DEPARTMENT OF COATINGS & POLYMERIC MATERIALS
NORTH DAKOTA STATE UNIVERSITY

1905: FIRST COATINGS COURSE

1962: DEPARTMENT ESTABLISHED

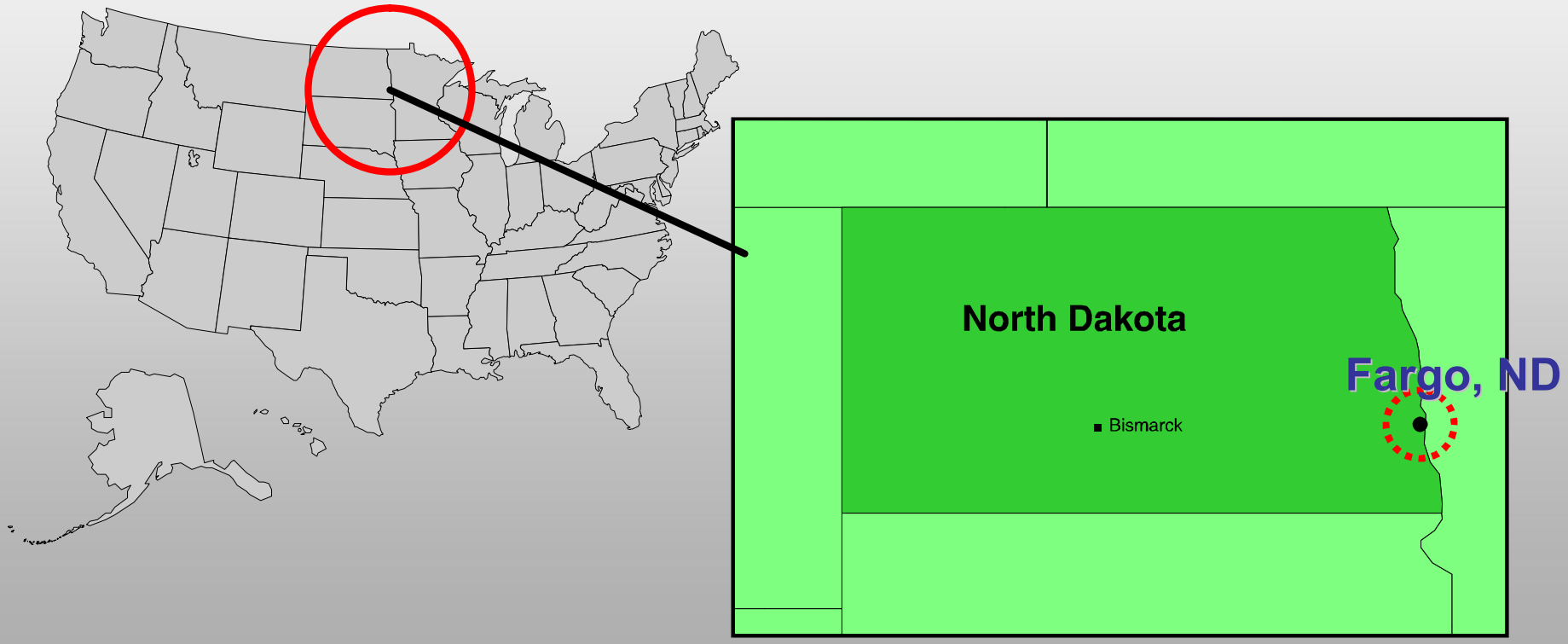
CURRENT OFFERINGS:

Minor in Coatings & Polymeric Materials

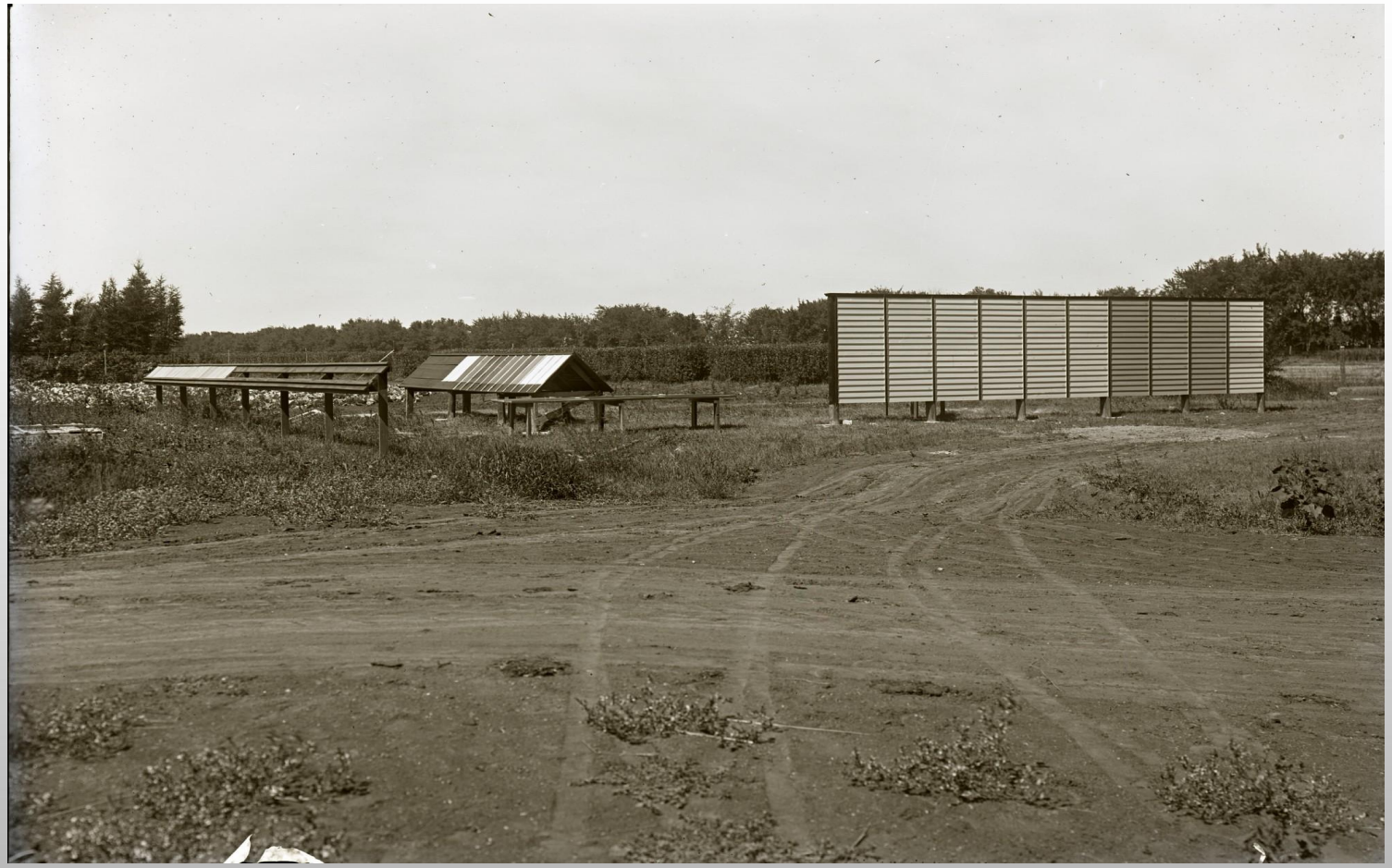
M.S.; Ph.D. in Coatings & Polymeric Materials

http://www.trekearth.com/gallery/North_America/United_States/Midwest/North_Dakota/photo258730.htm

North Dakota is missing.
"We think Canada took it," stated the auditors, "but every time we called up there to ask about it , they just laughed and hung up the phone."
- Dave Barry on North Dakota



NDSU – Coating Studies for 100 years



The first weathering exposure fence, *circa* 1907

Probably the very first coatings research program.

