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Electrochemical Characterization of Electronically Conductive Polypyrrole on Cyclic Voltammograms

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ABSTRACT

Experimental and theoretical cyclic voltammograms for electronically conducting polypyrrole film are obtained from the identical conditions and compared to each other to characterize electrochemical behavior of the polymer. A comparison of the simulated and experimental cyclic voltammograms shows quantitative agreement. The profiles of the dependent variables show that the switching process is governed by the availability of the counterion to the polypyrrole electrode and the amount of electroactive sites. Sensitivity analysis shows that the double layer effects have more influence in the cyclic voltammograms than the electrokinetic effects.

Electrochemically synthesized 1 μm thick polypyrrole film doped with perchlorate in 1M LiClO4-PC solution. A mathematical model, which is based on the conservation of mass and charged species, the porous electrode theory, the double layer theory, and the modified Butler-Volmer-type pseudo homogeneous electrochemical reaction rate expression, is developed. This model is an extension of previous work published in this laboratory (20, 21). Since the electrochemical properties and microscopic structure of polypyrrole film are locally defected, volume-averaged values are used to describe local variables throughout the polymer film to account for the effect of their nonhomogeneity (20, 21). The validity of the model is tested by comparing the model predictions to the experimental data.

The model is used to characterize dynamic behavior (i.e., the relationship between microscopic structure, charge transport, and electrochemical characteristics) within the polypyrrole films by studying the profiles of dependent variables. Also, the model is used to verify the interesting parameters to characterize the properties of polypyrrole by sensitivity analysis and studying the effect of each parameter. The efforts to estimate values for the parameters that would yield the best agreement between model predictions and experimental data are included.

Experimental Descriptions

All experiments are carried out in a single-compartment electrochemical cell with the classic three-electrode configuration; a platinum rotating disk electrode as a working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). A rotating disk electrode (RDE) is used here because of its well-defined hydrodynamics (22, 23). A Luggin capillary tip of the reference electrode is placed as close as possible to the center of the working electrode surface. This enables one to minimize ohmic loss and to use the reference electrode to detect the solution potential near the working electrode. The system is deoxygenated by nitrogen bubbling throughout experiments.

Electrochemical synthesis is carried out using an EG&G Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat equipped with a PAR Model 178 digital coulometer. Polypyrrole film is deposited electrochemically on the platinum rotating disk electrode surface at a constant current density of 1 mA/cm² in propylene carbonate solution containing 0.1M LiClO4 and 0.1M pyrrole monomer. The film thickness is controlled by monitoring the amount of total charge consumed during polymerization. That is, the film thickness is proportional to the total amount of charge consumed.

Fig. 1. A schematic diagram of a single-compartment electrochemical cell with a rotating disk electrode.
passed charge, and 0.24 C/cm² of passed charge yields 1 μm thick polypyrrole film (18, 19). The surface of platinum disk electrode is cleaned and polished to a mirror finish with 1, 0.3, then 0.05 μm alumina powder (Banner Scientific) on a Metron polishing cloth before polymerization.

After the electrochemical synthesis, the cell is thoroughly rinsed with propylene carbonate and then filled with 1M LiClO₄-PC electrolyte solution to perform the cyclic voltammetry. Cyclic voltammetry is accomplished using a PAR Model 173 potentiostat/galvanostat in conjunction with a PAR Model 175 programmer, and resulting current density responses are recorded on a Houston Instruments Model 2000 X-Y recorder.

All chemicals used are reagent grade (Aldrich Chemicals). Pyrrole is distilled twice in a vacuum and then stored under nitrogen. LiClO₄ is used without further purification. The propylene carbonate used as a solvent is further purified by fractional distillation and percolation through activated alumina. The water in the propylene carbonate is removed by adding molecular sieves for a few days. All electrolyte solutions are prepared in a glove box under nitrogen atmosphere.

**Model Descriptions**

The model presented here is for predicting the cyclic voltammetric behavior of the polypyrrole films doped with perchlorate. The modeling regions close to the rotating disk electrode, which are relevant to the development of the model equations, are schematically presented in Fig. 2.

The modeling regions consist of two main regions, two boundaries, and one interregional interface, and they must be modeled simultaneously. These are the boundary interface between a platinum current collector and the polypyrrole electrode (y = 0); the polypyrrole electrode region of width δpp; the inter-regional interface between the polypyrrole electrode and an electrolyte diffusion layer (y = ypp); the electrolyte diffusion layer of width δd; and the boundary at a bulk electrolyte solution (y = Yal).

