

Impedance Characteristics of Conducting Polypyrrole-poly(ethylvinylether) Graft Films

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Impedance characterization of graft copolymers of poly(2-(N-pyrrolyl)ethylvinylether) and polypyrrole (doped with BF_4^-) was elucidated in comparison with pure polypyrrole doped with BF_4^- .

Introduction

Conducting polymers have possible applications in electronic devices. Its poor mechanical and physical properties, however, prevents its application in certain cases. In studies conducted to improve the mechanical and physical properties of conducting polymers, several groups have reported that the electrochemical polymerization of the monomer can also occur on an electrode already coated with an ordinary insulating polymer, leading to conducting composites (1-5). Another method to enhance the mechanical and physical properties of the conducting polymer is to synthesize block and graft copolymers containing conventional and conducting sequences (6-8). This kind of conducting polymer synthesis not only improves the poor mechanical and physical properties of heterocyclic polymers, but also retains the conductivity at a desirable value. The grafting process leads to single phase conducting polymer matrice, in contrast to blending, which may yield heterogeneous systems. This makes the latter method more attractive.

Our purpose in this study is to investigate the impedance difference between polypyrrole (doped with BF_4^-) and graft copolymer of polypyrrole and poly 2-(N-pyrrolylethylvinylether) (doped with BF_4^-).

Experimental

Polypyrrole films with a thickness of 1.5 μm were electrochemically synthesized at a constant potential of 0.95 V(SHE) on a platinum wire (0.34 cm^2) in 50 mL dichloromethane (Aldrich) containing 0.1 M

tetrabutylammonium tetrafluoroborate as the supporting electrolyte and pyrrole (0.017 M) at 0°C. The anodic polymerization current during the process of the film formation was about 1.5 mAcm⁻².

Poly(2-(N-pyrrolyl)ethylvinylether) (poly(2-NEVE)) was synthesized from poly(2-chloroethylvinylether) (poly(2-CEVE)) through phase catalysis reaction. Poly(2-chloroethylvinylether) was first synthesized by means of photoinitiated polymerization with a 98% yield (9). A solution of 2-chloroethylvinylether (6.6 M) in dichloromethane containing 5 × 10³ M 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 5 × 10³ M diphenyliodonium hexafluorophosphate was outgassed with dry nitrogen prior to irradiation with a photoreactor equipped with a monochromator. After irradiation at λ=350 nm for 5 min, the viscous solution was precipitated in cold methanol. After decantation, the viscous polymer was dried in a vacuum oven. The following procedure was followed for synthesis of poly 2-(N-pyrrolylethylvinylether): to a solution of 18-crown-6 (3mmole) in dry THF, pyrrolyl potassium (Py⁻ K⁺) salt was added. The mixture was stirred for 15 min under nitrogen. Poly(2-chloroethylvinylether), obtained by means of photoinitiation, (35 mmole) was added. Stirring continued for 12 hours at room temperature. The solution was then concentrated in a rotary evaporator. The viscous solution was poured into ten-fold excess water (yield=60%). The polymer was finally dried in a vacuum oven for 2 days. Poly(2-NEVE) is soluble in dichloromethane.

A new polymer (PPy/poly(2-NEVE)) was electrochemically synthesized from poly(2-NEVE). The procedure is the same as in the synthesis of PPy. In this case, the solution contains poly(2-NEVE) along with pyrrole (10).

Impedance characterization of the produced PPy and PPy/Poly(2-NEVE) films with a thickness of about 1.5 μm was carried out at three different constant potentials: 0.6 V and 0.2 V (SHE) at the doped state and -0.6 V (SHE) at the reduced state. The frequency range was from 100 kHz to 10 mHz and the a.c. signal was 10 mV. The electronic equipment consisted essentially of a fast-rising potentiostat (rise time 0.3 μs), function generator and a frequency response Analyzer (Voltech;TF2000) (11). The potentiostat, function generator, interface and software were developed at the Institute of Physical Chemistry And Electrochemistry, Heinrich Heine University, Düsseldorf.