CPM Department

Department is located primarily in Tech' Park on north side of campus, "Research 1"

R2 broke ground on September 16, 2002 and occupants began moving in on March 15, 2004.

This 75,000 square-foot facility is dedicated primarily to nanoscale science and engineering research. In addition to five spacious cleanrooms, the building houses four laboratories for electronics and process engineering research, and eight well-equipped chemistry and instrument labs.

CPM Faculty Members

- Professor & Chair Gordon Bierwagen
  - Research Interests – Corrosion Control by Coatings, Particle Packing in Coatings, Physical Chemistry of Coatings, Aircraft Coatings, Lifetime Prediction in Coatings

- Professor Stuart Croll
  - Research Interests – Measurement of Mechanical & Physical Properties of Coatings, Durability of Coatings, Pigment Dispersion and Dispersion Stability

- Professor Dean Webster
  - Research Interests – Design and Synthesis of Coating Polymers and Oligomers, High Throughput Materials Synthesis – Combinatorial Materials Synthesis, Polymer Synthesis, Polymer Scale-Up and Reactor Design

Chemically Mediated Deposition of Polypyrrole on Aluminum Flake

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Katy Gohmann*, and Chris Vetter

Department of Coatings and Polymeric Materials
North Dakota State University

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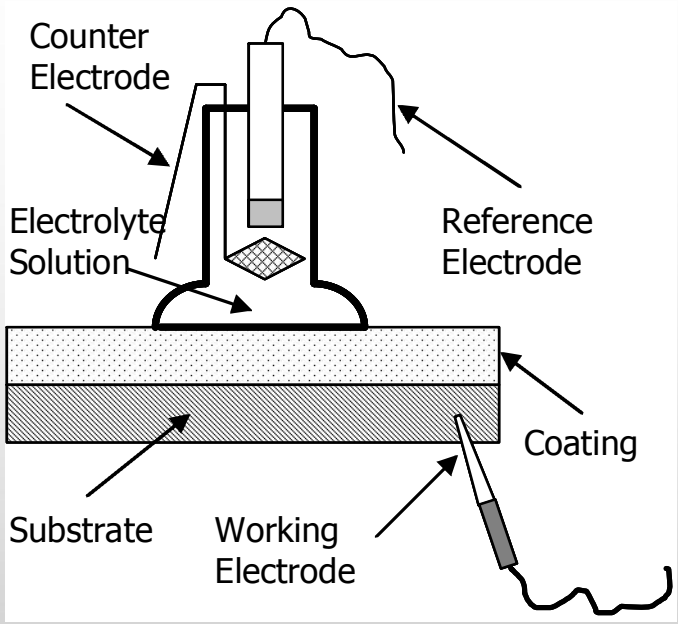
Outline

- Why Conducting Polymers?
- Flake Preparation
- Testing Methods and Results
  - Density
  - SEM
  - EIS Constant Immersion
- Future Work
- Conclusions

Electrochemical Impedance Spectroscopy (EIS)



Apply a sinusoidal potential (small) to the open circuit potential at varying frequencies

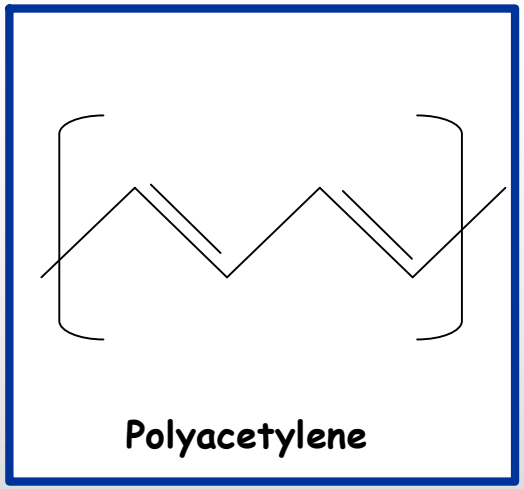
Measure phase lag (V- I) and current for varying applied frequencies

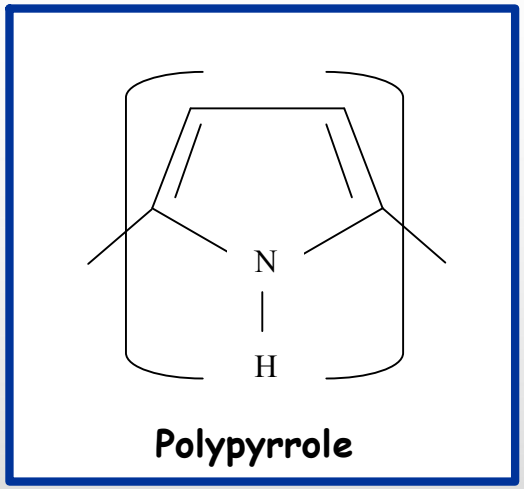
Easy testing variability: electrolyte, temperature, and time

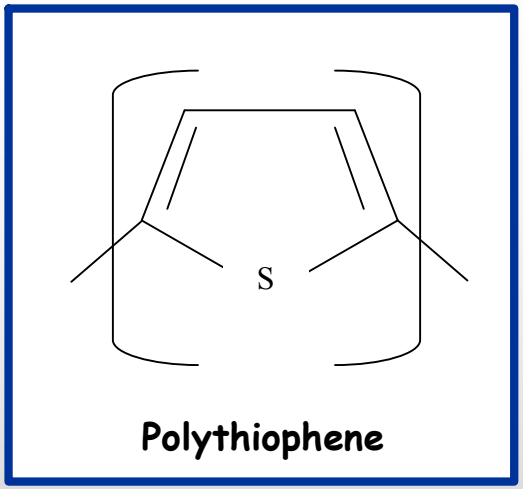
The solution was dilute Harrison's Solution (DHS) (0.05% NaCl and 0.35% $(NH_4)_2SO_4$).