In all of the regions, the dependent variables are: the concentration of Li⁺ (c⁺), the concentration of ClO₄⁻ (c⁻), the local faradaic charge per unit volume (Qf), the potential of the solid phase (Φs), and the potential of the solution phase (Φl). Because the cyclic voltammetry is controlled by sweeping potential at a constant scan rate, values for these unknowns depend on the perpendicular distance from the platinum current collector of the polypyrrole electrode (y) and applied potential (E), and they are obtained by solving the system of model equations for each region of the cell simultaneously.

The detailed discussion for the assumptions, mathematical treatment of properties of polypyrrole films, and derivation of the governing equations are given in previous works (20, 21). The system of model equations for each region and variable are summarized in Table I.

### Table I. System of model equations for cyclic voltammetry of polypyrrole.

<table>
<thead>
<tr>
<th>Region</th>
<th>Governing equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Polypyrrole electrode region.</td>
<td></td>
</tr>
<tr>
<td>Variables</td>
<td>Governing equations</td>
</tr>
</tbody>
</table>
| c⁺ | \[
\frac{∂c⁺}{∂t} = \frac{z⁺D⁺}{RT} \frac{∂}{∂y} \left( c⁺ \frac{∂c⁺}{∂y} \right) + \frac{∂}{∂y} \left( D⁺ \frac{∂c⁺}{∂y} \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| c⁻ | \[
\frac{∂c⁻}{∂t} = \frac{z⁻D⁻}{RT} \frac{∂}{∂y} \left( c⁻ \frac{∂c⁻}{∂y} \right) + \frac{∂}{∂y} \left( D⁻ \frac{∂c⁻}{∂y} \right) - \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]
| Qf | \[
\frac{∂Qf}{∂t} = \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) + \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \]
| Φs | \[
\frac{∂Φs}{∂y} = \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| Φl | \[
\frac{∂Φl}{∂y} = \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]
| B. Electrolyte diffusion layer. |  |
| Variables | Governing equations |
| c⁺ | \[
\frac{∂c⁺}{∂t} = \frac{z⁺D⁺}{RT} \frac{∂}{∂y} \left( c⁺ \frac{∂c⁺}{∂y} \right) + \frac{∂}{∂y} \left( D⁺ \frac{∂c⁺}{∂y} \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| c⁻ | \[
\frac{∂c⁻}{∂t} = \frac{z⁻D⁻}{RT} \frac{∂}{∂y} \left( c⁻ \frac{∂c⁻}{∂y} \right) + \frac{∂}{∂y} \left( D⁻ \frac{∂c⁻}{∂y} \right) - \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]
| Qf | \[
\frac{∂Qf}{∂t} = \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) + \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \]
| Φs | \[
\frac{∂Φs}{∂y} = \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| Φl | \[
\frac{∂Φl}{∂y} = \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]
| C. Boundary at current collector/polypyrrole electrode. |  |
| Variables | Governing equations |
| c⁺ | \[
\frac{∂c⁺}{∂t} = \frac{z⁺D⁺}{RT} \frac{∂}{∂y} \left( c⁺ \frac{∂c⁺}{∂y} \right) + \frac{∂}{∂y} \left( D⁺ \frac{∂c⁺}{∂y} \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| c⁻ | \[
\frac{∂c⁻}{∂t} = \frac{z⁻D⁻}{RT} \frac{∂}{∂y} \left( c⁻ \frac{∂c⁻}{∂y} \right) + \frac{∂}{∂y} \left( D⁻ \frac{∂c⁻}{∂y} \right) - \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]
| Qf | \[
\frac{∂Qf}{∂t} = \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) + \frac{∂}{∂y} \left( \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \right) - \frac{z⁺}{nF} \frac{∂Qf}{∂y} \frac{∂}{∂y} \left( \frac{∂Qf}{∂y} \right) \]
| Φs | \[
\frac{∂Φs}{∂y} = \frac{z⁺}{nF} \frac{∂Qf}{∂y} \]
| Φl | \[
\frac{∂Φl}{∂y} = \frac{z⁻}{nF} \frac{∂Qf}{∂y} \]

Where \( aj = \alpha_{ref} \left( 1 - \frac{c⁻}{c_{ref}} \right) \exp \left( \frac{α_F}{RT} \eta \right) - \theta_{ref} \exp \left( -\frac{α_F}{RT} \eta \right) \).
D. Interface at polypyrrole electrode/diffusion layer.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Governing equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$c_1 = c_{v,ref}$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$c_2 = c_{v,ref}$</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>$Q_f = 0$</td>
</tr>
<tr>
<td>$\Phi_1$</td>
<td>$\Phi_1 = 0$</td>
</tr>
<tr>
<td>$\Phi_2$</td>
<td>$\Phi_2 = \Phi_{v,ref}$</td>
</tr>
</tbody>
</table>

potential ($E$) sweeps between $-0.8$ and $+0.8$ V under the constant scan rates ($v_c$) of 10 and 20 mV/s at room temperature. The scan rate and the potential interval were selected in this study because a high doping level and a high efficiency have been observed for this thickness (2). All the potentials were referred to the SCE. The resulting anodic (oxidation) and cathodic (reduction) current densities are specified as being positive and negative, respectively.