Results and Discussion

As seen in Figure 1, the impedance responses of PPy and PPy/poly(2-NEVE) films in their electroconducting state (0.2 V/she) are very similar throughout the frequency range. The electrolyte resistance (R_{el}, 3.8 Ωcm² (Z' ~ R_{el} for f → ∞) and the charge transfer resistance (R_{ct}) were determined from the widths of the -Z''/Z'-semicircles (Fig 1a). The corresponding capacities (C_{dl}) of the polymer/solution interface can be determined from the values of the relaxation frequencies (f_{max}) (Figure 1a (3.3 Hz for PPy and 11.25 Hz for PPy/poly(2-NEVE))) by the equation

$$C_{dl} = \frac{1}{2\pi f_{max}} R_{ct} \quad (1)$$

The total resistance (R_T=R_{el}+R_{ct}+R_L), extrapolated to very low frequencies (Z' ~ R_T for f → 0), is about 26 Ωcm² in both cases, where R_L is the limiting resistivity of the polymer film. The other very important parameter of the electroconducting polymers, as far as their application in rechargeable batteries and/or supercapacitors is concerned, is C_L-limiting capacity, which was determined from the linear (-Z''/ω⁻¹)-plots, where d(-Z'')/d(ω⁻¹)=1/C_L (Fig.2).

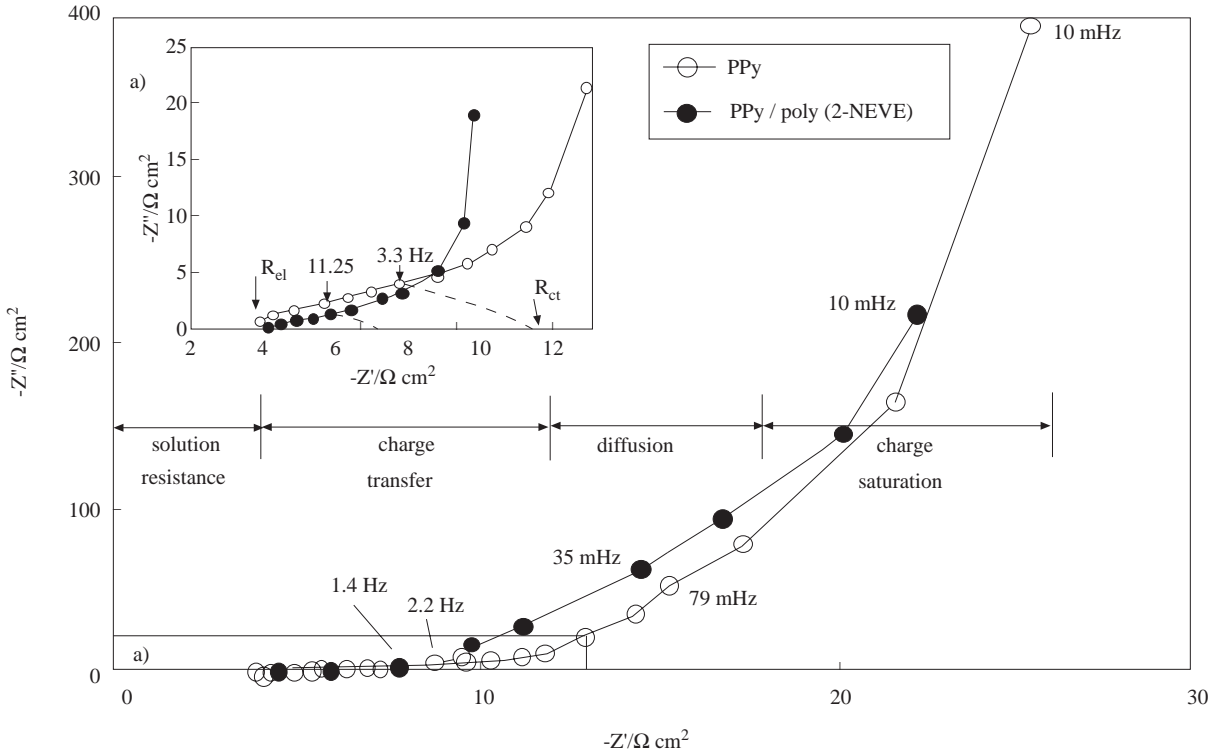


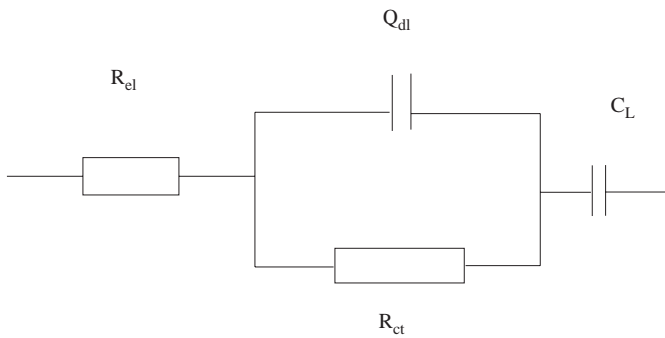
Figure 1. Z'' vs $\log Z'$ plot for \bullet : Ppy/poly(2-NEVE); \circ : Ppy at 0.2 V (SHE).