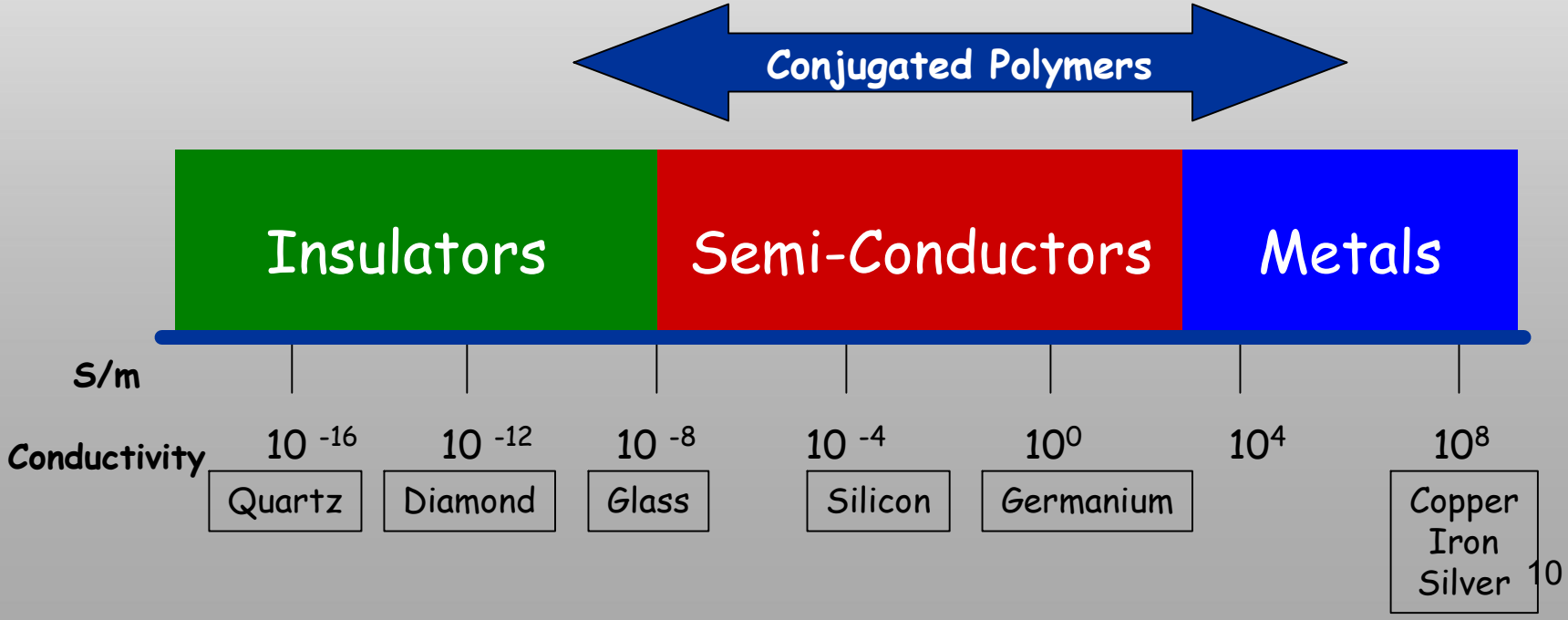
Presented usually as either a Bode (log modulus vs. log frequency)
or a Nyquist plot (Z' vs. Z")

