Electropolymerization of Polyaniline in the Presence of Ferricyanide

Farhad Akrami, Lucas Marinelli, and Ryan M. West
University of San Francisco, Department of Chemistry, San Francisco, CA 94117

Abstract

- Here, we demonstrate that electropolymerization of aniline (which is accompanied by deposition on the electrode) in the presence of ferricyanide leads incorporation of the ferricyanide anions into the resulting polyaniline (PANI) film.
- Electropolymerization with ferricyanide causes an increase of the apparent deposition rate compared to deposition of PANI alone.
- Simultaneous cyclic voltammetry (CV) and quartz crystal microbalance (QCM) measurements in background electrolyte show a change in counter ion ingress/egress during oxidation and reduction of the film.
- A novel “inverted” mass transport behavior is observed, suggesting a cation-exchange mechanism for maintaining charge neutrality during oxidation of the polymer.
- The behavior of the PANI-ferricyanide film is compared with films polymerized in the presence of potassium hexacyanoruthenate(II), FeCl₆, and RuCl₃.
- The potassium hexacyanoruthenate(II) enhances the polymerization rate and alters the electrochemical behavior of the film, much like ferricyanide, while FeCl₆ and RuCl₃ do not induce such an effect.
- Spectroscopic measurements confirm the presence of ferricyanide and hexacyanoruthenate(II) in the polymer.

Background

Polyaniline

- Polyaniline (PANI) is a conducting polymer with good long-term stability, high conductivity, and good biocompatibility, making it a promising candidate for chemical and biological sensors.
- Polyaniline thin films can be synthesized by oxidative electropolymerization of aniline from acidic solutions, resulting in electrically conducting thin films deposited on the working electrode (Pt or Au in this work).
- The properties of the resulting films depend on both the oxidation state and the protonation state. [1]

\[
\begin{align*}
\text{NH}_2 & \text{NH}_2 \\
\text{N}^+\text{t-C}_{2n} \text{H}_{4n} & \text{N}^+\text{t-C}_{2n} \text{H}_{4n} \\
\text{Fe(CN)}_6^3 & \text{Fe(CN)}_6^{3-} \\
\text{Cr} & \text{Cr} \\
\end{align*}
\]

1. LB = Leucoemeraldine Base – fully reduced, yellow color
2. PB = Pernigraniline Base – fully oxidized, purple color
3. EB = Emeraldine Base – partially oxidized, green color

Results

eQCM Deposition

- Polyainline
  - CV of PANI grows with each cycle as more aniline is oxidized.
  - Mass increases roughly exponentially in time.
  - The CV (current vs. time) appears roughly exponentially with each cycle.

- Polyainline + Fe(CN)_6^{3-}
  - CV shows Fe(CN)_6^{3-}
  - Rate of mass increase is over twice that of PANI alone for the same amount of PANI deposited.

Results and Outlook

- We have discovered a novel composite material consisting of polyaniline and Fe(CN)_6^{3-}.
- The material can be synthesized and deposited electrochemically on platinum and gold electrodes (and likely carbon as well) in one step.
- The films display a mass exchange behavior opposite of typical PANI films.
- Next, we will study the behavior of PANI with other transition metal complexes, particularly ones that also have a net negative charge.
- We hope these studies will allow us to elucidate the ion-exchange mechanism.

Acknowledgments

- The USF Faculty Development Fund was used to purchase materials for this work.

References