JAMS

Identification and Validation of Analytical Chemistry Methods for Detecting Composite Surface Contamination and Moisture

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A Center of Excellence AMTAS Advanced Materials in Transport Aircraft Structures

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CECAM center of excellence for composites and advanced materials

The Joint Advanced Materials and Structures Center of Excellence

FAA Sponsored Project Information

- PI & Researchers
  - Dwayne McDaniel, Richard Burton, Weihua Zhang, Wongbon Choi, Xiangyang Zhou
- Students
  - Yao Ge, Ling Wang, Tomas Pribanic, Kevin LaMott
- FAA Technical Monitor
  - Curtis Davies
- Industry Participation
  - Exponent, DME, Avborne, AeroMatrix

Introduction

- Motivation and Key Issues
  - Adhesive bonding is now used in manufacture and repair is beginning to predominate over mechanical fastening.
  - Adherend surface preparation is a critical issue to the structural integrity and durability of bonded structures.
- Objective
  - benchmark knowledge of surface preparation quality assurance methods
  - Identify, evaluate, and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.
- Approach
  - Literature review and analysis (completed)
  - Surface chemistry analysis
  - Electrochemical sensor evaluation
  - Experimental validation

Research Roadmap

Information collection and analyses →	Strength & durability versus surface pretreatment
	↓
Information collection and analyses →	Surface analysis methods
	↓
Technology evaluation →	Candidate field analysis technologies
	↓
Technology validation →	Effective field analysis technology

Results (2007)

- Literature database, completed
- Summary of literature review
  - Surface treatment, completed
  - Surface chemistry analyses, completed
- Proposed and evaluated electrochemical sensor for surface chemistry analysis.
- Proposed and evaluated carbon nano-tube sensor for humidity sensing.
- AFM/SEM study of surface-contamination (peel-plies, etc).

Results (2008)

- Evaluation of alternative mediators for sensor preparation
- Evaluation of both cyclic voltametry and electrochemical impedance spectroscopy methods
- Fabrication and testing of prototype sensors
- AFM force spectroscopy of peel ply samples and statistical analyses
- CFM imaging of the peel ply samples - in progress

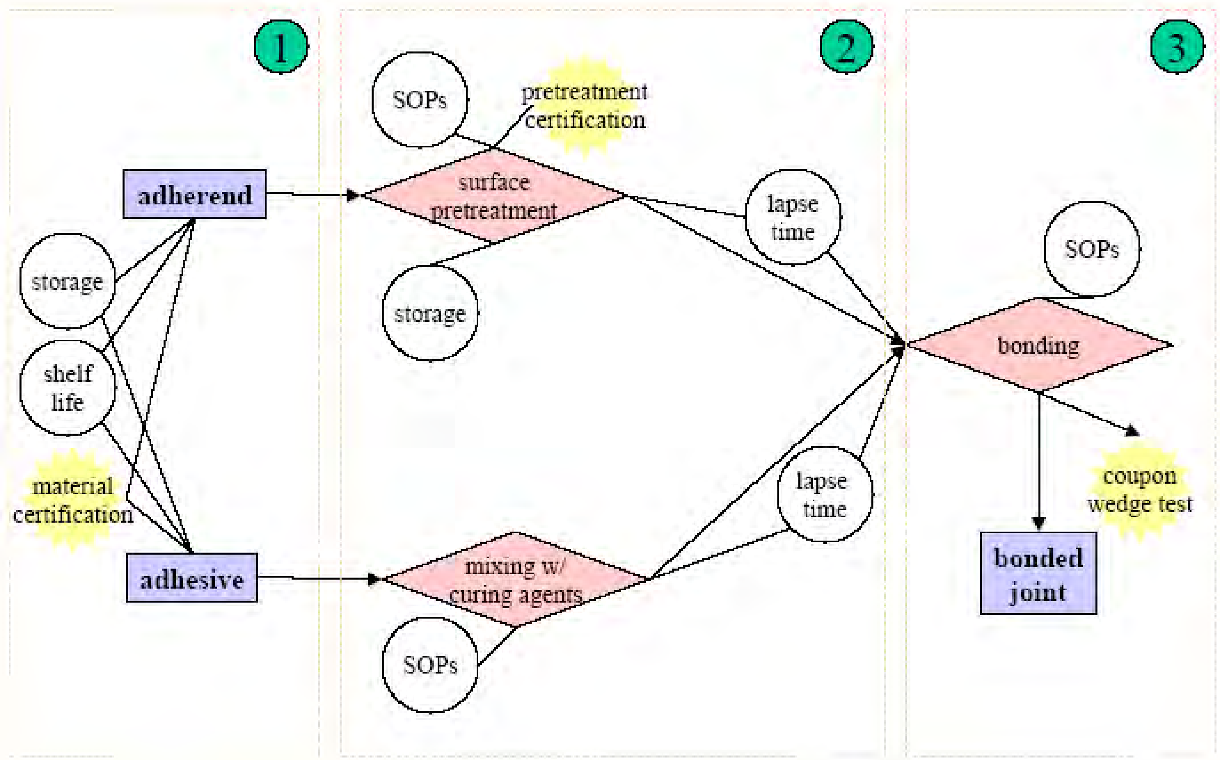
Literature Review: Concentration of Oxygen versus Strength

Polymer	Treatment	Surface composition (at%)		Failure load/N
		C	O	
HDPE	No treatment	100.0	0.0	400
	2.1 V, Pt edge, 50 passes	95.5	4.5	1330
	2.4 V, Pt edge, 50 passes	96.2	3.8	1320
	2.9 V, Pt disc, 5 min	92.4	7.6	1110
PP	No treatment	100.0	0.0	0
	3.25 M nitric acid, 60 s	—	—	267
	2.1 V, Pt edge, 50 passes	92.6	7.4	2060
	2.4 V, Pt edge, 50 passes	93.1	6.9	2560
	2.9 V, Pt edge, 50 passes ($H_2SO_4^-$)	100	0	50
	2.9 V, Pt disc, 300 s, not touching	—	—	270
	2.9 v, Pt disc, 300 s, far removed	—	—	390
SBS	No treatment	100.0	0.0	—
	2.5 V, Pt edge, 50 passes	83.6	14.6[b]	—
PS	No treatment	100.0	0.0	550
	2.9 V, Pt disc, 300 s	94.5	5.5	670

X-ray photoelectron spectroscopy (XPS)