Experimental results.—Experimental cyclic voltammograms for a 1 µm polypyrrole film in 1M LiClO$_4$-PC electrolyte at scan rates of 10 and 20 mV/s are presented in Fig. 3. The 1 µm polypyrrole film was deposited on polished platinum disk electrode surface with little difficulty by applying 1 mA/cm$^2$ for 240 s. Two main considerations can be derived from the analysis of these cyclic voltammograms, well-defined doping-undoping behaviors and large capacitance effects.

The current density is well-defined as positive and negative for doping and undoping processes, and immediately changes sign when the scan is reversed. The electrochemical behavior in cyclic voltammetry can be explained in relation to the diffusion of counterion. The electrochemical characteristics of the 1 µm polypyrrole film in the 1M LiClO$_4$-PC electrolyte obtained from these experimental cyclic voltammograms are summarized in Table III.

A large capacitive background current density ($i_c$) in the potential region between $-0.2$ and $+0.8$ V vs. SCE (where the film is not oxidized or reduced) is observed and is proportional to the scan rate. The related capacitance, $C_1$, may be obtained by simple calculation based on the expression 

$$C_1 = \frac{i_c}{v_c} $$

The related capacitance of fully oxidized polypyrrole from these experimental cyclic voltammograms have a value of about 33 mF/cm$^2$ (compared to the usual µF/cm$^2$ values for the bare electrodes), which is similar to values obtained by other laboratories (25, 4). The origin of such large capacitance in polymer films has been discussed in detail by Tanguy et al. (26) and Mermilliod et al. (27) The behavior observed is similar to that of a capacitor with very high capacitance and is due to the highly porous structure of polypyrrole films (16).

The polypyrrole film is very stable between $-0.8$ and $+0.8$ V vs. SCE. It is possible to obtain more than 200 cycles with no change in the coulombic capacity of the electrode. Extending the negative limit had little effect on the cyclic voltammogram characteristics. However, when the upper limit is taken to be more positive, there is a progres-

Table II. Operating conditions used for cyclic voltammograms of polypyrrole.

<table>
<thead>
<tr>
<th>Operating temperature ($T$)</th>
<th>298.15 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative potential limit ($E_{neg}$)</td>
<td>$-0.8$ V (vs. SCE)</td>
</tr>
<tr>
<td>Positive potential limit ($E_{pos}$)</td>
<td>$+0.8$ V (vs. SCE)</td>
</tr>
<tr>
<td>Potential scan rate ($v$)</td>
<td>10 and 20 mV/s</td>
</tr>
<tr>
<td>Disk rotation velocity ($\Omega$)</td>
<td>377 rad/s</td>
</tr>
<tr>
<td>Reference electrode potential ($\Phi_{ref}$)</td>
<td>0.0 V (vs. SCE)</td>
</tr>
<tr>
<td>Geometric electrode surface area ($A$)</td>
<td>1 cm$^2$</td>
</tr>
<tr>
<td>Thickness of polypyrrole film ($t$)</td>
<td>1 µm</td>
</tr>
<tr>
<td>Thickness of electrolyte diffusion layer ($t_0$)</td>
<td>0.01 cm</td>
</tr>
<tr>
<td>Reference concentration of Li$^+$ ($c_{ref}$)</td>
<td>0.001 mol/cm$^3$</td>
</tr>
<tr>
<td>Reference concentration of ClO$<em>4^-$ ($c</em>{ref}$)</td>
<td>0.001 mol/cm$^3$</td>
</tr>
</tbody>
</table>

Table III. Electrochemical characteristics of the 1 µm polypyrrole film in the 1M LiClO$_4$-PC electrolyte.