Electroactive Conducting Polymers

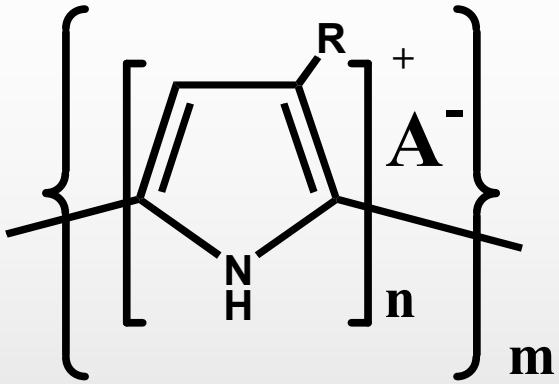


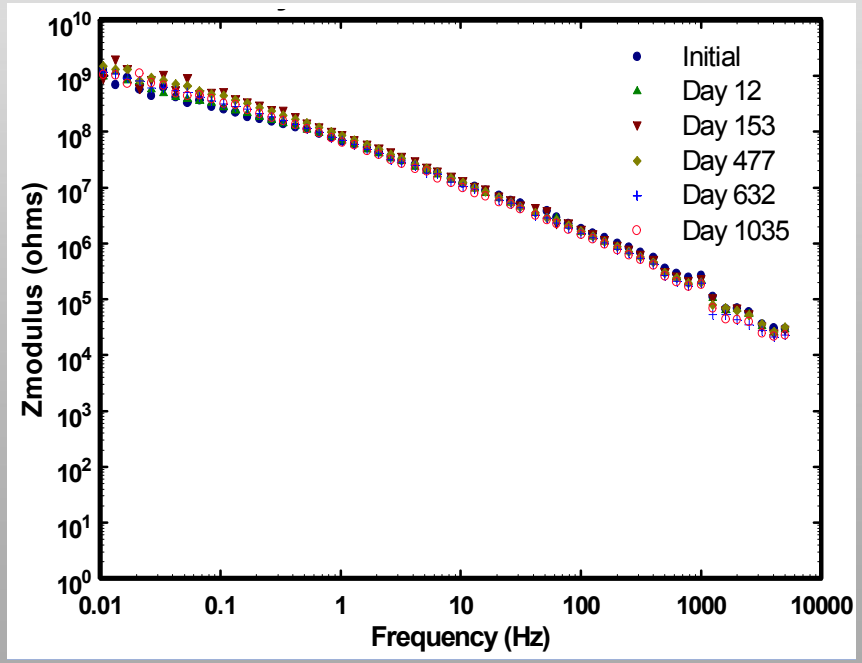


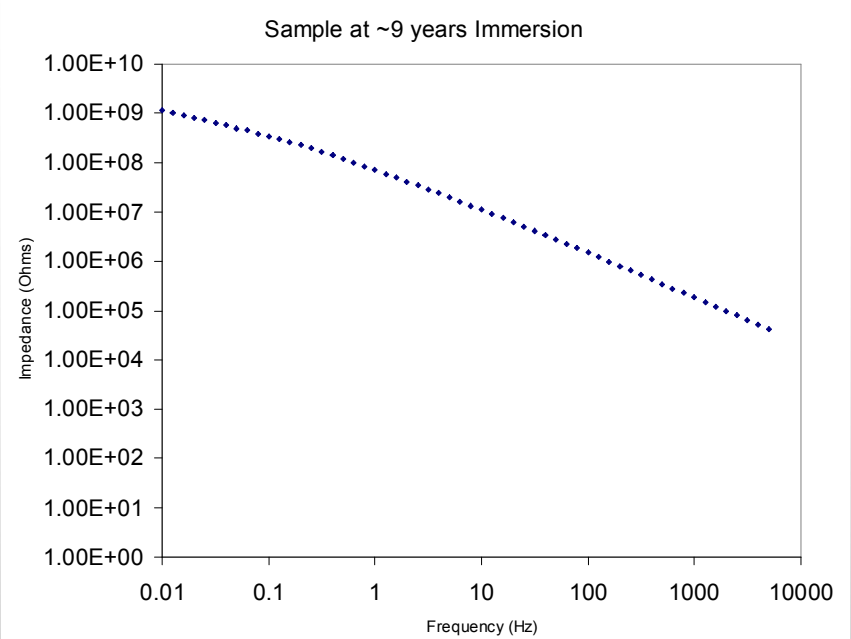


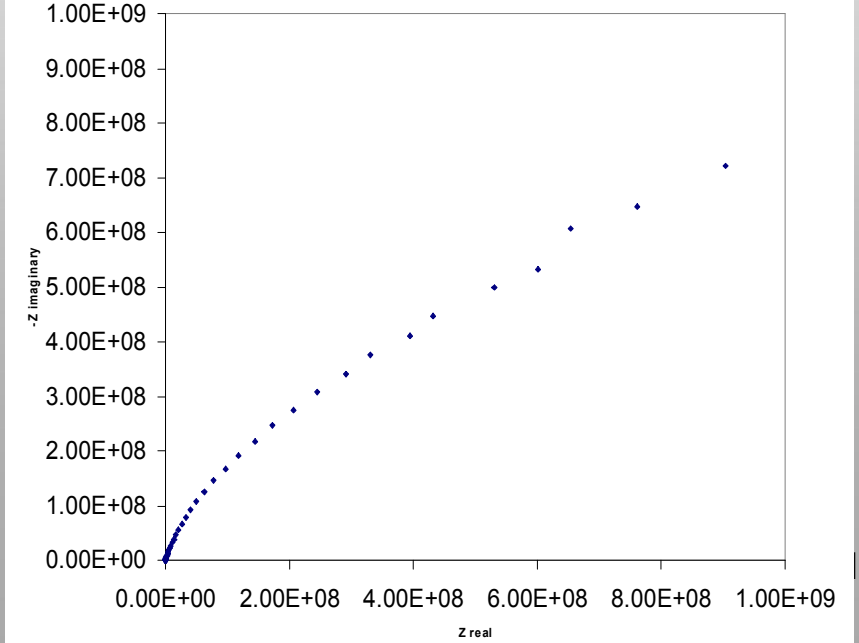


Polyurethane/POP/pTS$^-$/ClO$_4^-$/AA 2024-T3

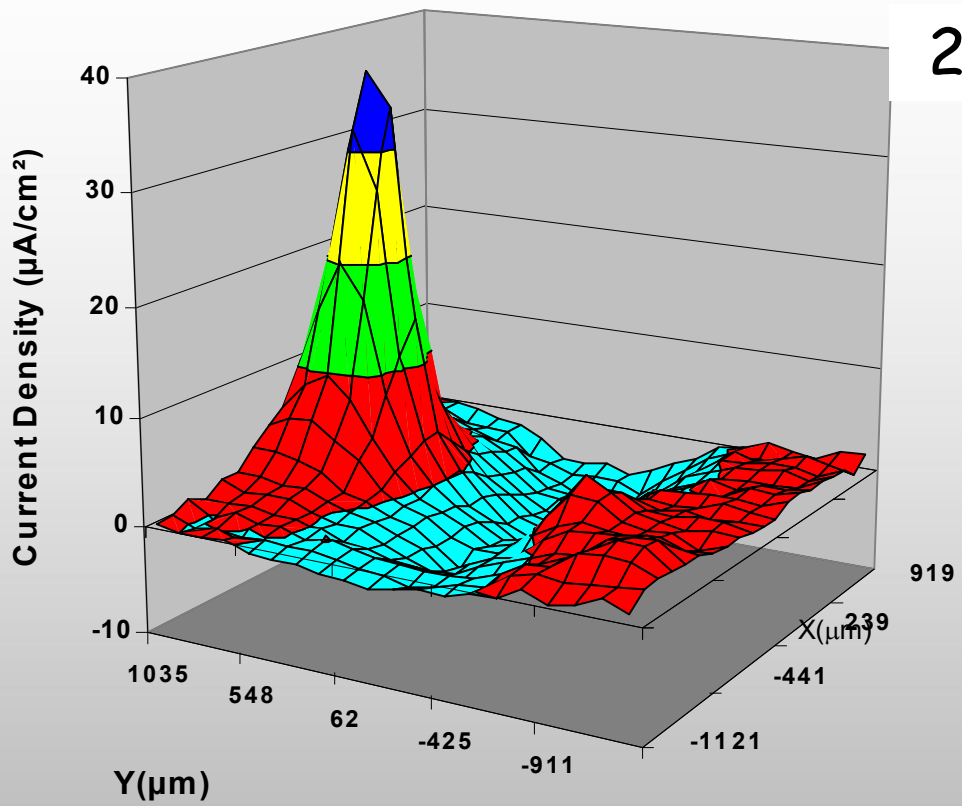






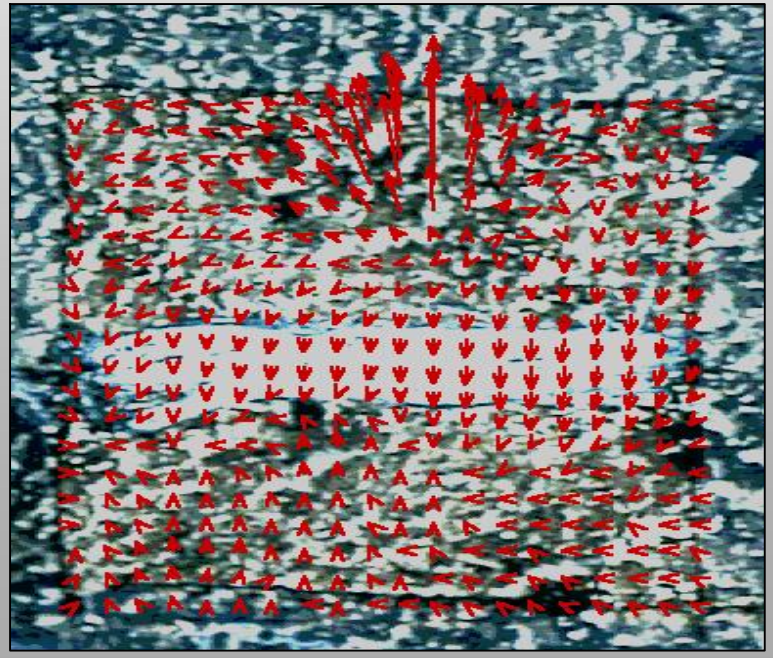


POP/pTS$^-$/ClO_4^- coated Aluminum 2024-T3



26.6 Hours

30-40
20-30
10-20
0-10
-10-0



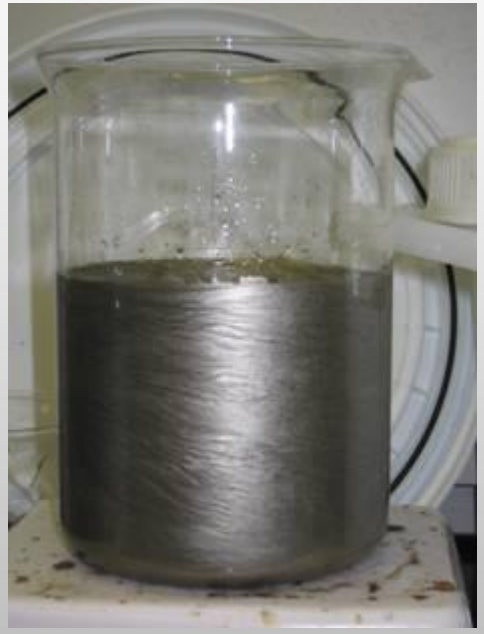
Why Polypyrrole/Aluminum Flake

- Easy coating incorporation
- Less quantity of conducting polymer required
- Solubility is not an issue

