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Capacitive Behavior in Conducting Polymers:
AC Impedance and Quartz Crystal Microbalance Studies

by

Katsuhiko Naoi, William H. Smyrl, Boone B. Owens and Mary M. Lien

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Corrosion Research Center
Department of Chemical Engineering and Materials Science
221 Church St. SE
University of Minnesota
Minneapolis, MN 55455

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Capacitive Behavior in Conducting Polymers: AC Impedance and Quartz Crystal Microbalance Studies

Katsuhiko Naoi, William H. Smyrl,
Boone B. Owens, and Mary M. Lien
Corrosion Research Center,
Department of Chemical Engineering and Materials Science,
University of Minnesota,
221 Church St SE
Minneapolis, Minnesota 55455

Conducting polymers (like polypyrrole) show super capacitive behavior (100-1000 F/cm²) at low frequencies (Eq. 2). In practical application, these materials (thin films) may be utilized in high energy capacitors. The low-frequency capacitive behavior in such films is ill defined and still unclarified because of the superposition of capacitive currents on the redox process which occurs at electroactive sites. The behavior has been explained in several ways, for example, double-layer formation (1,2), over-doping of anions (3), and non-Nernstian redox processes (3). In the present investigation, AC impedance analysis was adopted to clarify this behavior in electrically conducting polymers (4-6). From the impedance spectra at two different frequency regions, the diffusion coefficient, D , of dopant anions and the redox capacity, C_L , for polymer films were estimated.

The variations in redox capacity and diffusivity of anions for polypyrrole and other films are compared with the mass and volume changes that occur during the charge-discharge process. The electrochemical cells incorporated solutions of various lithium salts in either acetonitrile or propylene carbonate. The polymer doping process was facilitated by the transport of the anions across the electrolyte/electrode interface during the anodic reaction.

AC Impedance Analysis

The impedance spectra of polymers exhibits the behavior typical of thin redox and electronically conductive polymer films (like polyvinylferrocene), as shown in Fig. 1 (4-6).

At high frequencies (region A), charge transfer domination is observed with a semi-circle and, at lower frequencies (region B), diffusion of the anion in the polymer film dominates the impedance results. Finally at the lowest frequency (region C), the finite film thickness limits the extent of diffusion behavior, and the locus rises vertically, owing to the saturation of resistance and capacitance components.

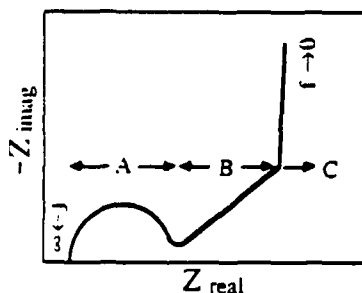


Fig. 1 Typical Cole-Cole plot for a conducting polymer electrode.

In the diffusion controlled region, where the impedance phase angle is $\pi/4$, the magnitude of the impedance is given by Eq. (1)

$$Z = \frac{C_L \cdot L}{\sqrt{D \cdot \omega}} \quad (1)$$

where C_L , D , and L are the low frequency redox capacitance, diffusion coefficient and the polymer film thickness, respectively. Values of C_L were estimated from the low frequency impedance

data (charge saturation region: $\omega \ll \frac{L^2}{D}$). In this range, the phase angle approached $\pi/2$ and C_L was calculated using Eq. (2).

$$C_L^{-1} = - \frac{d(-Z_{\text{imag}})}{d(\omega^{-1/2})} \quad (2)$$

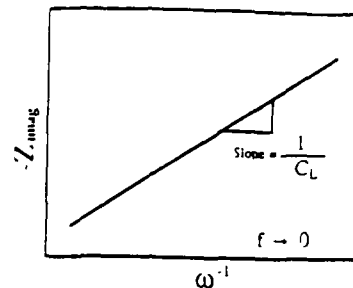


Fig. 2 Relationship between $-Z_{\text{imag}}$ vs. ω^{-1}

At very low frequencies ($< \text{ca. } 30 \text{ mHz}$), the locus for each film becomes vertical, and plots of $-Z_{\text{imag}}$ vs. $1/\omega$ become linear as shown in Fig. 2. From the slope of the curves in Fig. 2, the redox capacitance (C_L) of each film was calculated by using Eq. (2).

At intermediate frequencies ($\text{ca. } 40 \text{ mHz} < f < 210 \text{ mHz}$), each locus was linear with unit slope. In this region, a plot of Z vs. $\omega^{1/2}$ showed a straight line in agreement with Eq. (1). By combining the results for values of C_L with the Z vs. $\omega^{1/2}$ plots, values of the diffusion coefficient (D) were obtained.

QCM & PDIM Analysis

The mass changes during both electropolymerization and charge-discharge processes were monitored by using a Quartz Crystal Microbalance (QCM). In order to check the volume change in the polymer film during the redox process, Phase Detection Interferometric Microscopy (PDIM) was applied, and its dependence on charge/discharge rates was examined.

Charge-Discharge Characteristics

For example, polypyrrole behaved more like a capacitor with the linear increase/decrease in the charge/discharge curves, while polyazulene had a flat discharge. The latter behavior is due to the higher diffusivity (D) and higher redox potential (E_{pac}) of polyazulene ($D = 7.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$; $E_{\text{pac}} \approx \text{ca. } 3.05 \text{ V}$) compared to that of polypyrrole ($D = 1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$; $E_{\text{pac}} \approx \text{ca. } 3.35 \text{ V}$).

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