Doping and Undoping of OH\textsuperscript{−} during Redox Processes of Poly(vinyl ferrocene)

Maghana Sathe,a Lei Yu,a Yirong Mo,b and Xiangqun Zenga,*,z

aDepartment of Chemistry, Oakland University, Rochester, Michigan 48309, USA
bDepartment of Chemistry, Western Michigan University, Kalamazoo, Michigan 49008, USA

Poly(vinyl ferrocene) (PVF) electro-oxidation proceeds via coupled oxidation of uncharged ferrocene sites and entry of counterions and solvent into the film. Studies of PVF in the literature often neglect the OH\textsuperscript{−} doping in salt solutions due to its relatively low concentration compared to other major counterions. In this report, the role of OH\textsuperscript{−} ion in the redox processes of PVF in NaClO\textsubscript{4} solutions was studied by monitoring the dynamic changes of the pH near the PVF-modified electrode surface. Our study demonstrated that the OH\textsuperscript{−} ions share an important portion in the counterion doping/undoping processes in neutral NaClO\textsubscript{4} solution.

0 2005 The Electrochemical Society. [DOI: 10.1149/1.1859817] All rights reserved.

Electrodes modified with conductive polymers have been studied extensively for both practical and fundamental applications.1,6 Among all conductive polymers, poly(vinyl ferrocene) (PVF) is one of the most intensively studied polymers by electrochemical techniques because the redox behavior of the ferrocene/ferrocinium couple has already been well characterized and the redox processes of the repeat unit are simple, reversible one-electron transfer reactions. Electrochemical investigations show that the transports of solvent molecules and ions within the polymer films have great impact on the kinetics and thermodynamics of the redox behaviors and on the film surface structure.7 For example, Murray et al. studied PVF electrodes of different types in contact with various electrolyte/solvent systems.6,7 Inzelt and Szabo studied the effect of the concentration of counterions on PVF redox properties.8 These studies show that the movement of electrons within the PVF film requires coincident transport of ions to maintain electroneutrality, and the ion-transport process can influence the overall charge propagation rate. Hillman and Brukenstein,9 in a different approach, visualized the redox switching process of electroactive films as a sequence of several elementary steps: coupled electron/ion transfer, solvent transfer, and polymer reconfiguration. Each individual step could occur before or after coupled electron/ion transfer and on the same or different time scales. To simplify the model, they assumed that the totally oxidized and reduced polymer forms could exist in only two solvated and two-configuration forms and the counterions considered are the major salt anions; OH\textsuperscript{−} ions from water ionization are neglected.

In our previous work,10 X-ray photoelectron spectroscopy (XPS) studies indicated that counterions, such as ClO\textsubscript{4}\textsuperscript{−}, PF\textsubscript{6}\textsuperscript{−}, or BF\textsubscript{4}\textsuperscript{−}, were embedded in the oxidized PVF film from their solution. There was a minor discrepancy of atomic percentage between the iron charge centers and the counterions; for example, the Cl/Fe atom ratio was about 0.93 when PVF was oxidized in 0.1 mol/L NaClO\textsubscript{4} solution. The other 7% of counterions had not been identified by then. In this report, the pH change within the electrode vicinity was monitored by a fast-responding pH meter. The pH value changed and the cyclo-pH-gram showed two peaks during the potential sweep in the forward and the backward scans. It was demonstrated that OH\textsuperscript{−}, even at very low concentration in neutral NaClO\textsubscript{4} solution, shared a noteworthy portion in the counterion doping/undoping processes. This experimental finding was further validated by the quantum mechanical calculations.

Experimental

PVF was supplied by Polysciences, Inc. in polymerized form (molecular weight ca. 25,000). Methylene chloride (Fisher Scientific) was distilled in CaH\textsubscript{2}. Tetrabutylammonium perchlorate (TBAP, GFS Chemicals), NaClO\textsubscript{4}, (GFS Chemicals), and other chemicals (Aldrich) were all analytical grade and used as received. Aqueous solutions were prepared from 18 MΩ deionized water. The PVF film was electrochemically deposited on an evaporated gold electrode on quartz crystal from 2 mM PVF + 0.1 M TBAP/CH\textsubscript{3}Cl\textsubscript{2} solution as described in our previous publication.10 Experiments were carried out at room temperature in a conical cell with a quartz crystal Au electrode mounted at the bottom of the conical cell (Fig. 1). The quartz crystals (International Crystal Manufacturing Co., Inc., Oklahoma City, OK) are AT-cut, 10 MHz, 5 μm finished plates with gold electrodes (~900 Å) evaporated on both sides, of which one side was used as working electrode and another was in the air. The electrochemical active area is ~0.23 cm\textsuperscript{2}. A platinum wire or plate was used as counter electrode, and the reference electrode was a saturated calomel electrode (SCE). A Corning gel-filled combination pH semimicroelectrode (Corning Scientific Instruments, cat. no. 476345) was placed ~2 mm from the working electrode and connected to a digital pH meter (AR50 Accumet Fisher Scientific). The response time of the pH sensor is less than 1 s. The interface of the internal reference electrode for pH measurement and the measured solution has a zero distance from the geometrical center of the glass membrane (Fig. 1), so that the IR

