Properties of electrochemically grown polyaniline on ITO

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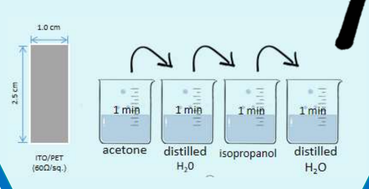
INTRODUCTION

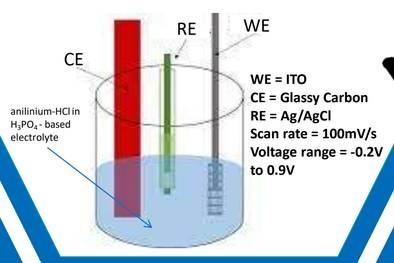
- Conducting polymers (CPs)
  ex. Polyaniline (PAni) known for its:
  - ✓ ease in synthesis
  - ✓ environmental stability and
  - ✓ easy to dope by protonic acids
- Applcations of electrochemical properties of PAni:
  - ✓ sensors
  - ✓ magnetic shielding
  - ✓ electrochemical capacitors
  - ✓ application of rechargeable power sources, etc.
- No reports were done on three electrode cell system utilizing ITO, Ag/AgCl and glassy carbon in anilinium-HCl and H_3PO_4 – based electrolyte in N_2 environment, except those that were done in our laboratory.
- In this study, utilization of N_2 was not included.

METHODS

SUBSTRATE CLEANING



POTENTIODYNAMIC ELECTROPOLYMERIZATION



CYCLIC VOLTAMMETRY ANALYSIS

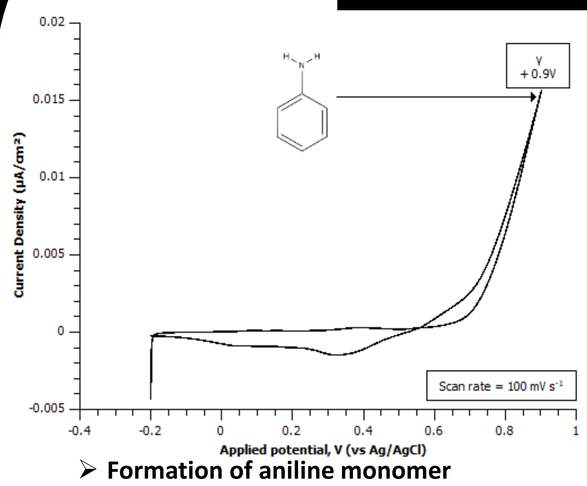
CAPACITANCE CALCULATION

$$C = \frac{S}{\Delta E \times v \times A}$$

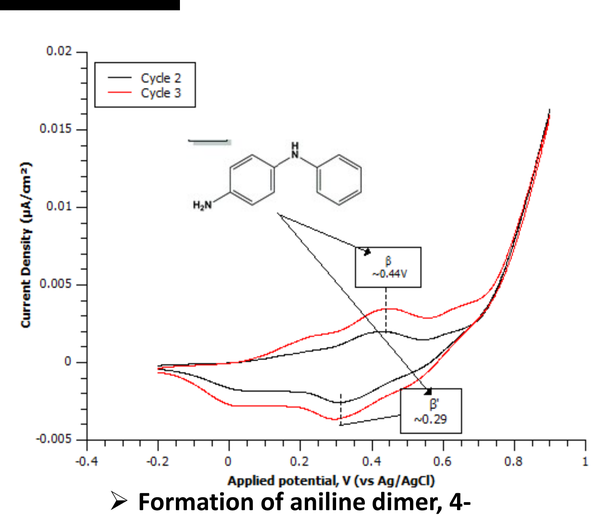
S = total area under the CV curve
ΔE = potential window applied
v = scan rate
A = surface area of the electrode material