PPy-Coated Aluminum Flake Preparation

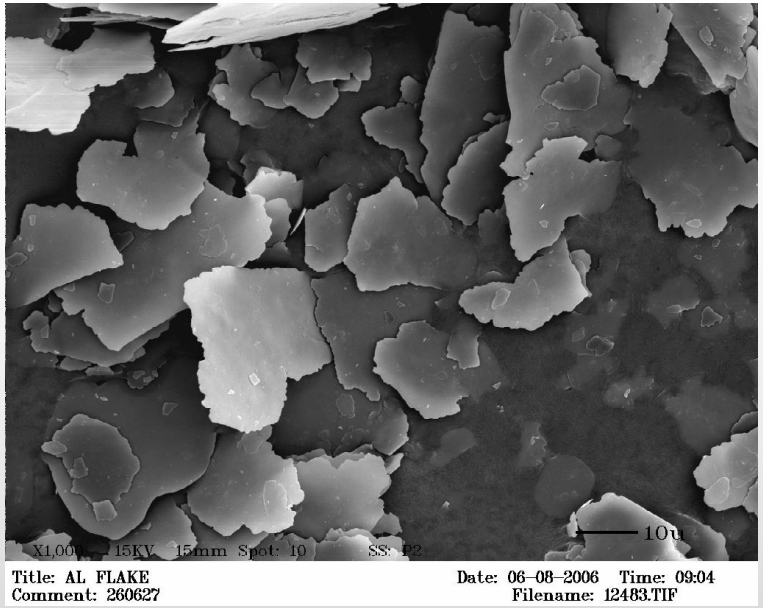
- Aluminum flake paste combined with:
  - DI water
  - Ammonium persulfate ($(NH_4)_2S_2O_8$) → Oxidizing Agent
  - Catechol (dihydroxybenzene, $C_6H_6O_2$) → Additive
  - Pyrrole monomer
- PPy was formed regardless of the presence of catechol, however, the coating of the flake seemed smoother when catechol was used
- In both cases the aqueous solution turned black indicating polymerization of the PPy monomer

PPy-Coated Aluminum Flake Preparation Cont.

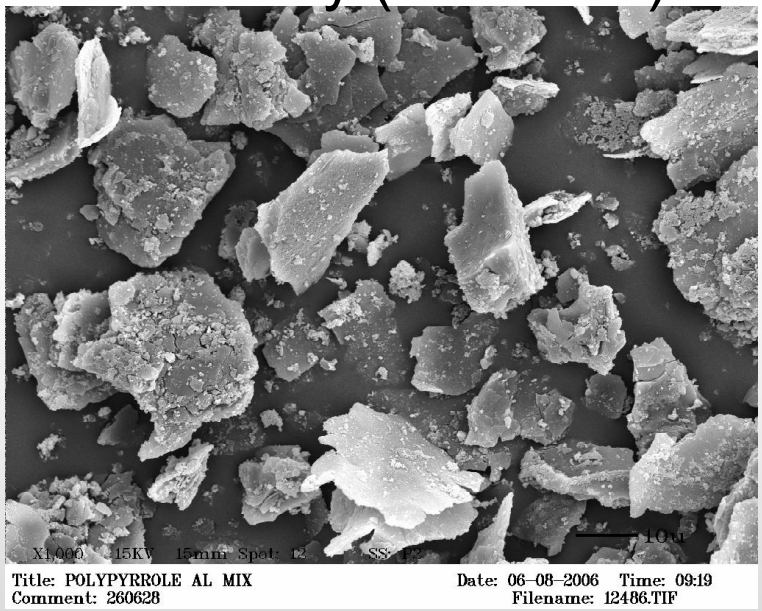


- Vacuum filtration
- Paste dried overnight, then ground using mortar and pestle and passed through a sieve with 150μm pore size