---

* Electrochemical Society Active Member.
\textsuperscript{z} E-mail: zeng@oakland.edu

---

Figure 1. Schematic diagram of experimental cell design and Corning combination pH semimicroelectrode.
As shown in Table I, the nature of counterions and their concentrations as well as the distance of the glass membrane from the PVF film all affect the values of absolute pH change measured during the dynamic PVF redox processes. Increasing either the basicity of the counterions or their concentrations reduces the absolute pH change. The farther the pH electrode was placed from the PVF film, the less the pH changed.

Interestingly, the rate of OH\(^-\) doping increases with the scan rate; bigger pH changes are observed for the faster scan rates (Fig. 3, top). The peak-to-peak separations increase slightly with increasing sweep rate. At scan rates higher than 50 mV/s, the peaks were not observable in the potential range owing to the limitation of the response time of the pH meter. The pH peaks, at 0.48 and 0.22 V, are at similar potentials to the current peaks observed in the CV, i.e., 0.43 and 0.23 V. Furthermore, the maximum pH change values were also proportional to the square root of the sweep rate (see Fig. 3, bottom).

**Discussion**

The pH change could originate from the OH\(^-\) ions’ ingress in and egress off the PVF film. Reactions 1 to 4 and Fig. 4 summarize the OH\(^-\) coupling process during oxidation and reduction of PVF films:

\[
\begin{align*}
\text{Fc} &\rightleftharpoons \text{Fc}^+ + e^- & [1] \\
\text{Fc}^+ + [\text{OH}^-](\text{solution}) &\rightleftharpoons \text{Fc}^+ [\text{OH}^-](\text{film}) & [2] \\
\text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- & [3] \\
\text{H}^+(\text{surface}) &\rightleftharpoons \text{H}^+(\text{bulk}) & [4]
\end{align*}
\]

The total oxidation reactions may be described as follows:

\[
\begin{align*}
\text{Fc}^+ + [\text{OH}^-](\text{film}) &\rightleftharpoons \text{Fc} + \text{H}_2\text{O} \rightleftharpoons \text{Fc}^+ + \text{OH}^- \rightleftharpoons \text{Fc} + \text{H}^+ + \text{OH}^- \rightleftharpoons \text{Fc}^+ + \text{H}^+ + \text{OH}^- \rightleftharpoons \text{Fc} + \text{H}^+ + 2\text{OH}^- \\
\end{align*}
\]

**Table I. Dependence of pH change on supporting electrolyte, their concentrations, and distance from electrode surface (d). Sweep rate = 5 mV/s.**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>0.01 M NaClO(_4) (d ~ 2 mm)</th>
<th>0.01 M NaClO(_4) (d ~ 4 mm)</th>
<th>0.01 M sodium tosylate (d ~ 2 mm)</th>
<th>0.01 M sodium tosylate (d ~ 4 mm)</th>
<th>0.1 M NaClO(_4) (d ~ 2 mm)</th>
<th>0.1 M NaClO(_4) (d ~ 4 mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔpH (oxidation)</td>
<td>0.28</td>
<td>0.15</td>
<td>0.16</td>
<td>0.14</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>ΔpH (reduction)</td>
<td>0.20</td>
<td>0.13</td>
<td>0.13</td>
<td>0.11</td>
<td>0.02</td>
<td>0</td>
</tr>
</tbody>
</table>
As shown in Reaction 6, the major counterion should be perchlorate. The preceding processes should combine with the diffusion of solvent molecules; these were omitted to simplify the model. Furthermore, in our present study, both proton and hydroxide migrate via the fast Grothuss mechanism\(^1\) in the form of hydrogen-bonded water wires instead of the slow diffusion mechanism that controls the diffusion of perchlorate. The difference between the Grothuss mechanism and the diffusion mechanism can be highlighted in the mobility of H\(^+\) (36.25 ± 10\(^{-8}\) m\(^2\) s\(^{-1}\) v\(^{-1}\)), OH\(^-\) (20.50 ± 10\(^{-8}\) m\(^2\) s\(^{-1}\) v\(^{-1}\)), and perchlorate (7.05 ± 10\(^{-8}\) m\(^2\) s\(^{-1}\) v\(^{-1}\))\(^1\)\(^2\).