<table>
<thead>
<tr>
<th>Scan rate ($v_c$)</th>
<th>10 mV/s</th>
<th>20 mV/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic peak potential ($E_{pa}$)</td>
<td>$-0.1$ V</td>
<td>$-0.04$ V</td>
</tr>
<tr>
<td>Cathodic peak potential ($E_{pc}$)</td>
<td>$-0.43$ V</td>
<td>$-0.45$ V</td>
</tr>
<tr>
<td>Anodic peak current density ($i_{pa}$)</td>
<td>$+0.95$ mA</td>
<td>$+1.18$ mA</td>
</tr>
<tr>
<td>Cathodic peak current density ($i_{pc}$)</td>
<td>$0.72$ mA</td>
<td>$1.42$ mA</td>
</tr>
<tr>
<td>Anodic charge density ($Q_{pa}$)</td>
<td>$+5.63$ mC/cm$^2$</td>
<td>$+56.3$ mC/cm$^2$</td>
</tr>
<tr>
<td>Cathodic charge density ($Q_{pc}$)</td>
<td>$-53.8$ mC/cm$^2$</td>
<td>$-53.8$ mC/cm$^2$</td>
</tr>
</tbody>
</table>
Table IV. Fixed parameter values used for polypyrrole.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faradaic charge of neutral polypyrrole (Qf,nd)</td>
<td>$1.0 \times 10^{-2}$ C/cm$^3$</td>
</tr>
<tr>
<td>Faradaic charge of oxidized polypyrrole (Qf,oc)</td>
<td>120.0 C/cm$^3$</td>
</tr>
<tr>
<td>Porosity of neutral polypyrrole ($e_{nd}$)</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Exponent on porosity term (ex)</td>
<td>0.5</td>
</tr>
<tr>
<td>Exchange current density (i_0)</td>
<td>10.0 A/cm$^3$</td>
</tr>
<tr>
<td>Anodic transfer coefficient (a_o)</td>
<td>0.7</td>
</tr>
<tr>
<td>Cathodic transfer coefficient (a_c)</td>
<td>0.3</td>
</tr>
<tr>
<td>Open-circuit potential ($U_{oc}$)</td>
<td>5.075 V (vs. Li)</td>
</tr>
<tr>
<td>Number of electron (n)</td>
<td>1</td>
</tr>
</tbody>
</table>

*Estimated values.

The local faradaic and capacitive transfer currents per unit voltammogram of the polypyrrole film consists of two regions as shown in Fig. 4. The estimated value of each parameter in Table IV is obtained by comparison between experimental and simulated cyclic voltammograms and is discussed in detail later.

The current density relative to the projected electrode area, $i$, is obtained by integrating the local transfer current per unit volume ($a_j$) over the porous polypyrrole electrode region

$$i = \int_{y=0}^{3-y_{wp}} a_j dy$$  \[2\]

It is noted that the value of the current density should be equal to the superficial current density in the solid phase ($i_s$) at the current collector/polypyrrole electrode interface ($y = 0$)

$$i = i_s \bigg|_{y=0}$$  \[3\]

This is because all of the current enters (reduction) or leaves (oxidation) the cell via the current collector.

As discussed earlier, the current density in the cyclic voltammogram of the polypyrrole film consists of two distinctive components: faradaic current density caused by the electrochemical reaction and capacitive current density caused by the double layer within the porous polypyrrole film. $i_1$ and $i_2$ are obtained by integrating the local faradaic and capacitive transfer currents per unit volume ($a_{j1}$ and $a_{j2}$) over the porous polypyrrole electrode region (see Eq. [2]). A typical cyclic voltammogram and its components of 1 μm polypyrrole film at a scan rate of 20 mV/s are presented in Fig. 5 as a function of the applied potential.

At potentials negative of -0.4 V, the entire polypyrrole electrode is in a fully neutral nonconducting state. For the anodic sweep of potential (increasing potential), neutral polypyrrole starts to converge to an oxidized conducting state at potentials positive of -0.4 V. The oxidation yields the consumption of both faradaic and capacitive charges within polypyrrole film. The faradaic current density ($i_f$) initially increases with time because of the increasing driving force (applied potential), then decreases because of the limited electroactive area (neutral polypyrrole sites) and the concentration of counterion within the polymer film as the polypyrrole electrode is significantly oxidized. However, the capacitive current density ($i_c$) increases continuously with time because the polypyrrole electrode is fully oxidized. At potentials positive of +0.2 V, the oxidation reaction is complete, and the entire polypyrrole electrode is in its fully oxidized conducting state. That is, the current density is entirely dominated by the double layer effect because no more oxidation of the polypyrrole can occur. The related capacitance ($C_f$) of fully oxidized polypyrrole from these simulated cyclic voltammograms has a value of about 38 mF/cm$^2$ and is well matched with that obtained from experiment.

When the scan is reversed in the cathodic direction (decreasing potential), the pure capacitive current density immediately changed sign. Oxidized polypyrrole starts to converge to the neutral state at potentials negative of +0.2 V and yields decreasing faradaic and capacitive charges. At a potential -0.6 V, the entire polypyrrole electrode is again in its fully neutral state.

Dependent variables profiles.—The dynamic profiles of the dependent variables in the porous polypyrrole electrode region at a scan rate of 20 mV/s are shown in Fig. 6. The concentration was made dimensionless relative to its reference concentrations ($c_{ref}$). It is noted that the concentration profiles of cation (Li$^+$) have similar distributions because of electro-neutrality.