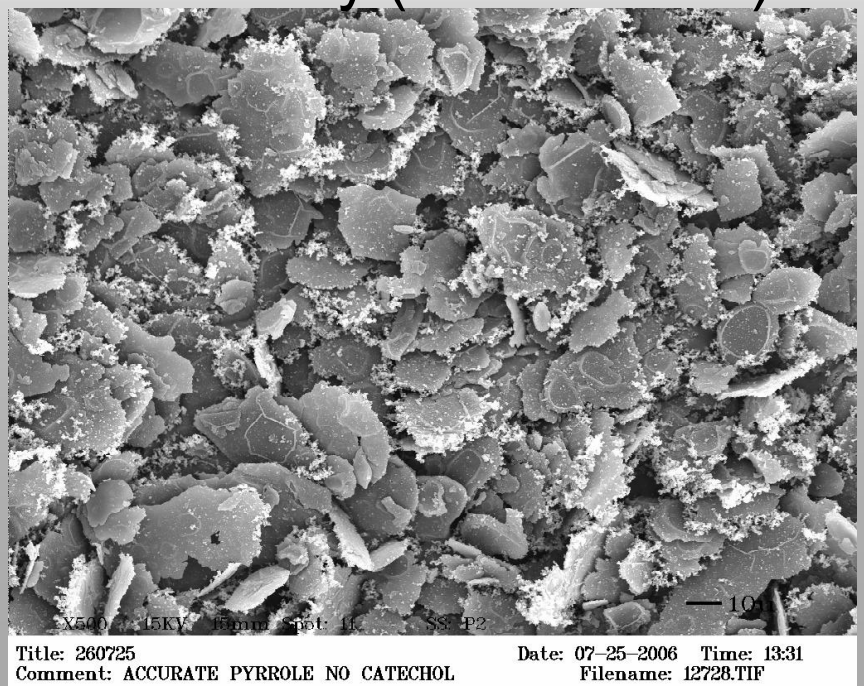
SEM Bare Aluminum Flake



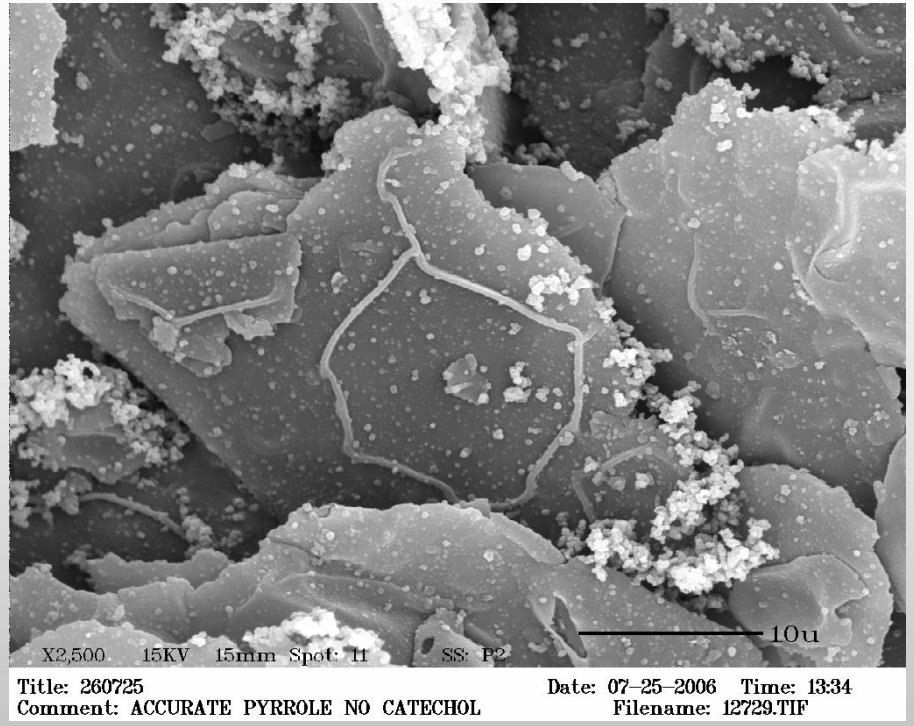
SEM PPy (Catechol)

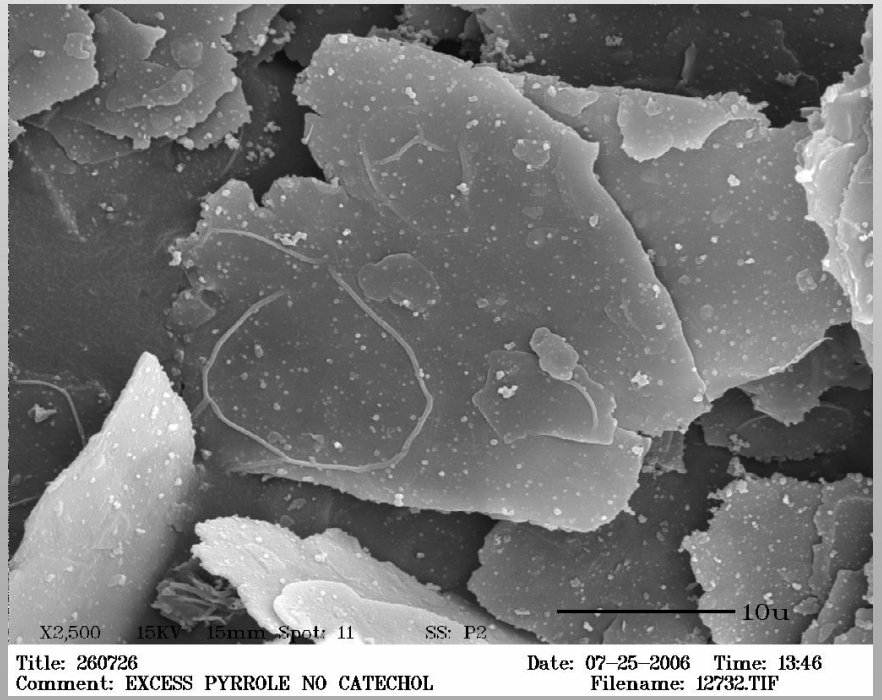


SEM PPy (no Catechol)



SEM PPy (no Catechol)