A quantitative analytical chemistry method

Quality Control

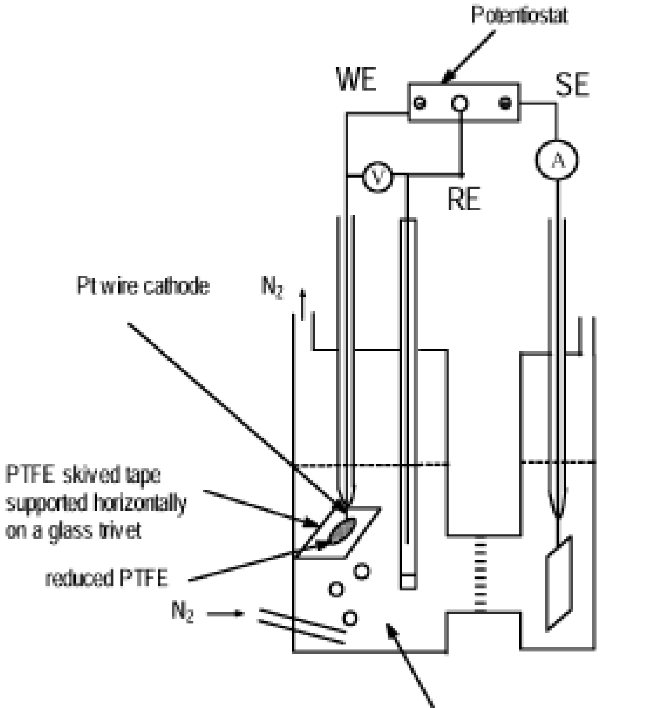


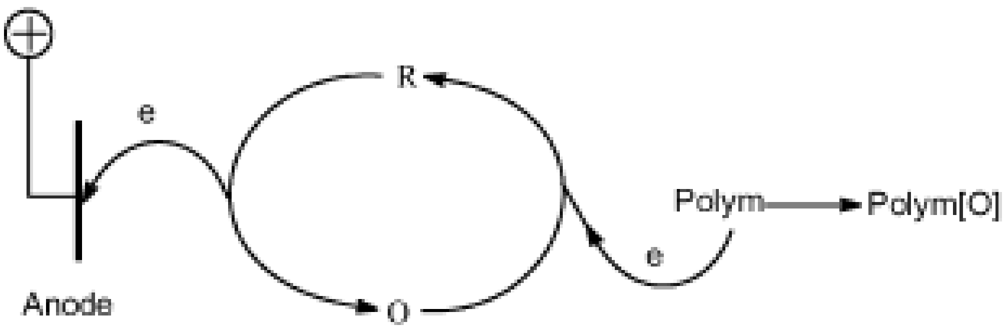
- Materials certification
- Pretreatment certification
- Adhesive application certification
- Bonding certification
- Technician certification
- Process flow management