Initially, the concentration of the counterion is uniform throughout the cell at the reference concentration ($c_{ref}$). For anodic scan, anions (ClO$_4^-$) are consumed at the porous polypyrrole electrode region because of the oxidation of neutral polypyrrole and the increase of double layer charge. The cation (Li$^+$) is transported from the bulk to the porous electrode region where it diffuses and migrates (c$-$,ref). It is noted that the concentration profiles of anions and cations have similar distributions because of electro-neutrality.
grates to electroactive sites within the porous region. After polypyrrole has been fully oxidized, the concentration distribution within the porous polypyrrole electrode region bounced back to a certain equilibrium state. This is because no more oxidation of polypyrrole occurs and counterions are consumed by double layer charge only.

For cathodic scan, the oxidized polypyrrole sites are reduced and the opposite phenomena occurred. Anions (ClO$_4^-$) are produced within the porous polypyrrole electrode region because of reduction of oxidized polypyrrole and decrease of double layer charge. The counterion (ClO$_4^-$) is transported from the porous electrode region to the bulk. Since the effective diffusivities of Li$^+$ and ClO$_4^-$ within the porous layer are much smaller than the free stream diffusivity of these species, the concentration gradients within the porous region must be larger to make up for the slower movement of the ions.

Figure 7 shows the distribution of faradaic charge per unit volume consumed within polypyrrole electrode due to the electrochemical reaction at a sweep rate of 20 mV/s. The faradaic charge per unit volume was made dimensionless by using the maximum faradaic charge value ($Q_{f,oxd}$) as the reference point.

Initially, the polypyrrole electrode is in fully neutral state ($Q_f = Q_{f,rel}$) and is ready to be oxidized. For the anodic scan, the faradaic charge accumulation in the outer layer of the polypyrrole electrode (electrolyte diffusion layer side) is faster because of the concentration gradient effect within the polypyrrole electrode as shown in Fig. 7. After polypyrrole has been fully oxidized, the faradaic charge distribution becomes uniform at $Q_f = Q_{f,oxd}$. During reduction, the faradaic charge is withdrawn more slowly in the inner layer of the polypyrrole electrode (current collector side) because of the diffusion limitation. Note that charge accumulates rapidly throughout the entire electrode.

The electrochemical properties (such as porosity, conductivity, diffusivity, mobility, etc.) have similar distribution throughout the polypyrrole electrode region because of the assumption that these properties are proportional to the faradaic charge per unit volume consumed within polypyrrole electrode (21).

Figure 8 shows the distribution of the potential difference between solid and solution phases, the driving force for the electrochemical reaction and the double layer charge within the porous polypyrrole electrode region at a sweep rate of 20 mV/s. For convenience, the potential difference is represented by $\Phi_I - \Phi_S - E$.

The potential difference increases with time indicating that the electrochemical reaction must proceed at a faster rate to compensate for the decreasingly available active surface area and reactive species in solution phase. It shows that the potential difference at the inner layer (current collector side) is higher because of diffusion limitation of counterion. The positive and negative values lead cathodic (reduction) and anodic (oxidation) reactions, respectively.

Sensitivity analysis.—Since the results predicted by the model depend on the physical and electrochemical parameters used, it is necessary to examine the sensitivity of the model predictions on these parameters and identify parameters which can be discarded from the further parametric analysis. If the model predictions are relatively insensitive to a parameter, then a fairly wide range of values for that insensitive parameter could be used without significantly affecting the predictions of the model. It is often the case that the more parameters that are estimated, the more uncertain are the estimates due to interaction between the parameters, poor seiling, and round-off errors (28).

The sensitivity coefficient of each parameter of interest, $S_k$, can be determined from the changes in the predicted anodic current density response as follows

$$S_k = \sum_{E=-0.8}^{E=0.8} \frac{\Delta i_a(E)}{m \Delta P_k}$$

where

- $\Delta i_a(E) = |i_a(E) - i_a(E)|$
- $\Delta P_k = |P_k - P_k'|$
- $i_a$ = predicted anodic current density with $P_k$
- $i_a'$ = predicted anodic current densities with $P_k'$
- $P_k$ = perturbed value of parameter $k$
- $P_k'$ = reference value of parameter $k$
- $m$ = number of data points
For convenience, only anodic (oxidation) current density responses are used to analyze the sensitivity of the model predictions here. Anodic current density responses shown in Fig. 4 and their conditions were used as the reference case. When an interesting parameter is perturbed slightly (i.e., multiplying by 1.05 to the reference value) while holding the values of all other parameters equal to that of the reference case, a new set of data of predicted anodic current density responses between the reference and perturbed cases (Δλ) is calculated at each potential interval and summed over the entire potential region used. The results of the sensitivity analysis are shown in Tables V and VI.