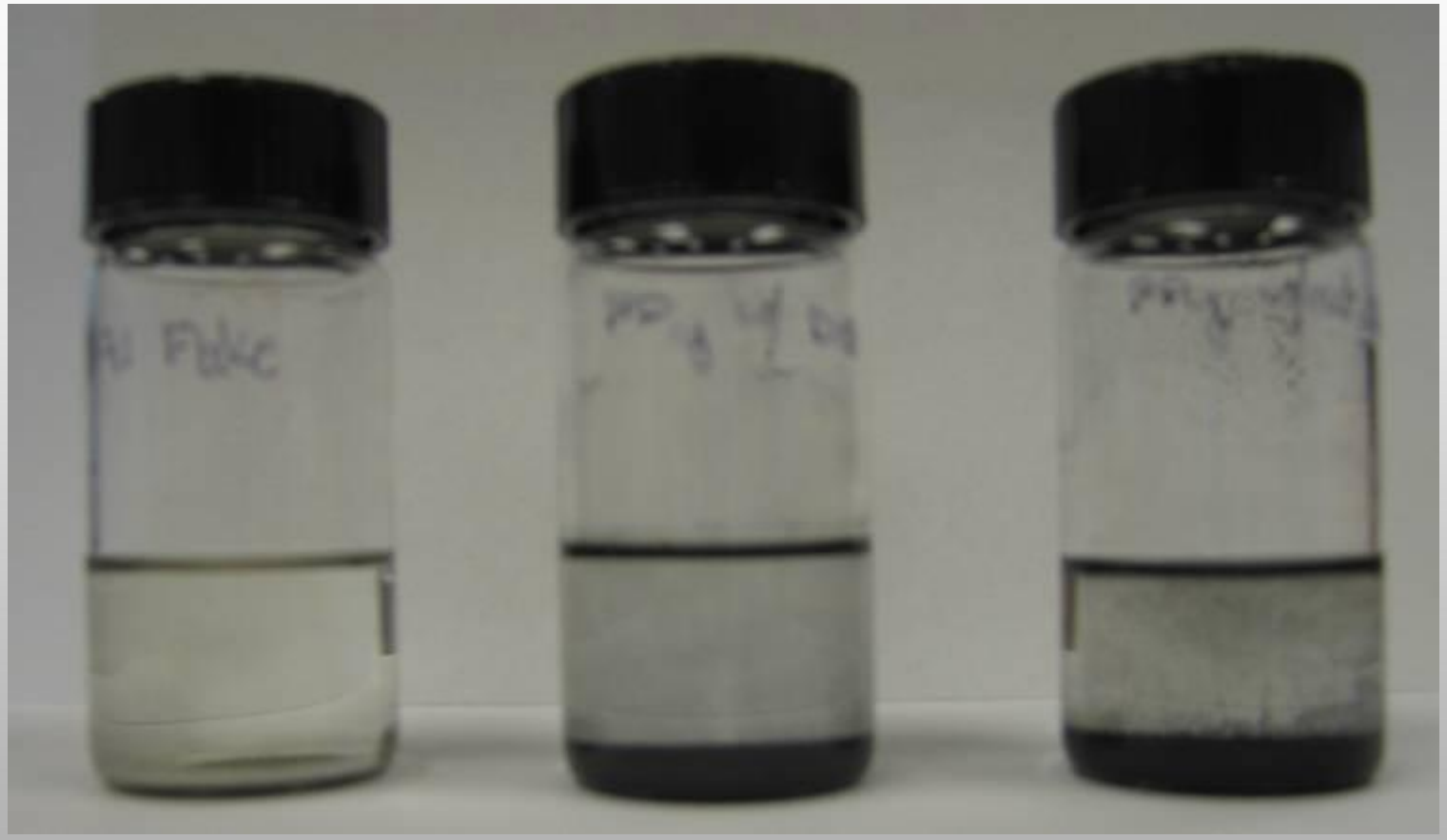


Density Tests

- Densities:
  - Tetrachloroethylene (1.622 g/cm^3)
  - Plain Aluminum Flake (2.70 g/cm^3)
  - Polypyrrole (0.967 g/cm^3)
- If the samples sank to the bottom, the flakes were coated
- If there was some sample floating at the top, the PPy did not completely coat the flakes

Test Performed	**Result**
Plain Aluminum Flake	Completely sank to bottom
Flake coated with PPy (with catechol and ammonium persulfate)	Almost completely sank to bottom, very few free-floaters on top
Flake coated with PPy (with ammonium persulfate)	Most sank to bottom, more free-floaters than with using catechol

Density Tests Cont.



Plain Flake

Flake, Py, Catechol, Ammonium Persulfate

Flake, Py, Ammonium Persulfate

Formulations of PPy coated Aluminum flake

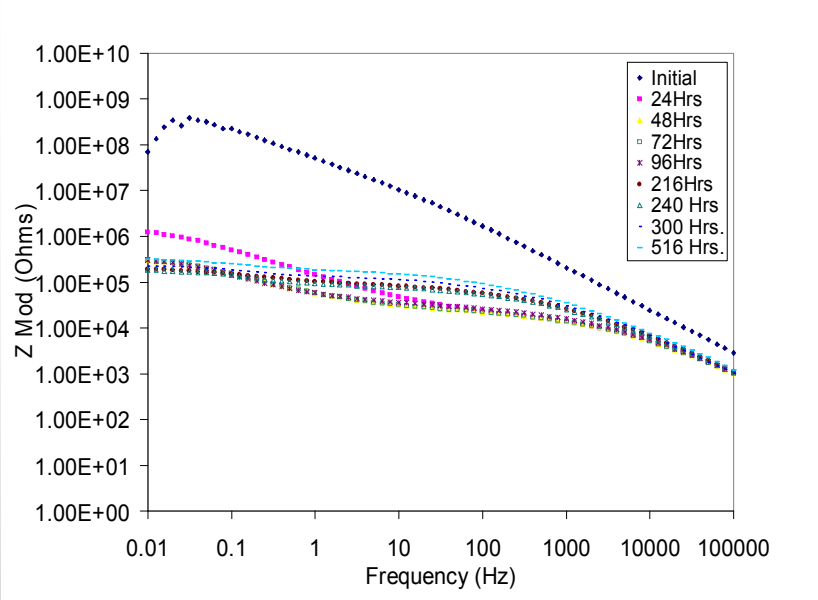
- Formulations were calculated at PVCs of 33%, 40%, 45%, 51%, 56% and 61%
- Coated pigment was combined with:
  - Epikure 3175 Curing Agent
  - Epon Resin 828
  - Methyl Isobutyl Ketone (MiBK) → solvent

Al 2024-T3 panel application of formulation

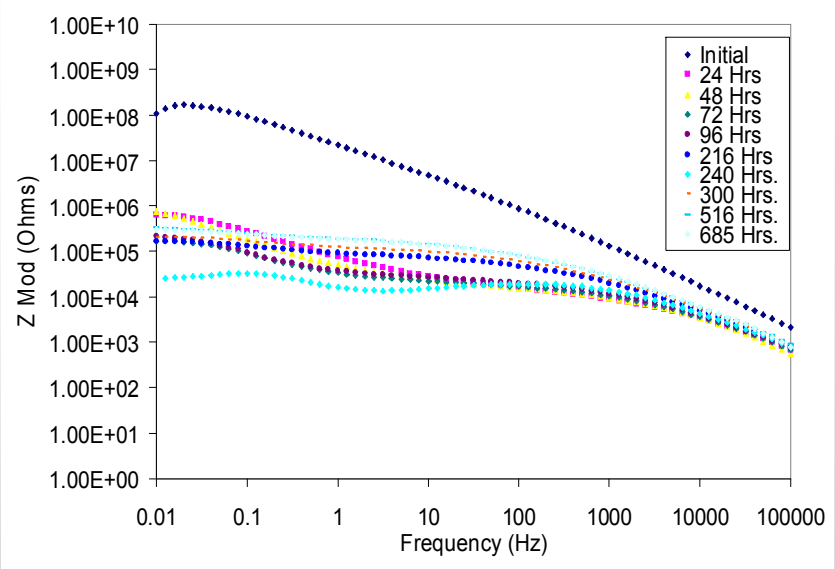
- Coatings were applied to sanded and degreased 8”x4” Al 2024-T3 panels using a 3” drawdown bar at 8 mils