The impedance parameters of PPy and PPy/poly(2-NEVE) films are summarized in Table 1.

Table 1. Impedance data for PPy and PPy/poly(2-NEVE) films ($1.5 \mu\text{m}$) in oxidized (0.2 V/SHE) state at room temperature

Polymer film	$R_{el}/\Omega\text{cm}^2$	$R_{ct}/\Omega\text{cm}^2$	$C_{dl}/\text{mF cm}^{-2}$	$R_I/\Omega\text{cm}^2$	$C_L/\text{mF cm}^{-2}$	Specif. capacity/Ahkg $^{-1}$
PPy	3.8	8.0	6.0	14.2	41	50
PPy/poly(2-NEVE)	3.8	3.5	4.0	18.7	74	90

In accordance with these results, the following electric equivalent circuit (EEC), describing the impedance behavior of PPy and PPy/poly(2-NEVE)-films in their conductive (oxidized) state, can be proposed (12,13):



Scheme 1.

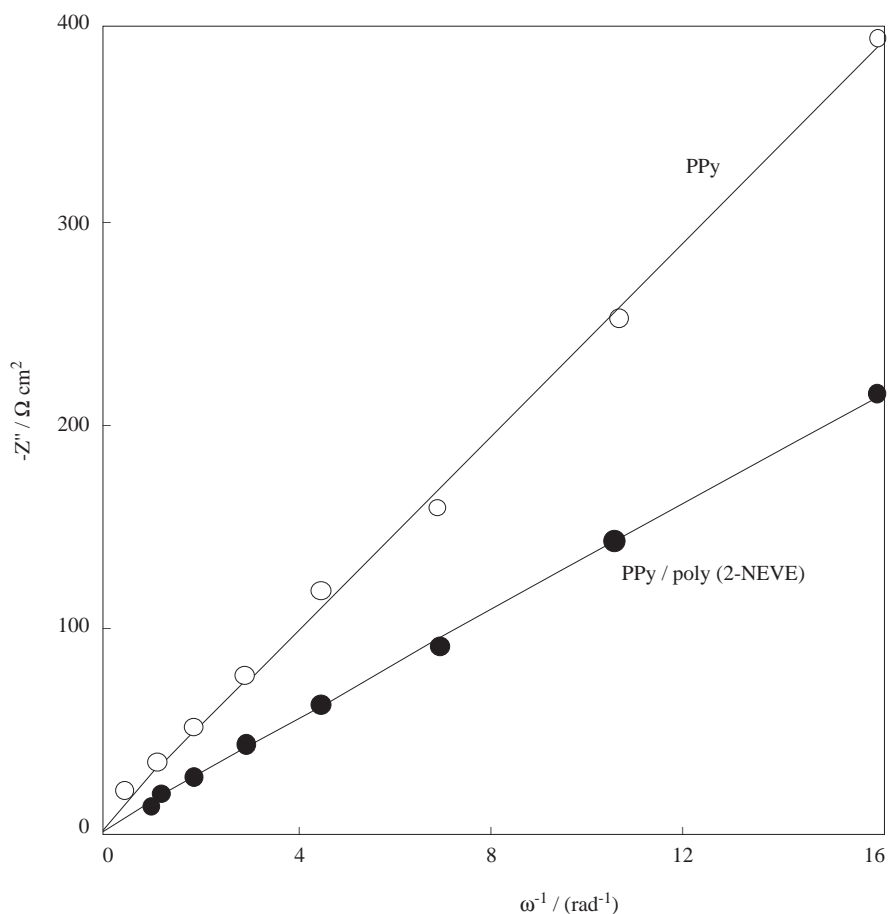


Figure 2. Z'' vs ω^{-1} plot for \bullet : Ppy/poly(2-NEVE); \circ : Ppy

The capacities of the polymer/solution interface (C_{dl}), Table 1, are for about two orders of magnitude higher than expected ones ($20\text{-}60 \mu\text{Fcm}^{-2}$), indicating very rough polymer surfaces and/or the existence of micropores in the outer part of the film.