Table V. Sensitivity analysis on various physical parameters.

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>Sensitivity coefficient (Sk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of polypyrrole film (δpp)</td>
<td>0.66469</td>
</tr>
<tr>
<td>Porosity of polypyrrole film (εpp)</td>
<td>0.52389</td>
</tr>
<tr>
<td>Thickness of diffusion layer (δh)</td>
<td>0.12216</td>
</tr>
<tr>
<td>Exchange current density (αιoxd)</td>
<td>0.08758</td>
</tr>
</tbody>
</table>

Table VI. Sensitivity analysis on various electrochemical parameters.

<table>
<thead>
<tr>
<th>Electrochemical parameters</th>
<th>Sensitivity coefficient (Sk)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximal Faradaic charge (Qf,oxd)</td>
<td>0.66469</td>
</tr>
<tr>
<td>Double layer constant (α*)</td>
<td>0.52389</td>
</tr>
<tr>
<td>Zero charge potential (εpzr)</td>
<td>0.49472</td>
</tr>
<tr>
<td>Anodic transfer coefficient (αιa)</td>
<td>0.12216</td>
</tr>
<tr>
<td>Exchange current density (αιoxd)</td>
<td>0.08758</td>
</tr>
</tbody>
</table>

Effects of parameters.—Many factors come into play when calculating the sensitivity coefficients. For example, the exchange current density and transfer coefficient strongly influence the initial slope in the cell current density. On the other hand, the maximum faradaic charge and double layer constant have more influence later when polypyrrole films are significantly oxidized. Thus, it is necessary to understand the detailed effects of each parameter, which is identified as relatively sensitive on model prediction. The effects of the maximal faradaic charge (Qf,oxd), the double layer constant (α*), the anodic transfer coefficient (αιa), and the exchange current density (αιoxd), on the cyclic voltammograms are examined and estimated.

Figure 9 shows the effects of the maximum faradaic charge (Qf,oxd) in the cyclic voltammograms. This parameter affected both faradaic and capacitive current densities. The value does not influence the initial slope of the current density. However, the larger value of maximal faradaic charge yields higher and broader peak current densities, and higher background capacitive current density. This is because the amount of electroactive material is proportional to this value.

Figure 10 shows the effects of the double layer constant (α*) in the cyclic voltammograms. The region where polypyrrole is significantly reduced is not affected because this parameter only influences the double layer charging. Since the local capacitive transfer current per unit volume is proportional to this parameter (21), the larger value of double layer constant (α*) yields higher capacitive current density.

Figures 11 and 12 show the effects of the electrokinetic parameters describing the electrochemical reaction of polypyrrole. These parameters show significant effects in the region where polypyrrole is oxidizing or reducing. No effects are observed in the background capacitive current density. Figure 11 shows the effects of anodic transfer coefficient (αιa) in the cyclic voltammograms. This value strongly influences the shape of the peak current density. Increasing the anodic transfer coefficient (αιa) yields higher and narrower anodic
peak current density. The opposite is true for the cathodic direction because the sum of anodic and cathodic transfer coefficients ($\alpha_a$ and $\alpha_c$) is set equal to 1.

Figure 12 shows the effects of exchange current per unit volume ($i_{\text{io,ref}}$) in the cyclic voltammograms. This parameter shows a most significant influence in the peak current density. Increasing exchange current per unit volume yields both an increase in anodic and cathodic peak current densities and reducing potential difference between anodic and cathodic peak. This is because the electrochemical reaction rate is proportional to this value.

The value of each independent parameter discussed above has been estimated by comparing the peak and background current densities predicted by the model with the experimental results, and this has been summarized in Table IV. The dependent parameters (diffusion coefficients, mobilities, conductivities, etc.) can be calculated from the relationships given in the model development using the values of the independent parameters estimated here. For example, the effective diffusion coefficients of the counterion ($\text{ClO}_4^-$) within the doped and undoped states of the polypyrrole film are $4.0 \times 10^{-11}$ cm$^2$/s and $1.0 \times 10^{-9}$ cm$^2$/s, respectively. These values are smaller than those obtained from experimental measurements. This may be due to the large capacitive and uncompensated resistance effects in polypyrrole films which are not addressed properly in experiments.

Conclusions and Recommendations

The electronically conducting polypyrrole film has been synthesized electrochemically and used in cyclic voltammetry to study the electrochemical characteristics. The experimental results show that:

1. The simple one-step electrochemical oxidation of pyrrole monomer yields a flexible, metallic, and organic polymer film.
2. The polypyrrole film has a quasi-reversible switching behavior with large capacitive background effects.
3. The switching process of the polypyrrole film is accompanied by distinctive color changes, brown-black at doped state and light yellow at undoped state.
4. The polypyrrole film can be cycled more than 200 times without significant loss of the coulombic capacity of the electrode.