In neutral NaClO\(_4\) solution (pH 7.1), the OH\(^-\) concentration is as low as 10\(^{-6.9}\) mol/L. The magnitude of pH changes observed is surprising in such a low OH\(^-\) concentration. To understand exactly what the driving force is for the OH\(^-\) doping in neutral NaClO\(_4\) solution, we employed the density functional theory at the B3LYP level in combination with a continuum solvation model PCM.\(^1\)\(^3\) In this model, the solutes are treated by the quantum mechanics directly but embedded in a dielectric continuum of permittivity equal to that of the solvent to compute the standard binding free energy Δ\(G_{\text{bind}}\) between anion (ClO\(_4^\text{-}\) or OH\(^-\)) and a PVF monomer in solution phase:

\[
\text{ClO}_4^\text{-}(aq) + [\text{CP-Fe-Cp}]^+(aq) \rightarrow \text{CP-Fe(CIO}_4\text{)}\text{-Cp}(aq) \quad [7]
\]

\[
\text{OH}^-\text{(aq)} + [\text{CP-Fe-Cp}]^+(aq) \rightarrow \text{CP-Fe(OH)-Cp}(aq) \quad [8]
\]

based on the following thermodynamic cycle:

\[
\begin{align*}
\text{ClO}_4^\text{-}(g) + [\text{CP-Fe-Cp}]^+(g) & \rightarrow [\text{CP-Fe(CIO}_4\text{)}\text{-Cp}](g) \\
\Delta G_{\text{g}} & \rightarrow \Delta G_{\text{sol}} \\
\text{ClO}_4^\text{-}(aq) + [\text{CP-Fe-Cp}]^+(aq) & \rightarrow [\text{CP-Fe(CIO}_4\text{)}\text{-Cp}](aq) \\
\Delta G_{\text{sol}} & \rightarrow \Delta G_{\text{aq}}
\end{align*}
\]

and

\[
\Delta G_{\text{bind}} = \Delta G_{\text{g}} + (\Delta G_{\text{aq}} - \Delta G_{\text{sol}} - \Delta G_{\text{aq}}) \quad [9]
\]

The basis set we adopted is 6-31G (d,p), and all geometries are optimized in the gaseous phase and assumed unchanged in solution. This level of theory, i.e., B3LYP/6-31G (d,p), has been extensively used to compute standard redox potentials for metallocenes in solution phase.\(^1\)\(^4\) Table II compiles the computational results for our cases in standard states. If we consider [OH\(^-\)] = 10\(^{-7}\) M while all other species are in unitary molarity, the binding free energy between hydroxide and ferrocenium is...
Both facts favor our rationale that OH$^-$ vs. E near the PVF-modified Au electrode. It is not the pH of the bulk that there is a maximum pH peak, which was observed at 0.22 V.

Note that the pH measured is at a dynamic and nonequilibrium state that the percentage of OH$^-$ that the pH change value at 2 mm from the electrode represents the blockage of the working electrode by glass membrane. If we assume even though this experiment is not practical due to the possibility of much bigger than what was measured at 2 mm from the interface, there is a maximum pH peak, which was observed at 0.22 V.

1 The percentage of OH$^-$ that the pH change value at 2 mm from the electrode represents the blockage of the working electrode by glass membrane. If we assume even though this experiment is not practical due to the possibility of much bigger than what was measured at 2 mm from the interface.

...which confirmed that the pH changes were not caused by the electronic effects.

As shown in Fig. 3, a square root proportionality between the anodic and cathodic peak current ($i_p$) and sweep rate is observed. This is characteristic for systems where semi-infinite diffusion conditions are fulfilled. Of particular interest, the change of pH was also proportional to the square root of the sweep rate (Fig. 3). As the $i_p$ vs. $v^{1/2}$ diffusion behavior is promoted by the small charge transport diffusion coefficient $D_{OH}$, the release of all the anions in a short time (fast scan rate) results in a very high concentration of anions at the film surface. Because the hydroxides and protons migrate via the fast Grotthuss mechanism in the form of hydrogen-bonded water wires instead of the slow diffusion mechanism mentioned earlier, this leads to the pH change following the square root of the scan rate and little hysteresis of pH peaks compared to the current peaks in the CV. Consequently, the inverse square root of scan rate dependence of the concentration is not observed based on the diffusion distance $x = \sqrt{D \Delta t}$. At higher sweep rates, the pH peaks were not clear in the potential range owing to the slow response time of the pH meter.

Conclusions

Shinohara et al. studied the electrically controlled ion transfer and pH changes near a polypyrrole-modified electrode. Because polypyrrole is a basic polymer, they explained that the discrepancy they observed between the amounts of major electrolyte anion incorporation and the electrochemical doping charge suggested the simultaneous doping of OH$^-$ other than the major anion in the solution. In this work, we have successfully demonstrated for the first time the transfer of OH$^-$ ions during the doping and undoping of anions in PVF film along with the major anions in solution. Little hysteresis of pH peaks is observed in comparison to the current peaks in the CV owing to the hydroxide and proton migration via the fast Grotthuss mechanism in the form of hydrogen-bonded water wires instead of the slow diffusion mechanism. The change of pH is proportional to the square root of the sweep rate.

Acknowledgments

This research was supported by Oakland University start-up funds, ACS PRF 36833-GB5, and partly by NIH 4R33 EB000672-02. We thank Dr. Quinxi Xie for help in modifying the WinWedge software for pH data acquisition.

Oakland University assisted in meeting the publication costs of this article.

References