Electropolymerization of Polyaniline in the Presence of Ferricyanide

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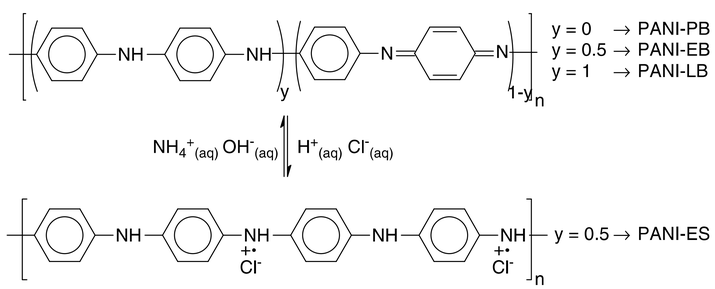
Abstract

- 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), $FeCl_3$ and $RuCl_3$.
- The potassium hexacyanoruthenate(II) enhances the polymerization rate and alters the electrochemical behavior of the film, much like ferricyanide, while $FeCl_3$ and $RuCl_3$ do not induce such an effect.
- Spectroscopic measurements confirm the presence of ferricyanide and hexacyanoruthenate(II) in the polymer.

Background

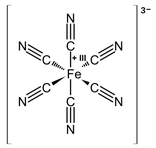
Polyaniline

- 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]



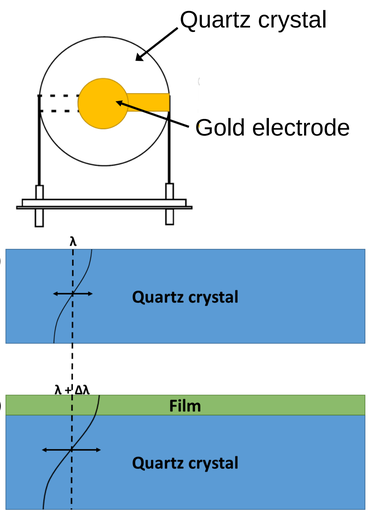
1. LB = Leucoemeraldine Base – fully reduced, yellow color
2. PB = Pernigraniline Base – fully oxidized, purple color
3. EB = Emeraldine Base – partially oxidized, green color

$Fe(CN)_6^{3-/4-}$ in 2 M HBF_4



In neutral pH:
$Fe(CN)_6^{3-} + e \rightarrow Fe(CN)_6^{4-}$ $E^0 = 0.356$ V vs SHE
In acidic solution (used here) [3]:
$2H^+ + Fe(CN)_6^{3-} + e \rightarrow H_2Fe(CN)_6^{2-}$ $E^0 \sim 0.7$ vs SHE

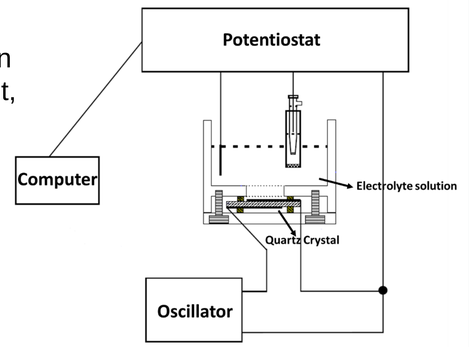
Quartz Crystal Microbalance (QCM)



- When an electrode on the crystal is used as the working electrode during an electrochemical experiment, the mass changes associated with electrodeposition can be monitored (known as **electrochemical quartz crystal microbalance, eQCM**).
- The use of quartz crystals enables the possibility of measuring a change in mass by monitoring the crystal frequency [3].
- The Sauerbrey equation describes the relationship between frequency and mass:

$$\Delta f = -sensitivity \times \Delta m$$

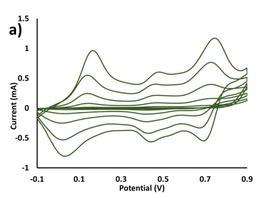
- The *sensitivity* depends on the fundamental resonance frequency, piezoelectric active area, density of quartz, and the shear modulus of the crystal.