- Panels were allowed to flash off and were then placed in an oven to fully cure

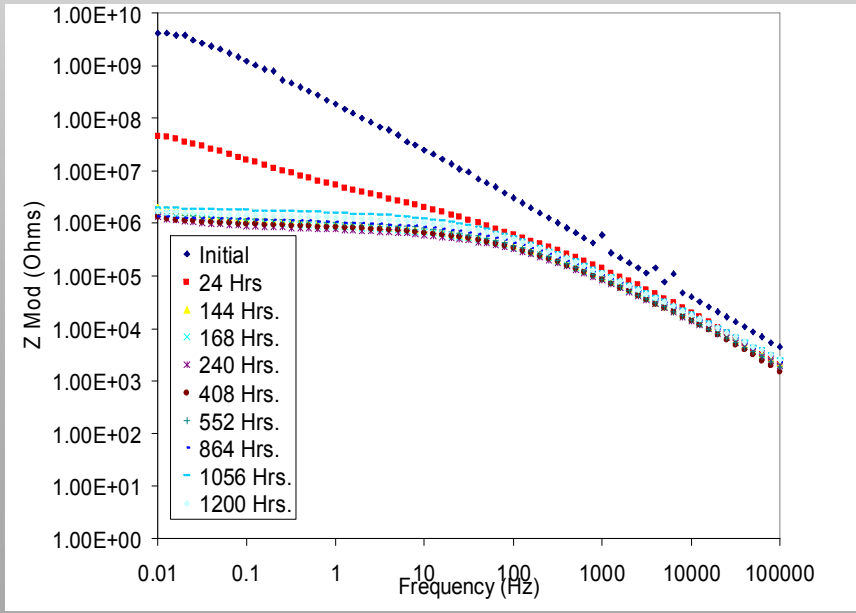
33% Formulation



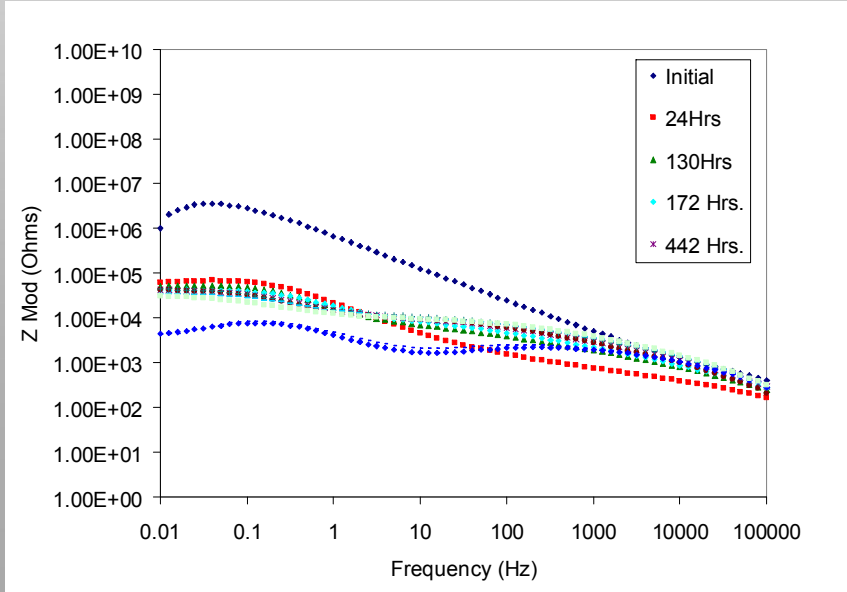
40% Formulation



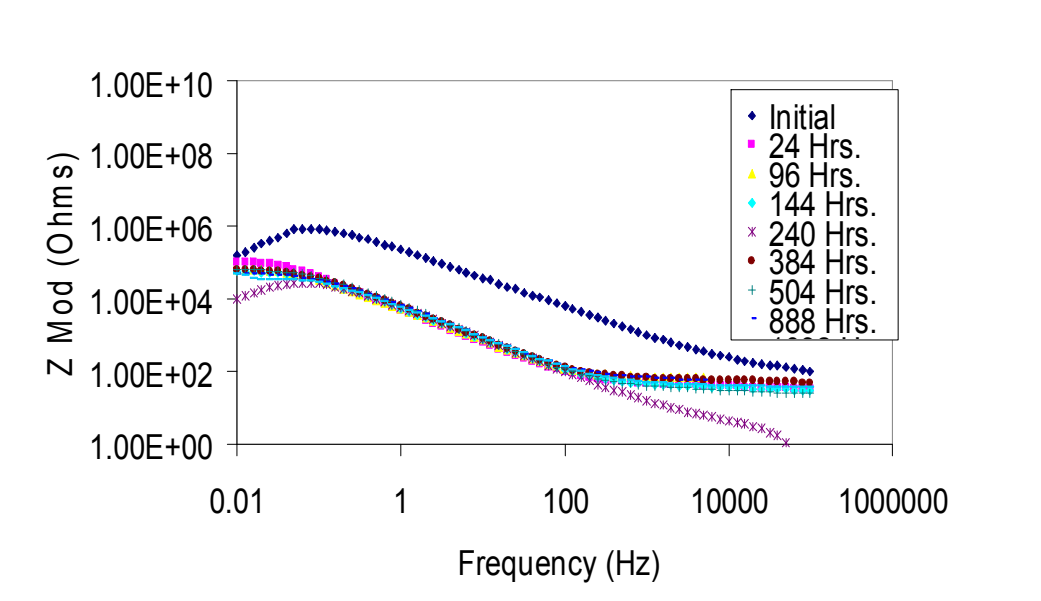
45% Formulation



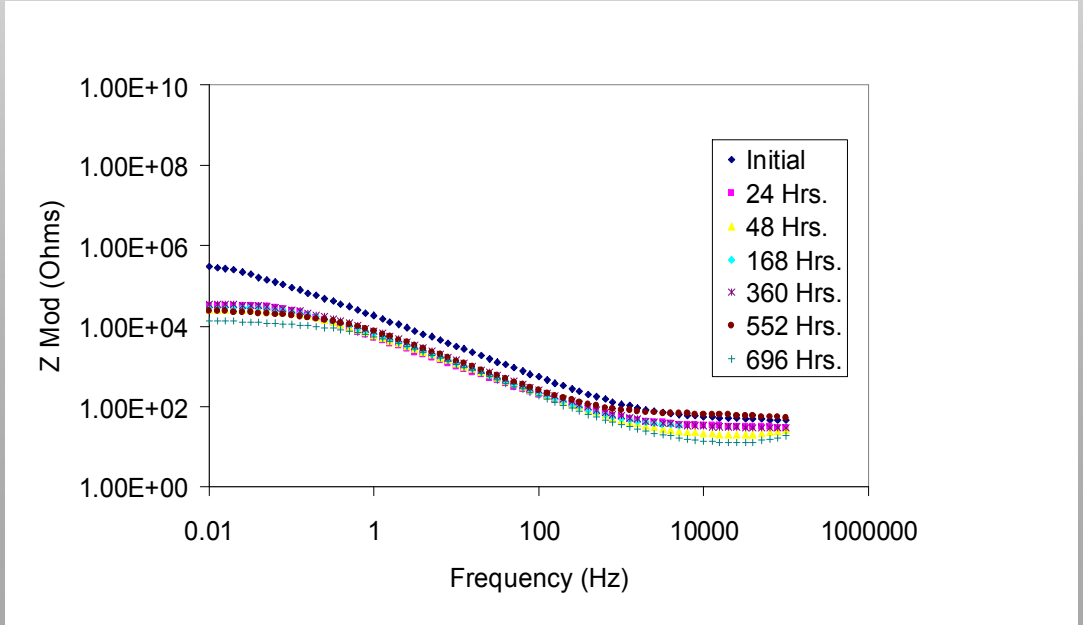
51% Formulation



56% Formulation



61% Formulation



Conclusions

- Right now, CPVC is believed to be somewhere in the vicinity of 51-56%
  - Similar EIS results
- From density tests, we see that although polymerization occurs without catechol, it causes adherence of PPy to the flake to be better

Future Work

- Continue property testing to find optimal PVC for this coating
- Conductive AFM
- Elemental Analysis
- Spray new panels
  - Accelerated exposure with topcoats
- Investigate the roles of ammonium persulfate and catechol in the polymerization of pyrrole
  - Hydroquinone? o-Benzoquinone?