$$N_{adsorbed} < N_{adsorbed}(critical)$$

$$N_{O-\&N-} > N_{O-\&N-}(critical)$$

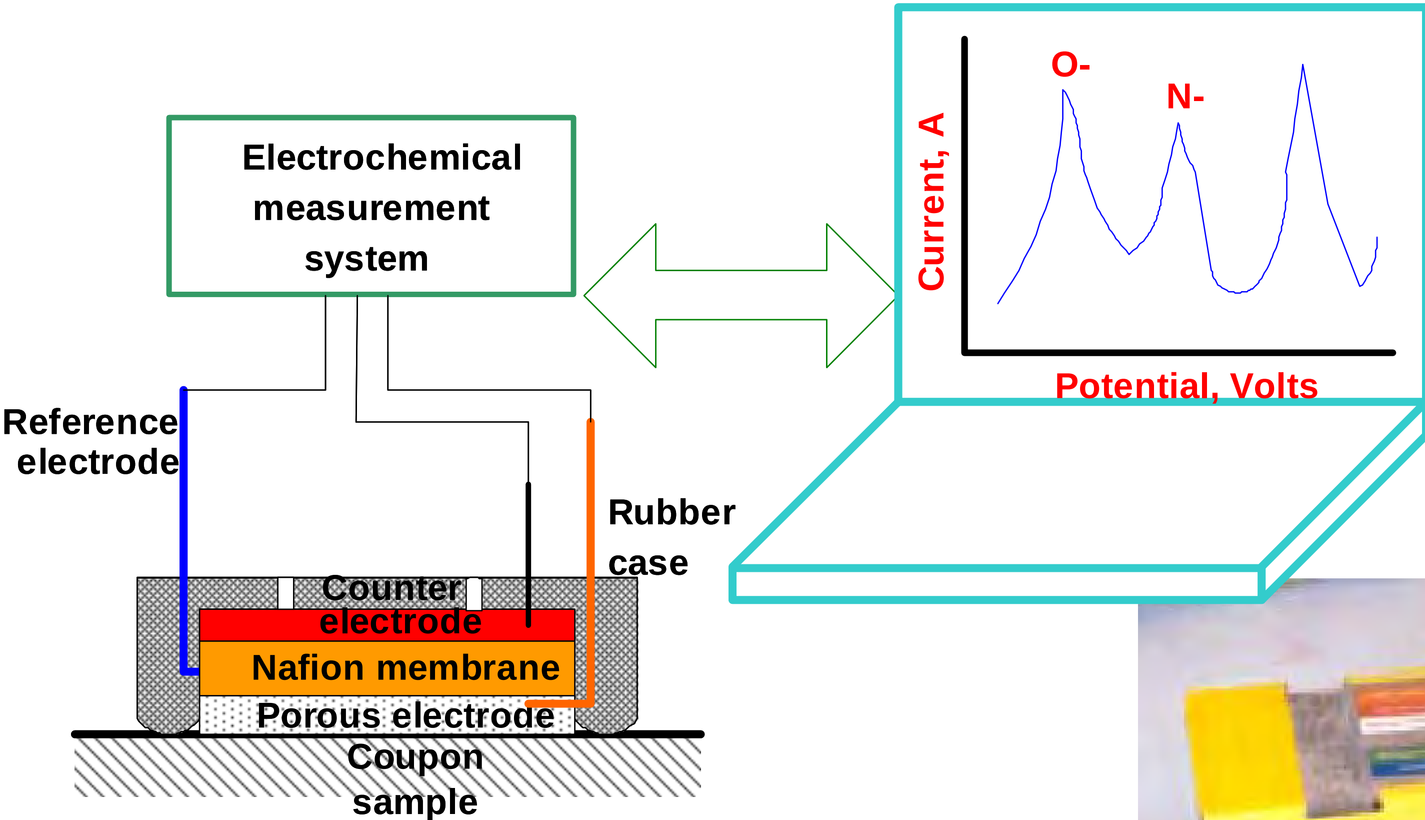
Mediated Electrochemical Cell



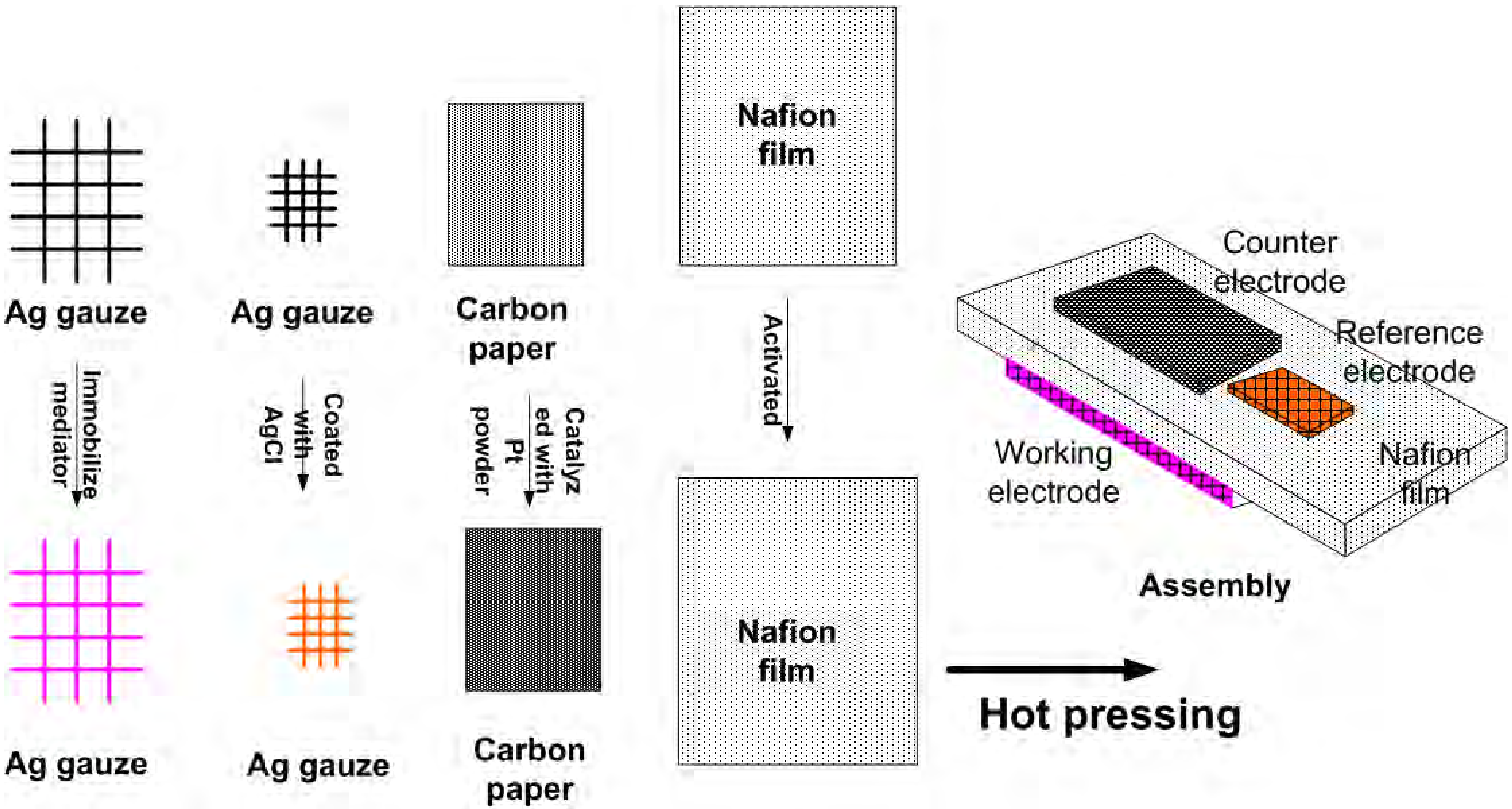


D.M. Brewis, R.H. Dahm / International Journal of Adhesion & Adhesives 21 (2001) 397–409