These observations make polypyrrole a prospective candidate in the area of energy storage devices.

The mathematical model based on the porous electrode, dilute solution, and double layer theories, coupled to the Butler-Volmer-type rate expression has been developed to predict the cyclic voltammograms of a polypyrrole film under identical conditions of the experiments. The simulated results show that:

1. Despite the fact that the present model involves a number of simplifications such as the presumption that the electronic conductivity varies linearly with the doping level, a comparison of the simulated and experimental cyclic voltammograms shows quantitative agreement.
2. The modified Butler-Volmer-type rate expression can be applied for the quasi-reversible switching behavior or polypyrrole. This assumes that the appearance of the quasi-reversible peak in the cyclic voltammograms for conducting polymers is not necessarily evidence for the presence of an additional redox process.
3. The profiles of the dependent variables show that the switching process is governed by the availability of the counterion to the polypyrrole electrode and the amount of electroactive sites. Thus, the performance of the polypyrrole-based devices could be improved by physical modifications that increase the electroactive surface area and optimize the rate of ionic charge transport.
4. Sensitivity analysis shows that the parameters describing the double layer effects have more influence than those describing the electrokinetic process. This observation suggests that more emphasis should be placed on evaluating the capacitive effects affiliated with the doping state of polypyrrole.
Better agreement between the simulated and experimental data will be obtained if different charge transport mechanisms are considered for the doping and undoping processes. In addition, the factors which determine the electrochemical characteristics of polypyrrole are the doping level and its functional relationship to the microscopic structure, conductivity, and capacitance. In the absence of any experimental or theoretical data, the presumptions used are adequate for these preliminary analyses. With pertinent experimental or theoretical data to quantify these factors, the model can be used, together with parameter estimation techniques, to determine the electrochemical characteristics of polypyrrole.

The model developed here can be modified to study cyclic voltammetric behavior of other conducting polymers, such as polythiophene, polyaniline, polycarbajole, etc., by simply adjusting the input parameters and their relationships. Also, the model can be extended to predict other electroanalytical techniques, such as ac impedance, chronocoulometry, and chronoabsorptometry. AC impedance can be useful in obtaining more details of the double layer effects.

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LIST OF SYMBOLS

A
a
A'
C'
c
C_{ref}
D
D_{p}
E
E_{eq}
E_{pa}
E_{pp}
E_{po}
E_{pos}
ex
F
f
i
i_{a}

geometric electrode surface area, cm²
specific surface area of polypyrrole film, cm²
rotating disk electrode constant, 0.51023
double layer constant, V
related capacitance of polypyrrole film
concentration of species i, mol/cm³
reference concentration of species i, mol/cm³
diffusion coefficient of species i, cm/s
effective diffusion coefficient of species i within the polypyrrole film, cm²/s
applied potential (potential difference between the current and reference electrode), V
negative potential limit, V
anodic peak potential, V
cathodic peak potential, V
positive potential limit, V
exponent on the porosity term, 0.5
Faraday’s constant, 96,487 C/mol

current density based on projected electrode area, A/cm²
anodic current density with perturbed value of parameter k, A/cm²
anodic current density with reference value of parameter k, A/cm²
capacitive current density based on projected electrode area, A/cm²
faradaic current density based on projected electrode area, A/cm²
exchange current density based on projected electrode area at reference concentrations, A/cm²
anodic peak current density based on projected electrode area, A/cm²
cathodic peak current density based on projected electrode area, A/cm²
superficial current density within the solid phase based on projected electrode area, A/cm²
difference of anodic current densities between reference and perturbed values of parameter k, A/cm²
local capacitive transfer current density within the polypyrrole film based on electrode area, A/cm²
local faradaic transfer current density within the polypyrrole film based on electrode area, A/cm²
local transfer current density within the polypyrrole film based on electrode area, A/cm²
number of data points for sensitivity analysis
current density based on projected electrode area, A/cm²
perturbed value of parameter k

Greek

α
κ
φ
ν
π
σ
ε
δ
γ

anodic transfer coefficient
cathodic transfer coefficient
thickness of the electrolyte diffusion layer, cm
kinematic viscosity, cm²/s
electronic conductivity of the polypyrrole film,
fractional doping level of polypyrrole film
free-stream solution conductivity, β-cm
bulk viscosity
overpotential, V
overpotential at the point of zero charge, V
free-stream solution conductivity within the polypyrrole film, β-cm
effective diffusion coefficient of species i within the polypyrrole film
potential at the solution phase, V