RESULTS AND DISCUSSION

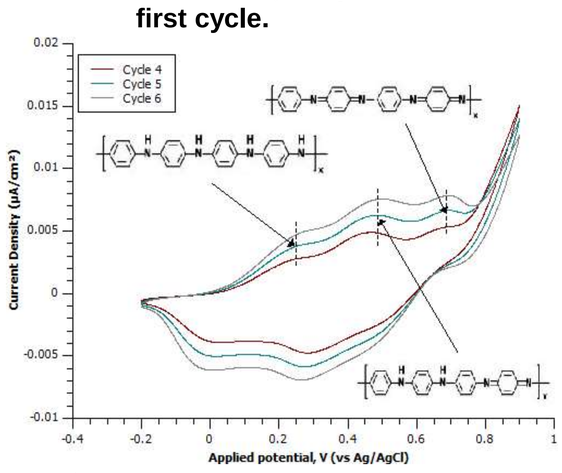
CYCLIC VOLTAMMETRY



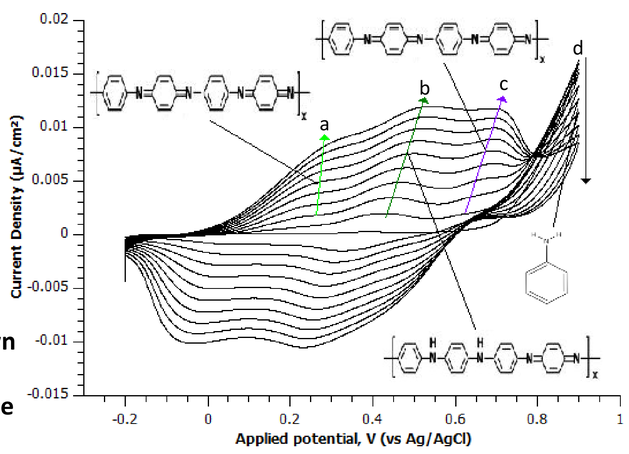
- Formation of aniline monomer
  - ❖ Presence of peak γ at +0.9V on the first cycle.



- Formation of aniline dimer, 4-aminodiphynelamine (4-ADA)
  - ❖ The CV exhibited a redox couple ββ' at ~0.2V and ~0.4V.

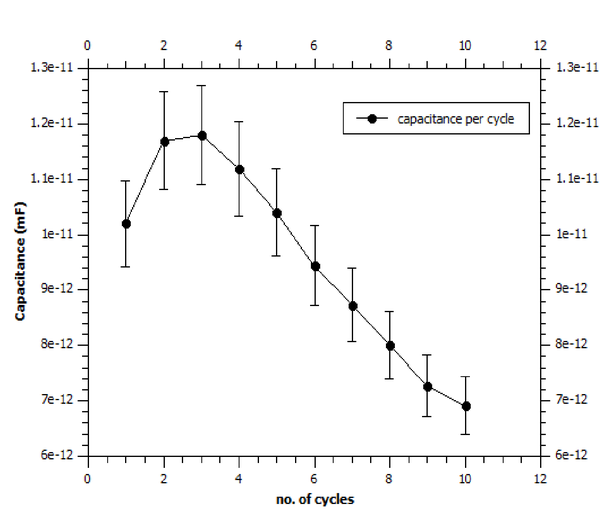


- Formation and growth of polyaniline shown in the oxidation.
- Peak ~0.2V - conversion of leucoemeraldine base (LEB) to emeraldine salt (ES).
- Peak ~0.6V - conversion of ES to pernigraniline base (PNB).
- Transformation of aniline dimer, 4-ADA into emeraldine.



(a) LEB to ES, (b) ADA to ADA oxidation,
(c) ES to PNB, (d) AnH^+ oxidation

CAPACITANCE



- Loss in capacitance value
  - ❖ Diffusion of electron ion into electrode internal structure and pore become difficult.
  - ❖ Occurence of non-uniform interaction between the electrolyte and electrode materials.

Rate Equation of PAni Electropolymerization

Starting $An + H^+ \rightleftharpoons AnH$, $K_{eq} = \frac{[AnH^+]}{[An][H^+]}$ Eq. 1

then

Step 1 $AnH^+ \rightarrow AN^+ + H^+ + e^-$, $\frac{d[An^+]}{dt} = k_1[AnH^+] - 2k_2[An^+]^2 = 0$ Eq. 2,

Step 2 $2An^+ \rightarrow ADA + 2\,H^+$, $\frac{d[ADA]}{dt} = 2k_2[An^+]^2 - k_3[ADA] = 0$ Eq. 3,

Step 3 $ADA \rightarrow ADA^+ + e^-$, $\frac{d[ADA^+]}{dt} = k_3[ADA] - 2k_4[ADA^+]^2 = 0$ Eq. 4, and

Step 4 $2ADA^+ \rightarrow PANI + 2\,H^+$, $\frac{d[PANI]}{dt} = 2k_4[ADA^+]^2$ Eq. 5.

Thus, the rate of equation of polyaniline growth for the 3-electrode-electrolyte system used in the present study is

$$\frac{d[PANI]}{dt} = k_1[AnH^+] \quad \text{Eq. 6.}$$

CONCLUSION

The growth of the peaks as the number of cycle increased suggests a successful electrochemical deposition of PAni films. PAni exhibited a pseudocapacitive behavior which is an evidence of a long life potential cycle stability. Evaluation for various applications are ongoing.

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