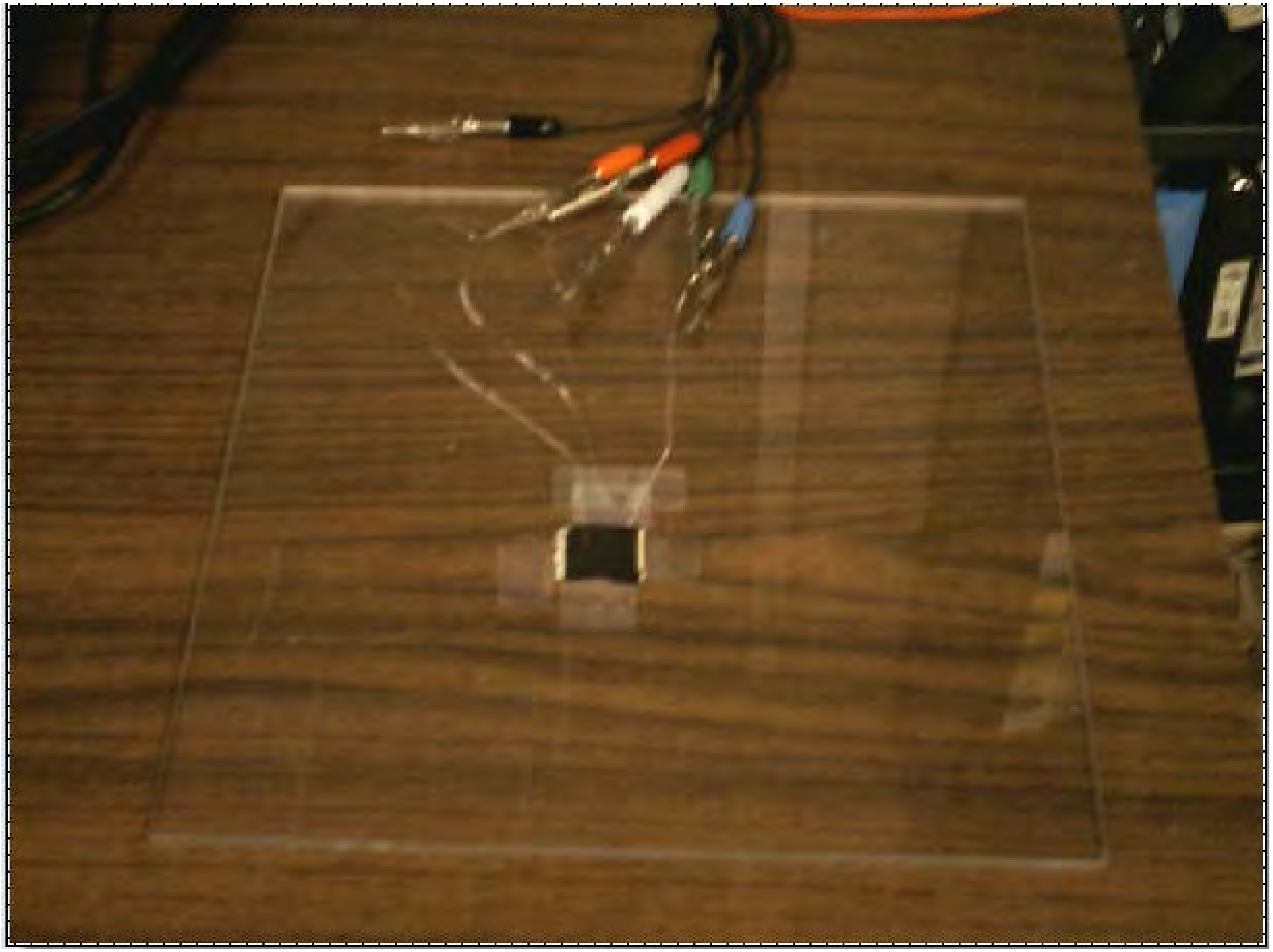
Solid-State Electrochemical Sensor



Fabrication



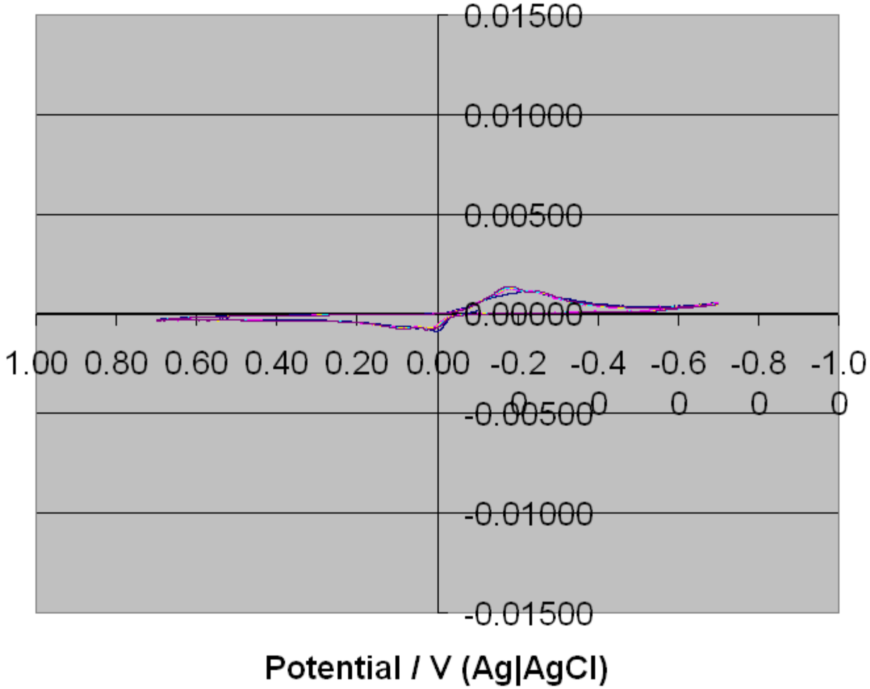
Solid-state Electrochemical Sensor

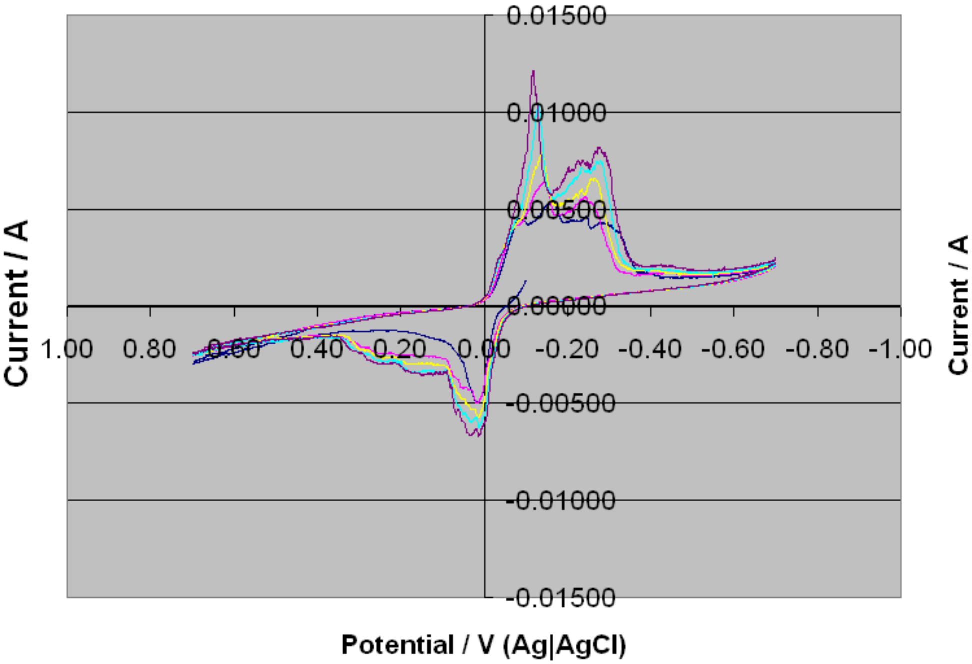


Tests on Polyester Peel Ply Samples

- Original surface: after removing peel ply
- Polished surface: polished using polishing paper (#600), and wiped with paper.
- Sulfuric acid etched: immersed in 50% sulfuric acid for 1-2 seconds, washed with DI water, and dried.