Subscript

c
cation, Li⁺
anion, ClO₄⁻

REFERENCES

Hydrous Oxide Film Growth on Amorphous Ni-Co Alloys

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ABSTRACT

The electrochemical behavior of a Ni51Co23Cr10Mo2Fe1.5B3.5 (weight percent) amorphous alloy ribbon has been investigated in alkaline solutions. When the metal is initially subjected to anodic potentials, an enriched Cr (and possibly B) surface layer is dissolved. Following this, a hydrous oxide film can be readily formed on the electrode surface by a continuous potential cycling method, to a thickness of up to one micron. The film, which has an electrochemical signature which is very similar to the Ni(II)/Ni(III) transition, is electrochromic in nature and displays interference colors when thin. The maximum growth rate of the film per cycle of potential has been found to be 0.15 to 0.20 mC/cm2, achieved by optimization of the magnitude and time spent at the upper and lower potential limits.

There has been a significant amount of interest in the electrochemical behavior of glassy alloys since the earliest reports of their superior corrosion resistance and interesting mechanical, electrical, and magnetic properties (1-10). The low corrosion susceptibility of these materials is not unexpected, due to the virtual absence of classical grain boundaries and other crystalline defects, as well as the frequent presence of elements such as Cr, Ti, Nb, etc. (7, 11-20), which are known to promote the formation of protective oxide films in most environments. There have also been numerous reports concerning the electrocatalytic nature of particular amorphous alloys toward reactions such as hydrogen and oxygen evolution (21-27) and the hydrogenation of carbon monoxide (28, 29). This is also reasonable, as surface defect sites are known to play an important role in heterogeneous electrocatalytic reactions. In the present study, an investigation of the electrochemical oxidation of an amorphous alloy, containing primarily Ni [51 weight percent (w/o)] and Co (23 w/o), was undertaken. Alkaline solutions were utilized in order to minimize the dissolution of these metals, and oxide growth behavior was compared with that observed at polycrystalline Co electrodes. Polycrystalline Ni electrodes have been studied extensively in the past in alkaline solutions (30-39), due to their important application in heterogeneous electrocatalytic reactions such as hydrogen and oxygen evolution (21-27) and the hydrogenation of carbon monoxide (28, 29). This is also reasonable, as surface defect sites are known to play an important role in heterogeneous electrocatalytic reactions. In the present study, an investigation of the electrochemical oxidation of an amorphous alloy, containing primarily Ni [51 weight percent (w/o)] and Co (23 w/o), was undertaken. Alkaline solutions were utilized in order to minimize the dissolution of these metals, and oxide growth behavior was compared with that observed at polycrystalline Co electrodes. Polycrystalline Ni electrodes have been studied extensively in the past in alkaline solutions (30-39), due to their important application in heterogeneous electrocatalytic reactions such as hydrogen and oxygen evolution (21-27) and the hydrogenation of carbon monoxide (28, 29).

At a fresh polycrystalline Co electrode, several different oxidation/reduction steps can be seen in the first sweep of a CV experiment (47-49). With continued potential cycling, the buildup of a hydrous oxide film occurs readily (47, 48, 50, 51), similar to the case at numerous other metals (40-46), where it is believed that new oxide film is formed during each excursion to positive potentials, while negative potentials are required in order to release the newly formed oxide from the metal surface to the overlying hydrous oxide film (40, 41). The principal electrochemical reaction [Co(III)/IV] occurs in the range of 1.0 to 1.5 V vs. RHE. Oxidized Co electrodes, as well as Co/Ni oxide electrodes, have also been investigated (52-54) with respect to the kinetics of the oxygen evolution reaction (OER) at these materials.

The purpose of this research was to determine how the presence of both Co and Ni, as well as several secondary elements (Cr, Mo, and B) influence the nature of oxide growth and the properties of the resulting oxide film. Also, it was of interest to examine the impact of the amorphous structure of the substrate on the properties of the electrochemically formed oxide films. Both electrochemical and ex situ surface analytical techniques were employed in this work in an attempt to answer these questions.

Experimental

Cyclic voltammetry was carried out with the use of a Hokuto-Denko HA301 potentiostat and a Tacussel GSATP function generator, or with the EG&G PARC 175/173 combination when infrared compensation was required. Either a HP 7045B X/Y recorder or a Nicolet 3091 digital oscilloscope was employed to record the electrochemical data. The working electrode (WE) used in all of these experiments was a melt-spun Ni51Co23Cr10Mo2Fe1.5B3.5 composition given in terms of w/o glassy alloy, provided by Allied-Signal Corporation in the form of a ribbon 25 mm wide.