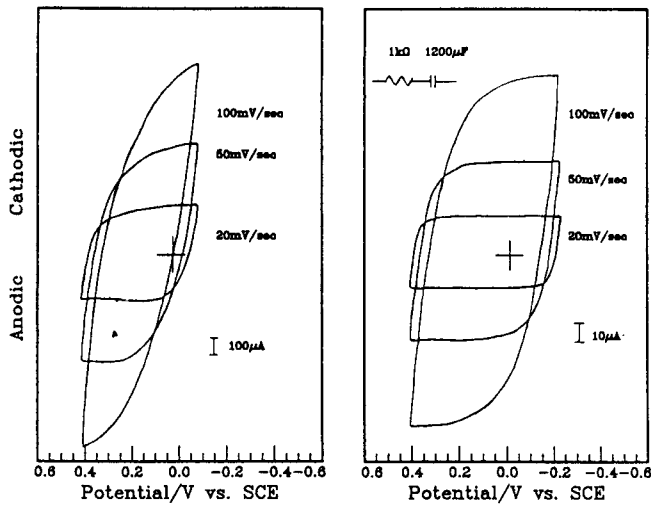
Figure 3. Current responses to a cyclic potential scan of a PPy-Nafion electrode (a) and of an equivalent circuit consisting of a capacitance and a resistance connected in series (b). The scan rates are marked on the curves.

resistive and the capacitive components can be evaluated by applying square pulses between the film electrode and the reference electrode from the potentiostat and analyzing the current response.

$$I = \frac{V_o}{R} \exp\left(-\frac{t}{RC}\right), \tag{2}$$

where V_o is the pulse height.

From Figure 4b, which is an oscilloscope recording of the current response of a PPy-Nafion film electrode to positive and negative pulses (Figure 4a), it can be seen that the electrode exhibits a single RC transient time component. The pulse height was limited to ± 10 mV in order to minimize the contribution from the oxidation/reduction activity of the polymer. The PPy-ClO$_4$ film also gave same type of response. The resistance is obtained from the initial current, V_o/R, and the capacitance is obtained from the transient time using equation (2).

In the modern literature often the charge accumulated or expended in the course of oxidation and reduction of the polymer is taken to be associated also with "capacitance" in the broader sense of the term, thus making the distinction between battery and capacitor obscure.[1~5] The capacitance

(a)
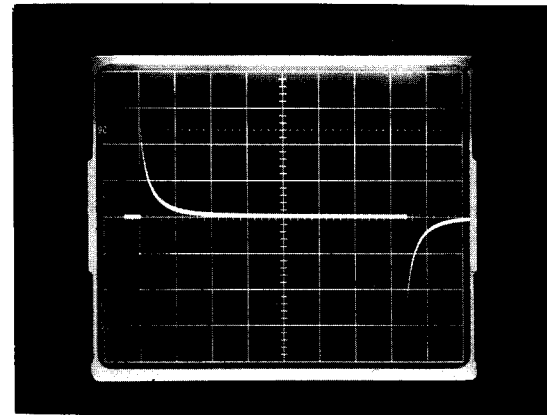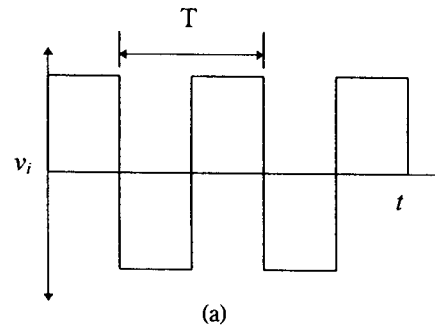
(b)

Figure 4. Potential pulses applied to the polymer film electrodes (a) and the typical transient current response obtained from PPy-Nafion film electrode in the conducting state (b). Geometric area of the electrode : 0.157 cm^2; Pulse height : 10 mV; pulse duration : 15 s; Scale in the oscillograph X : 2.5 s/div, Y : 0.05 mA/div.

measured in the present work is the double layer capacitance because the measurements were made in such a way to exclude the faradaic current by applying small potential pulses superposed on the electrode potential that is well within the range in which the polymer is in the fully oxidized (electronically conductive) state.