Results

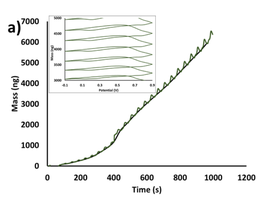
eQCM Deposition

Polyaniline



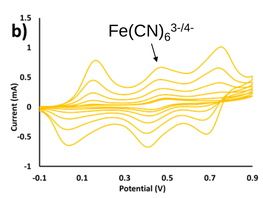
Current vs. E

- CV of PANI grows with each cycle as more aniline is oxidized.
- Mass increases roughly exponentially in time.



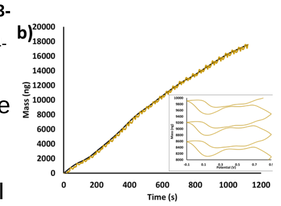
Mass vs. time (and E)

Polyaniline + $Fe(CN)_6^{3-}$



Current vs. E

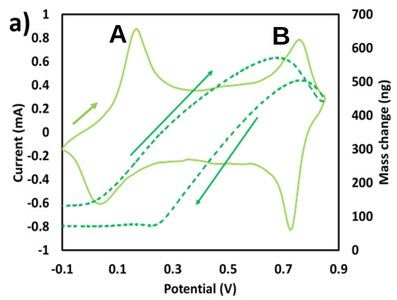
- CV shows $Fe(CN)_6^{3-/4-}$ redox wave
- Rate of mass increase is over twice that of PANI alone for the same amount of PANI deposited.



Mass vs. time (and E)

eQCM while cycling in HBF_4

eQCM (CV) of PANI

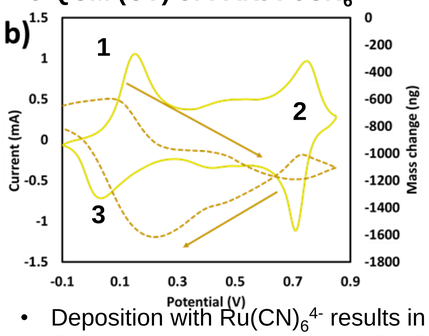


Mass changes are typical of PANI:
B. 1st oxidation of PANI:
Leucoemeraldine → Emeraldine
Accompanied by ingress of BF^- from solution to compensate (+) charge on polymer

B. 2nd oxidation of PANI:
Emeraldine → Pernigraniline
Accompanied by loss of H^+ to compensate (+) charge on polymer

- Deposition with $FeCl_3$ and $RuCl_3$ result in the same behavior.
- Spectroscopic results suggest that these compounds are not incorporated in the films.

e-QCM (CV) of PANI-$FeCN_6$

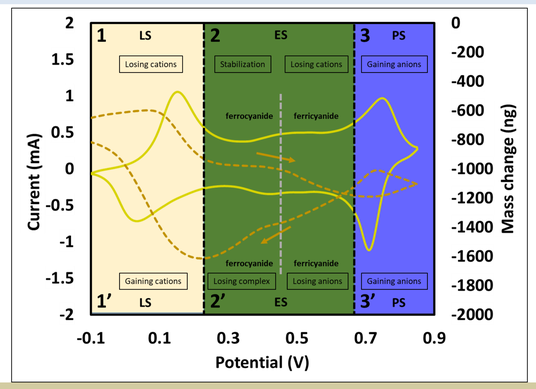


The CV (current vs. time) appears to be very similar to that of PANI-alone. **But the mass changes are different:**

1. During the first oxidation, mass is lost
2. Mass increases slightly during second oxidation before decreasing again
3. Mass is rapidly gained during reduction to initial state

- Deposition with $Ru(CN)_6^{4-}$ results in similar behavior.
- Spectroscopic results suggest $Fe(CN)_6^{3-}$ and $Ru(CN)_6^{4-}$ can be incorporated in the film.

Working Model



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
[1] D.W.Hatchett, M. Josowicz, J. Janata, *J. Phys. Chem. B*, 1999, 103, 10992-10998
[2] M. T. Ramirez, A. Rojas-Hernandez, I. Gonzalez, *Talanta*, 1997, 44, 31-37
[3] J. Janata, Principles of Chemical Sensor, 2nd ed. 2009