Ag(I)/Ag(II) mediator

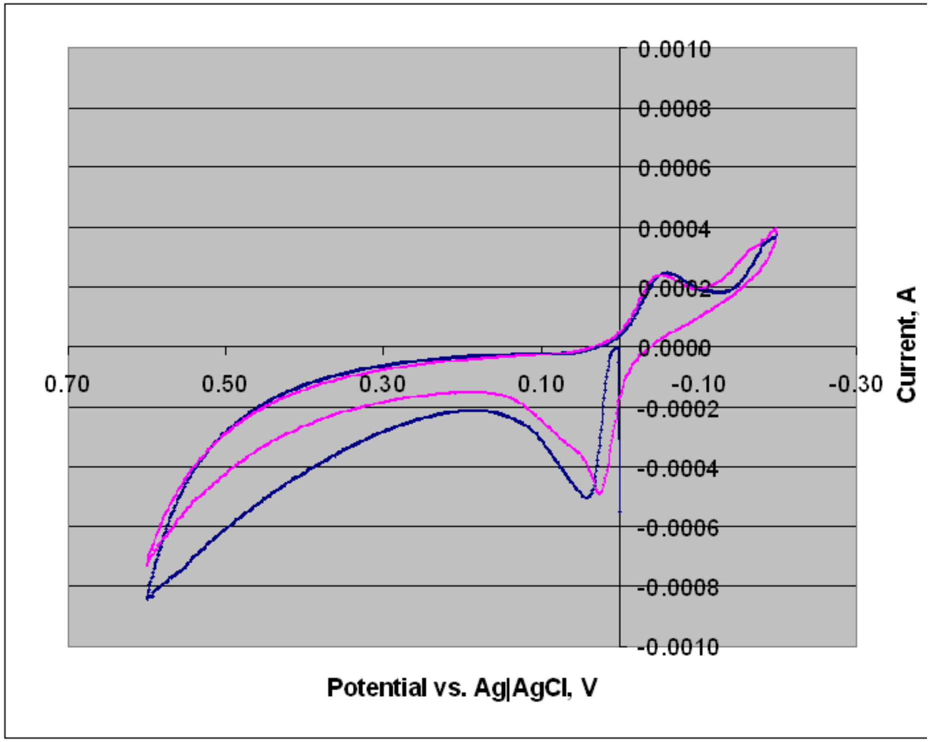


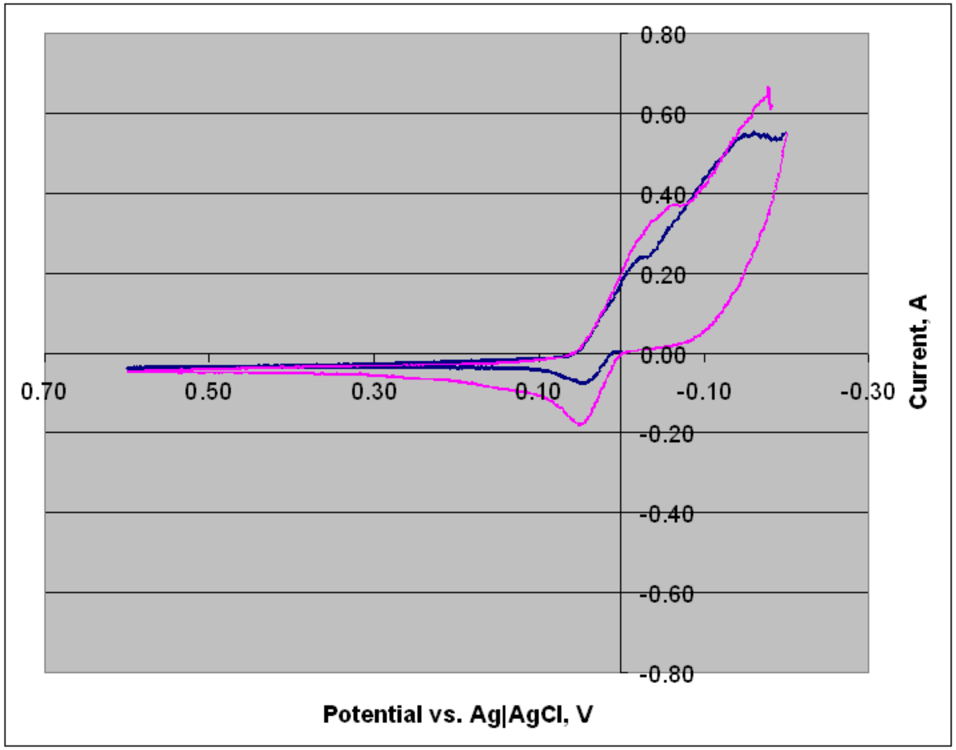


Original surface

Treated with sulfuric acid

Mn(II)/Mn(III) Mediator

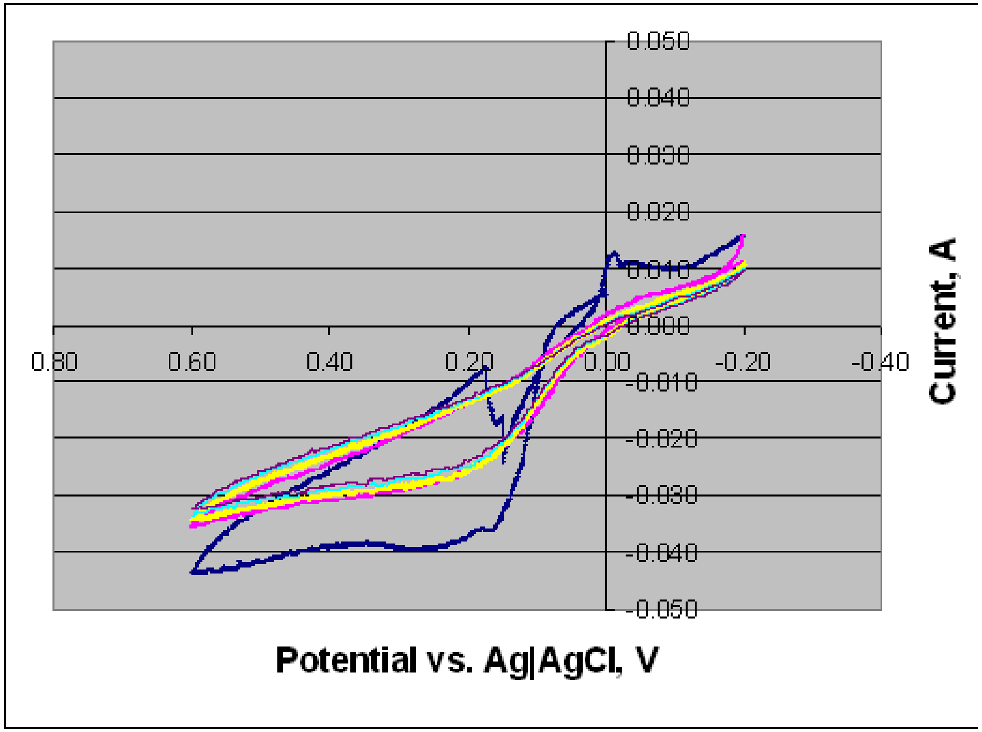


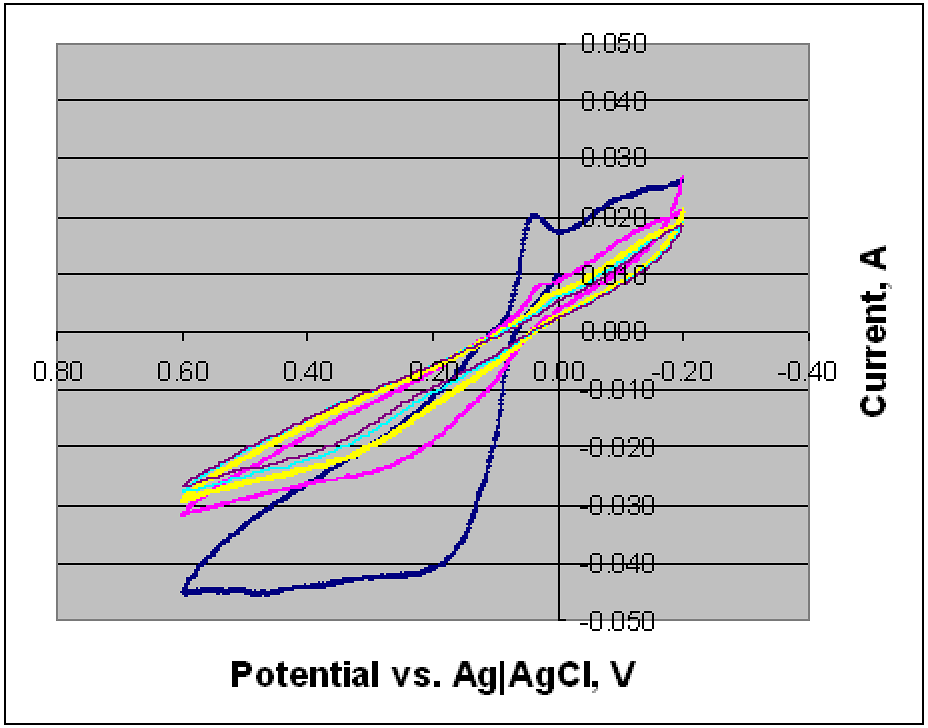


Original sample

Sulfuric acid treated sample

Ce(III)/Ce(IV) Mediator

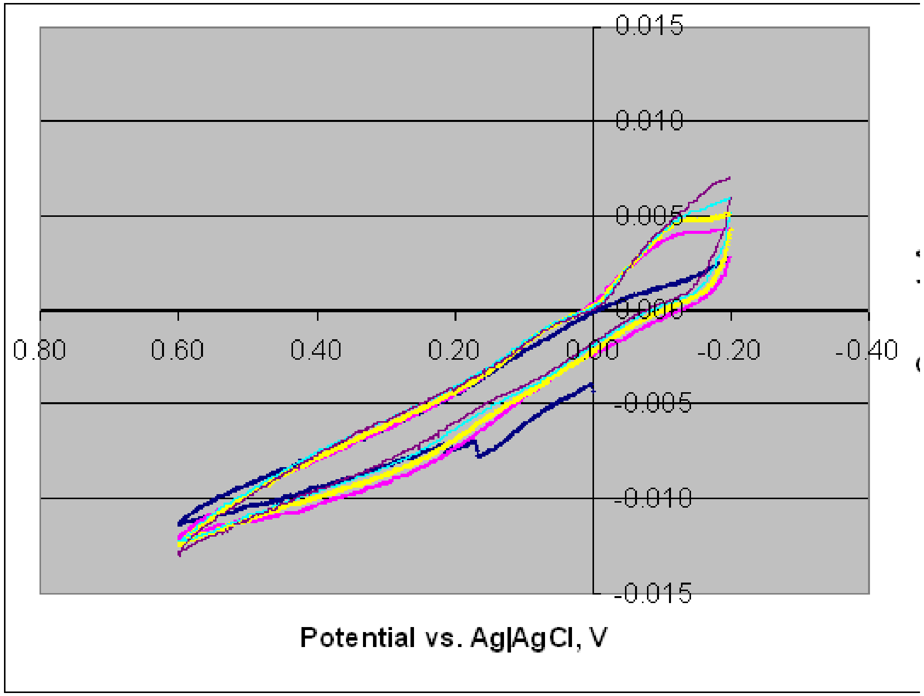




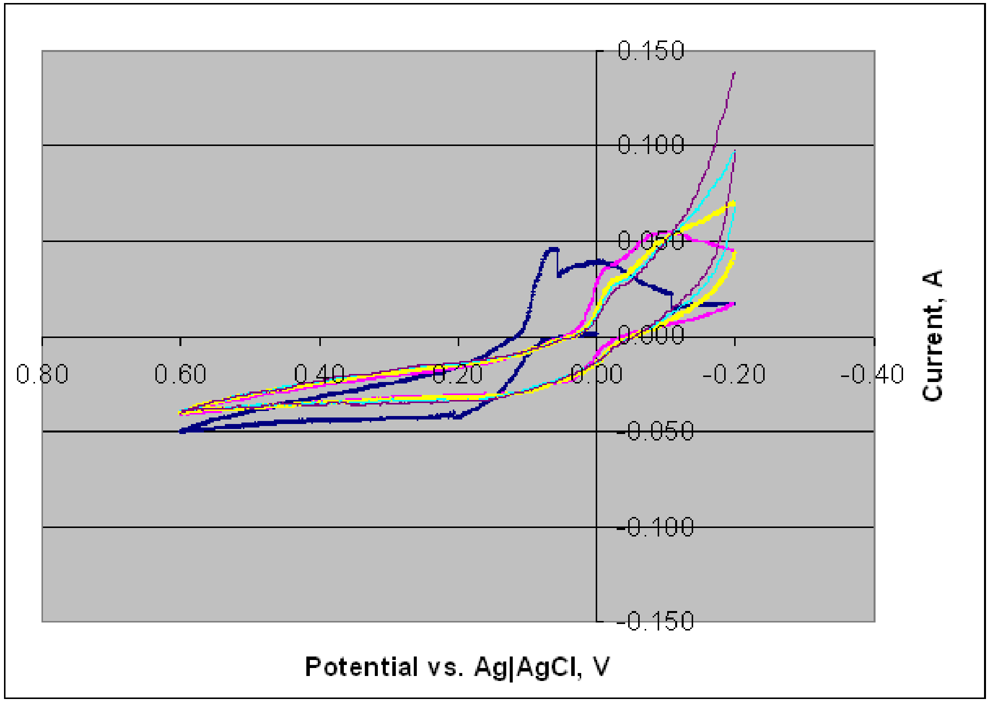
Original sample

Sulfuric acid treated sample

Cu(I)/Cu(II) Mediator



Original sample