Using the “finite diffusion model” of Ho and et al.(14), the diffusion coefficient for the doping anions in the polymer film can be determined by equation

$$D = L_{pf}^2 / 3R_L C_L \quad (2)$$

where L_{pf} is the thickness of the polymer film.

Thus, the values 1.3×10^{-8} and $5.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ were calculated for PPy and PPy/poly(2-NEVE) polymer films, respectively. These values are in good agreement with literature data for PPy and and/or similar systems (12,13).

The significant difference between the values of the limiting capacitance of PPy film and that of PPy/poly(2-NEVE) film can be attributed to the change in the morphology (Fig. 4), which influences the doping level of the electrochemically obtained films. It is known that usual value of the doping level of PPy film in $\text{AN}/\text{C10}_4^-$ solution ranges between 0.25 and 0.3. In the case of graft copolymer PPy/poly(2-NEVE) films, the doping level is higher (0.41-0.5), in accordance with the ratio of C_L (PPy/poly(2-NEVE))/ C_L (PPy) ≈ 1.65 . According to the obtained value of the limiting capacitance of PPy film at 0.2 V(SHE), the effective volume capacity is approximately 280 Fcm^{-3} or 0.185 Fmg^{-1} ($\cong 50 \text{ Ahkg}^{-1}$), and

that for PPy/poly(2-NEVE) film is about 460 Fcm^{-3} or 0.31 Fmg^{-1} ($\cong 80 \text{ Ahkg}^{-1}$). These results indicate that PPy/poly(2-NEVE) is preferable as a cathode material as far as application in rechargeable batteries is concerned.

Table 2. Best-fitting parameters for PPy and PPy/poly(2-NEVE) -films at -0.6 V/SHE) and room temperature

Polymer films	$R_{el}/\Omega\text{cm}^2$	$C_{dl}/\mu\text{F cm}^{-2}$	$R_{ct}/\text{k}\Omega\text{cm}^2$	$W/\Omega\text{s}^{1/2}$
PPy	4.4	70	3.72	1.32×10^{-3}
PPy/poly(2-NEVE)	4.4	80	2.90	2.75×10^{-4}

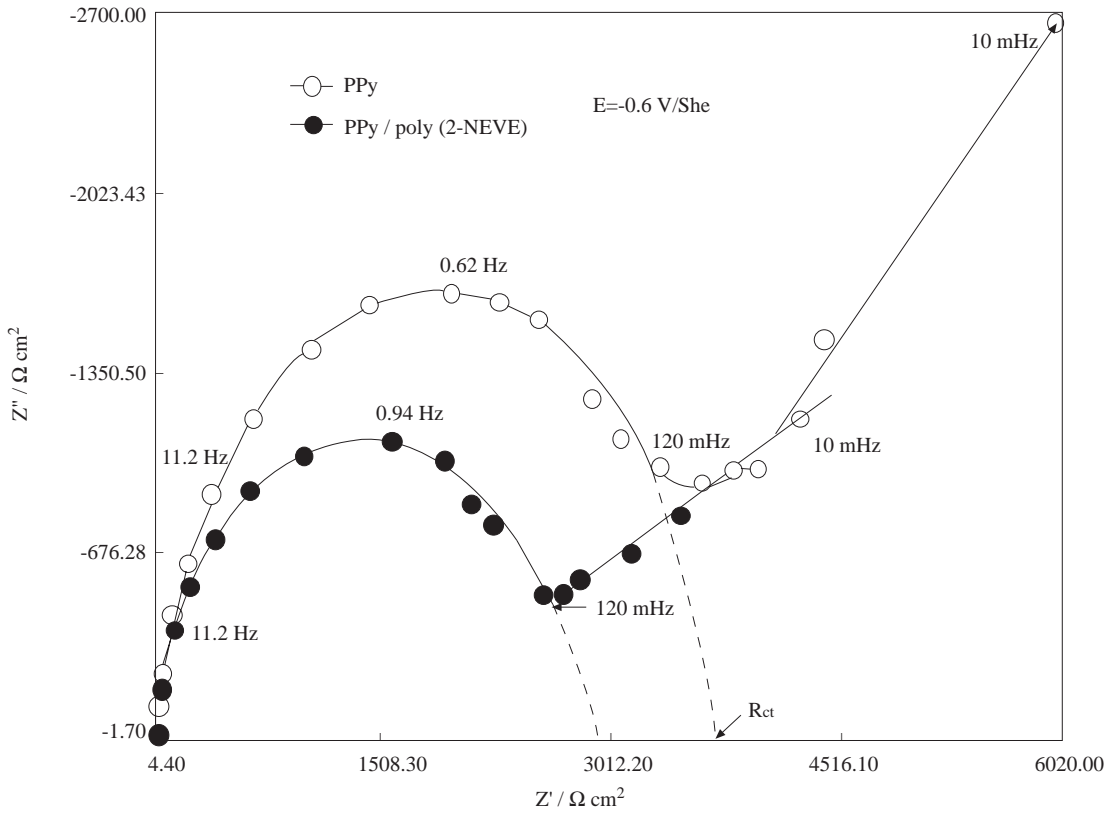
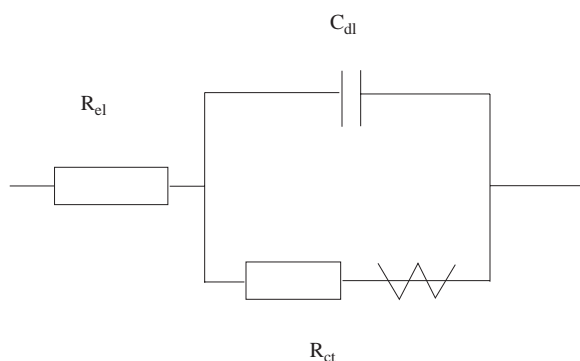