The capacitance values measured by the response to the pulse (equation (2)) were converted to capacitance per unit geometric area of the electrode and are tabulated for different polymerization charges and different potentials (Table 1). The values agreed with those estimated from the CV's using equation (1). The capacitance showed a slight potential

Table 1. Capacitance of the conducting polymer/electrolyte interface, measured with the PPy-Nafion and PPy-ClO4 film electrodes in aqueous 0.1 M LiClO$_4$ solution, in units of mFcm^{-2}

Polymerization charge	0.32 C cm^{-2}		1.13 C cm^{-2}		3.53 C cm^{-2}	
Pot'l (V vs SCE)	PPy-Nafion	PPy-ClO$_4$	PPy-Nafion	PPy-ClO$_4$	PPy-Nafion	PPy-ClO$_4$
0.4	9.55	14.0	45.9	66	121	191
0.3	12.1	14.0	45.9	59	121	153
0.2	8.9	12.7	28.0	67	115	140
0.1	15.9	14.0	38.2	67	138	140
0	19.1	12.7	33.1	67	145	115
−0.1	19.1	14.0	28.0	72	140	102
−0.2	19.7	12.7	39.5	57		76

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dependence and near-linear increase with the film thickness, which in turn is considered to be proportional to the electrical charge expended during the polymerization. The measured resistance was between 55 and 110 ohms without systematic potential dependence and with a tendency of slight decrease with thickness. Therefore, the resistance can not be considered to be that of the film. The resistance of the circuit including the solution between the working electrode (geometric area : 0.157 cm^2) and the Luggin capillary of the reference electrode is considered to be the major part of the measured resistance.

The capacitance values for PPy-Nafion were almost consistently smaller than those for PPy-ClO$_4$ polymerized by same coulombic charge. This seems to imply that PPy-ClO$_4$ film is more porous than PPy-Nafion. This was confirmed to be the case by the scanning electron micrographs; PPy-ClO$_4$ appeared to be more rough on the surface with well-developed cauliflower-like structure which may have many buried voids underneath, whereas the SEM picture of PPy-Nafion showed finer surface.

We also made measurements on PPy-Fe(CN)$_6$ films. Both the resistance and the capacitive components measured for PPy-Fe(CN)$_6$ films were of comparable magnitudes as those for PPy-Nafion and PPy-ClO$_4$. However, the capacitance of PPy-Fe(CN)$_6$ appeared to be more than 50% larger in the potential region above 0 V where the electrochemical activity of the ferro/ferricyanide ion might be responsible for the increased current response. Therefore, the measured apparent capacitance may be far from the pure double layer capacitance.

Supposing that in one unit segment of the polymer there are about 3 pyrrole moiety and 1 positive charge which is neutralized by 1 negative charge of the associated anion, we can estimate that 4 electronic charge units are used for polymerizing 3 pyrrole molecules and forming 1 positive charge of the unit segment. For the PPy-Nafion, 1 equivalent weight of the segment is *ca.* 1300 (195 for the 3 monomer units + 1100 for a Nafion segment containing a sulfonate group). One equivalent weight of PPy-ClO$_4$ is *ca.* 300. Therefore, the mass of the polymer film formed on 1 cm^2 of the substrate electrode with the charge of 3.53 C (last column of Table 1), is estimated to be 1.2×10^{-2}g for PPy-Nafion, and 2.7×10^{-3} g for PPy-ClO$_4$. Taking the approximate capacitance to be 120 mF cm^{-2} for the 3.53 C films from the table, the specific capacitance values as defined as capacitance per unit film mass are 10 F g^{-1} and 44 F g^{-1} for PPy-Nafion and PPy-ClO$_4$, respectively. These large values are due to large real surface area of the porous polymer. Considering the fact that the double layer capacitance is typically about 20 μF cm^{-2} (One estimation reported in the literature[11] is 37 μF cm^{-2}, based on a roughness factor of 100.), the

specific surface area comes out to be *ca.* 50 m^{2}g^{-1} for PPy-Nafion, and 220 m^{2}g^{-1} for PPy-ClO$_4$.

Although these values are somewhat smaller than the highest values reported for solid materials such as carbon,[12] and organic electrolyte solutions with wider potential windows are preferable to aqueous solutions for direct applications,[6] it is interesting to note that this large capacitance is actively present in the materials that are electroactive. Both PPy-Nafion and PPy-ClO$_4$ appear to be good candidate to be used for their large capacitances; PPy-ClO$_4$ being better for larger specific capacitance and PPy-Nafion better with respect to the stability against anion exchange.

Summary

Electrical capacitance at the interface between electrolyte solution and conducting polypyrrole film electrode was measured by a simple method for the polymers associated with perchlorate anion and Nafion. Both polymers exhibited large double layer capacitance which is slightly potential dependent within the potential range where the polymers are conductive. The capacitance increased in proportion to the polymer thickness.

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