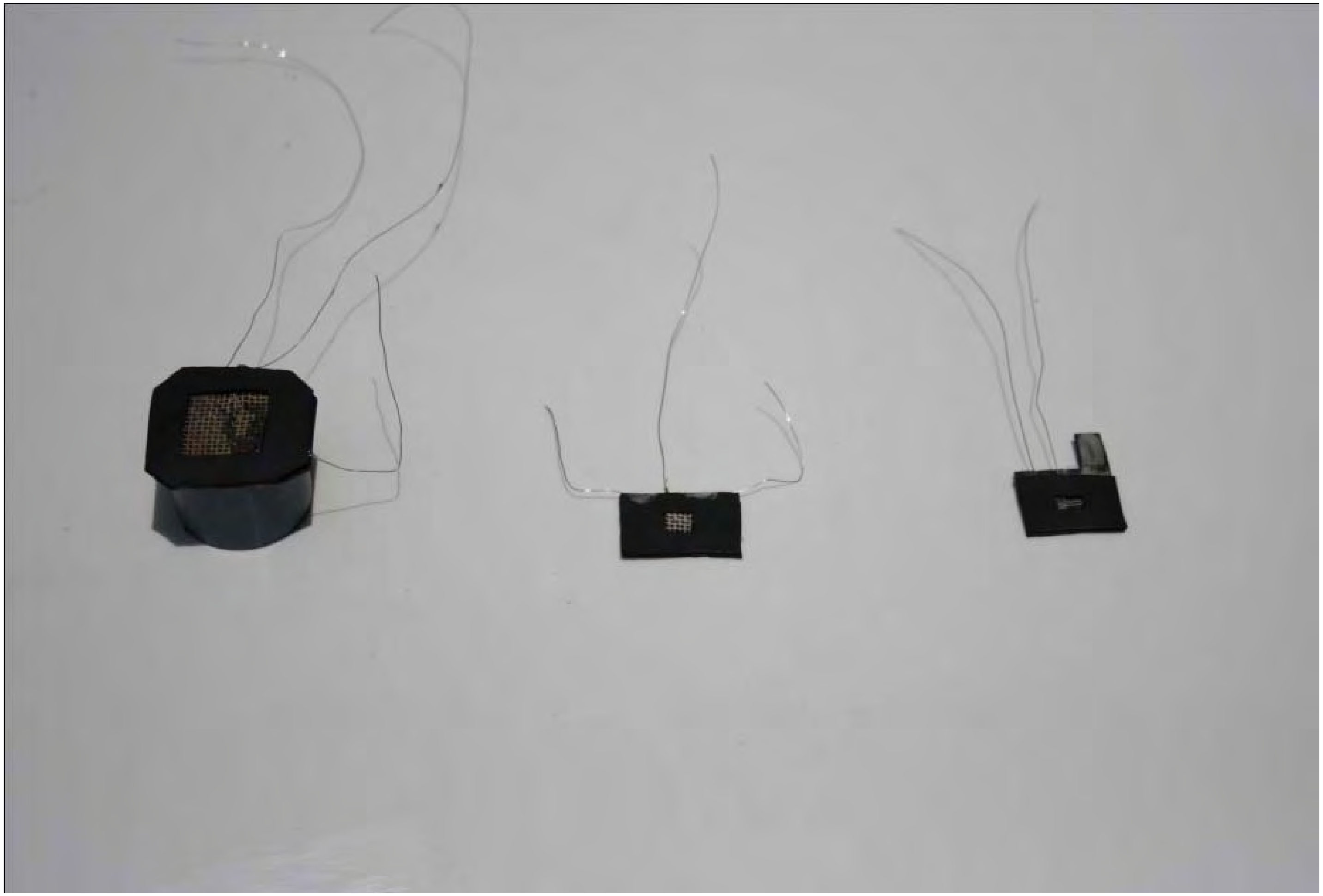


Sulfuric acid treated sample

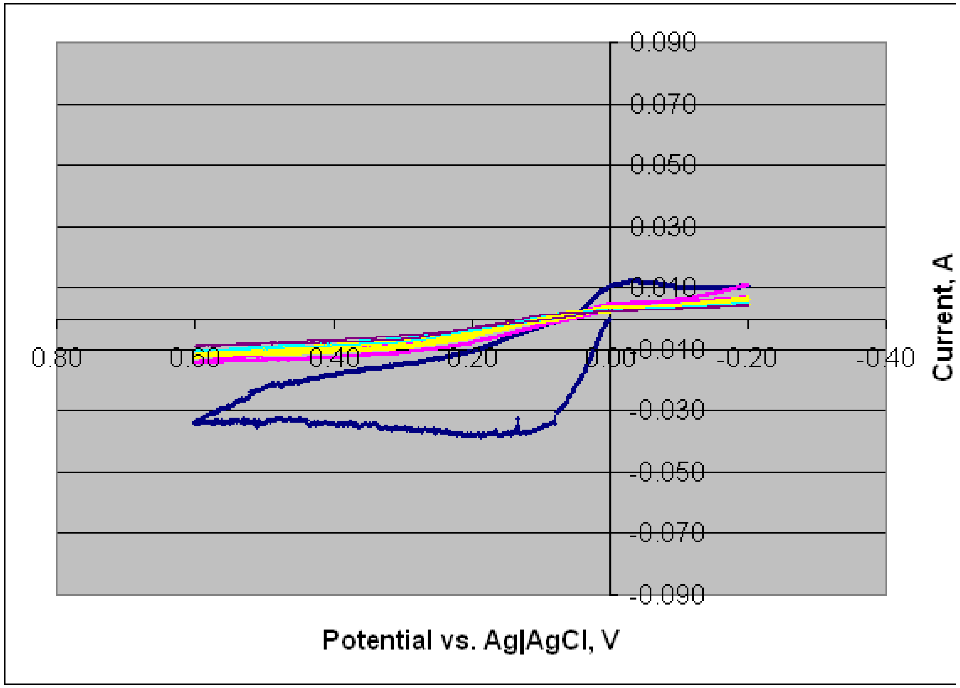
Sensitivity

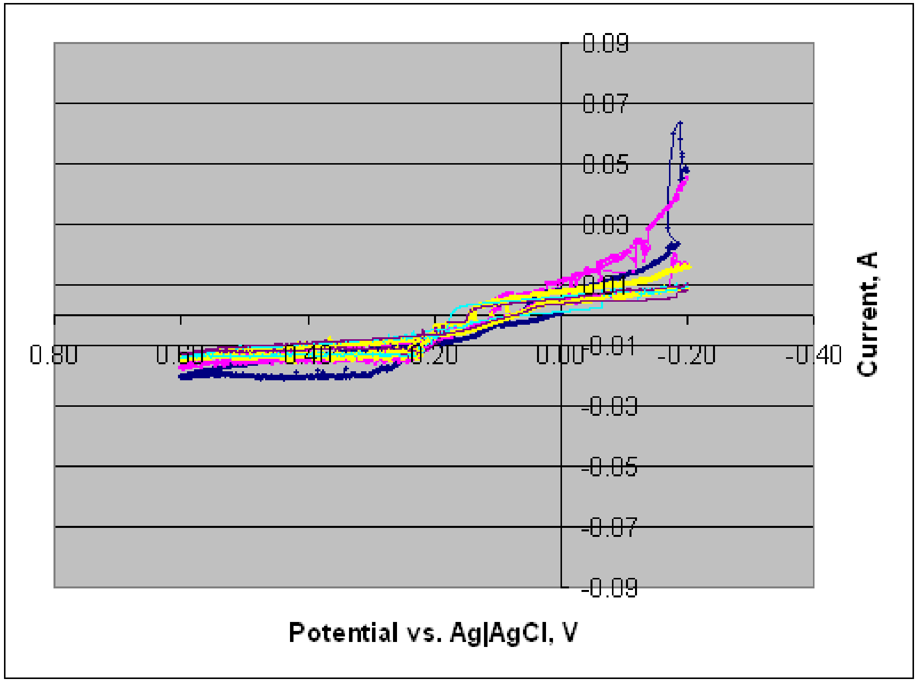
	I_{ca} (ori), A	I_{an} (ori), A	I_{ca} (sul), A	I_{an} (sul). A	I_{ca} (sul)/ I_{ca} (ori)	I_{an} (sul)/ I_{an} (ori)
Ag(I)/Ag(II)	0.001	0.0005	0.0125	0.006	12.5	12
Mn(III)/Mn(IV)	0.0004	0.00081	0.65	0.18	1625.0	222.2
Ce(III)/Ce(IV)	0.015	0.042	0.026	0.045	1.733	1.071
Cu(I)/Cu(II)	0.0055	0.0125	0.145	0.05	26.36364	4.0

Prototype Sensor