Figure 3. Z'' vs Z' plot for \bullet : PPy/poly(2-NEVE); \circ : PPy at -0.6 V(SHE).

The impedance response of these polymers at -0.6 V/SHE (insulating-reduced state) is presented in Figure 3. The dominating semicircle curves ($-Z''/Z'$), due to the charge transfer processes at the polymer/solution interface, and the linear ($-Z''/Z'$) dependencies at a very low frequencies (Warburg, diffusion, impedance), can be represented with the following EEC:



Scheme 2.

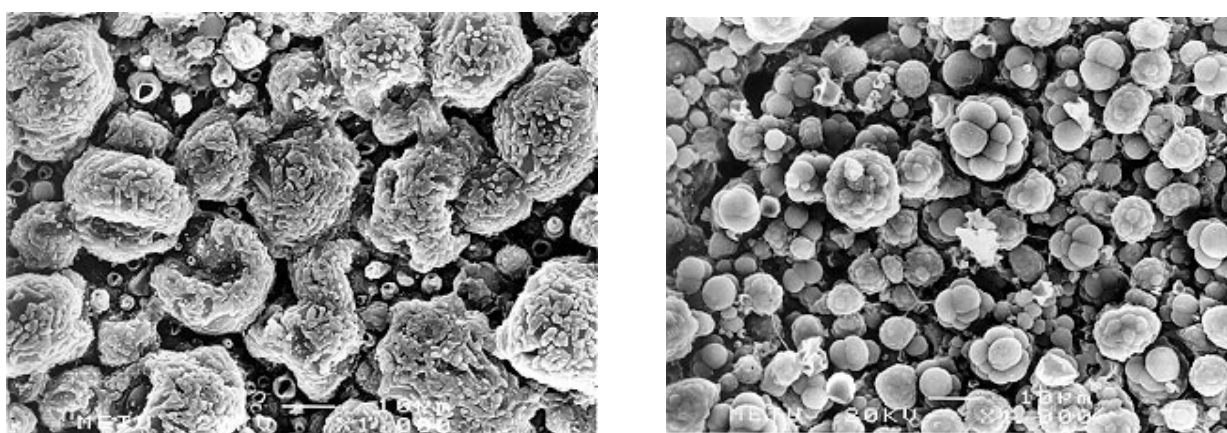


Figure 4. SEM films of a) PPy (solution side) b) PPy/poly(2-NEVE) (solution side)

The best-fitting parameters were obtained using a Boukamp program (15) (EQUIVCRT. PAS) (developed by Bernard A. in the Institute of Phys. Chem. And Electrochem., Heinrich Heine University, Düsseldorf).

As shown, the impedance responses of the PPy and PPy/poly(2-NEVE)-films in their conducting (0.2 V) and insulating state are essentially different. The limiting capacity (C_L), which determines the charge (energy) density of the conducting polymer, is practically zero when it undergoes a change to the insulating state. On the other hand, the charge transfer resistance at a polymer/solution interface, in its insulating state, is about three orders higher than that of the conductive state, indicating a sharp decrease of the exchange current densities ($i_0 = RT/zFR_{ct}$)

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