Prototype Sensor





Original sample

Sulfuric acid treated sample

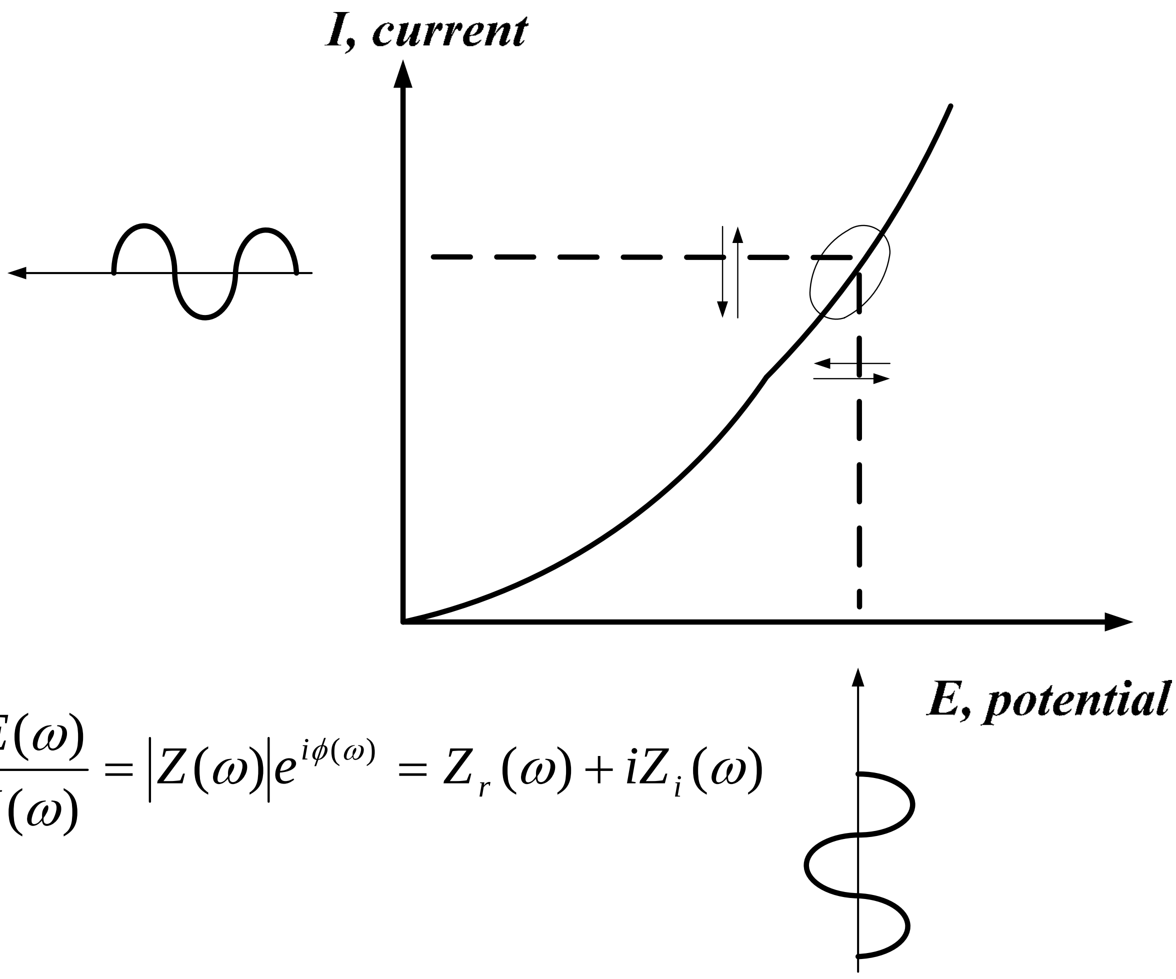
Reaction Mechanisms

Treatment with sulfuric acid produces

Hydroxyl, carbonyl, carboxylic acid, phenol, and sulfonated groups, ions, or fragments that may be very unstable and can be reduced or oxidized at certain potentials. The surface chemistry can be analyzed using XPS and FTIR.

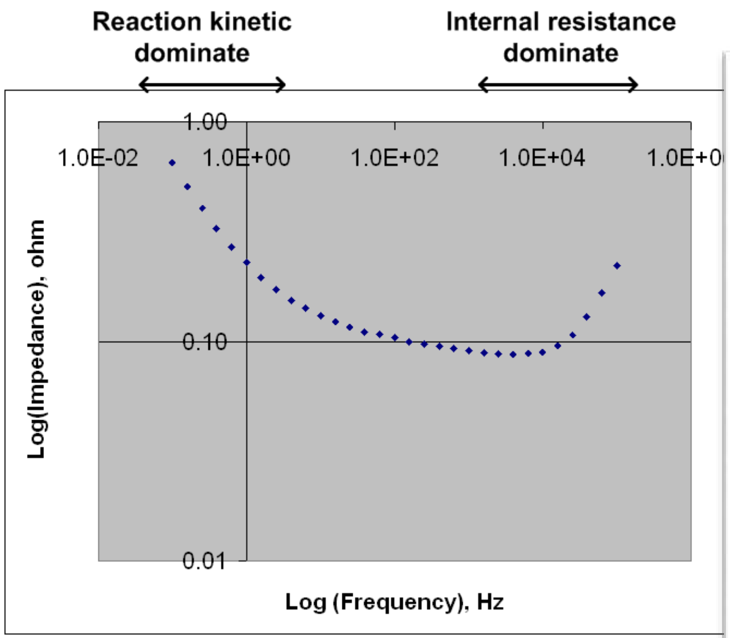
The electrochemical sensor can detect these groups, ions, or fragments on the surfaces.

Electrochemical Impedance Spectroscopy



$$Z(\omega) = \frac{E(\omega)}{I(\omega)} = |Z(\omega)| e^{i\phi(\omega)} = Z_r(\omega) + iZ_i(\omega)$$

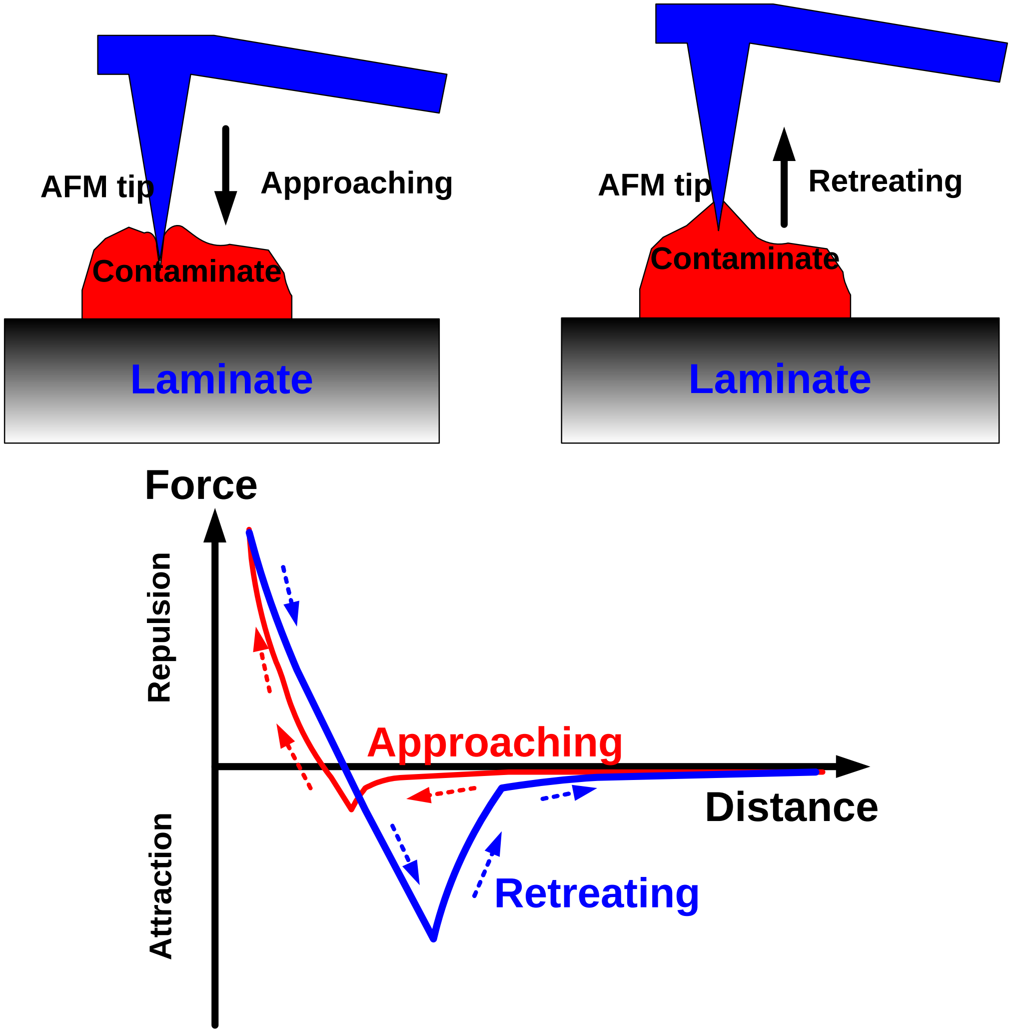
Electrochemical Impedance Spectroscopy



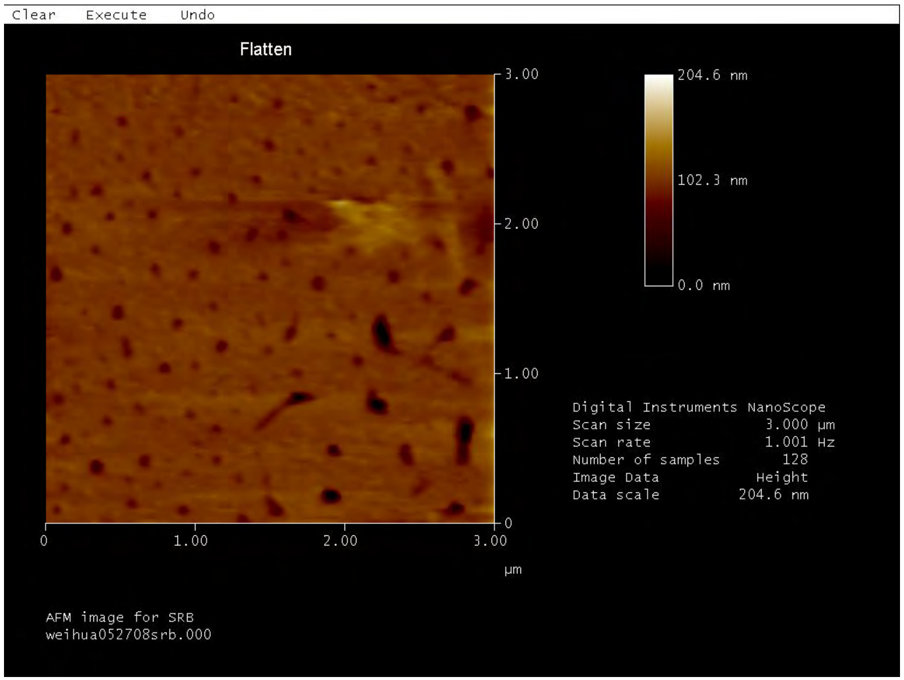
	Imp(Hi), ohm	Imp(Lo), ohm	Imp(Lo)-Imp(Hi) ohm	Ratio (Ori/Sul)
Ag-ori	8.369	6.36×10^4	6.36×10^4	150
Ag-sul	1.34	4.24×10^2	4.24×10^2	
Mn-ori	2.81	81.7	78.9	183
Mn-sul	**0.221**	**0.652**	**0.431**	
Ce-ori	2.62	55.6	53.0	2.16
Ce-sul	**0.336**	**24.8**	**24.5**	
Cu-ori	0.199	97.8	97.6	21.7
Cu-sul	**0.426**	**4.93**	**4.50**	
Ce-ori	0.441	1.58	1.139	3.07
Ce-sul	**1.14**	**1.51**	**0.37**	

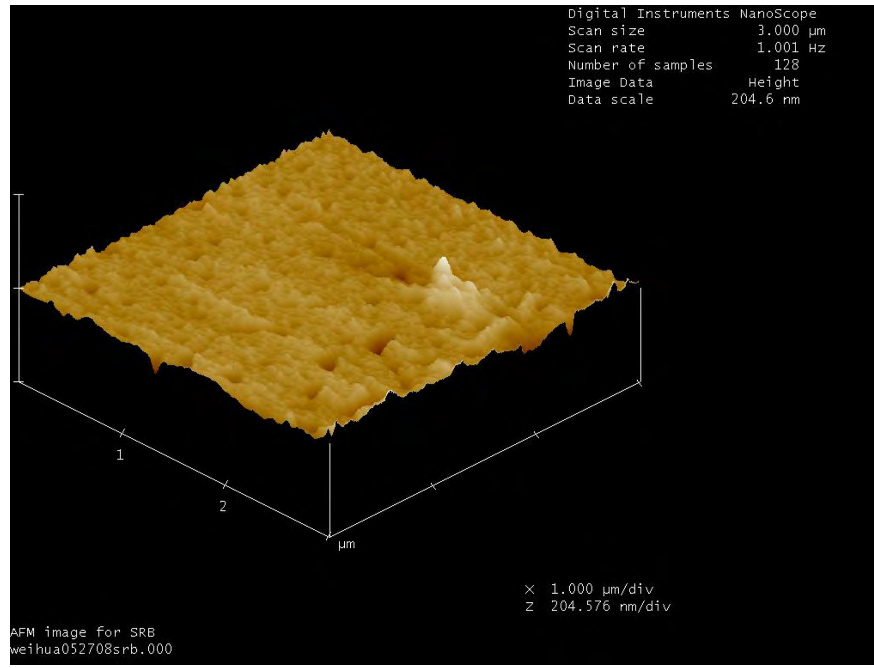
Sulfuric acid treated surface
Sensor with Mn(II)/Mn(III) mediator

AFM Force Spectroscopy

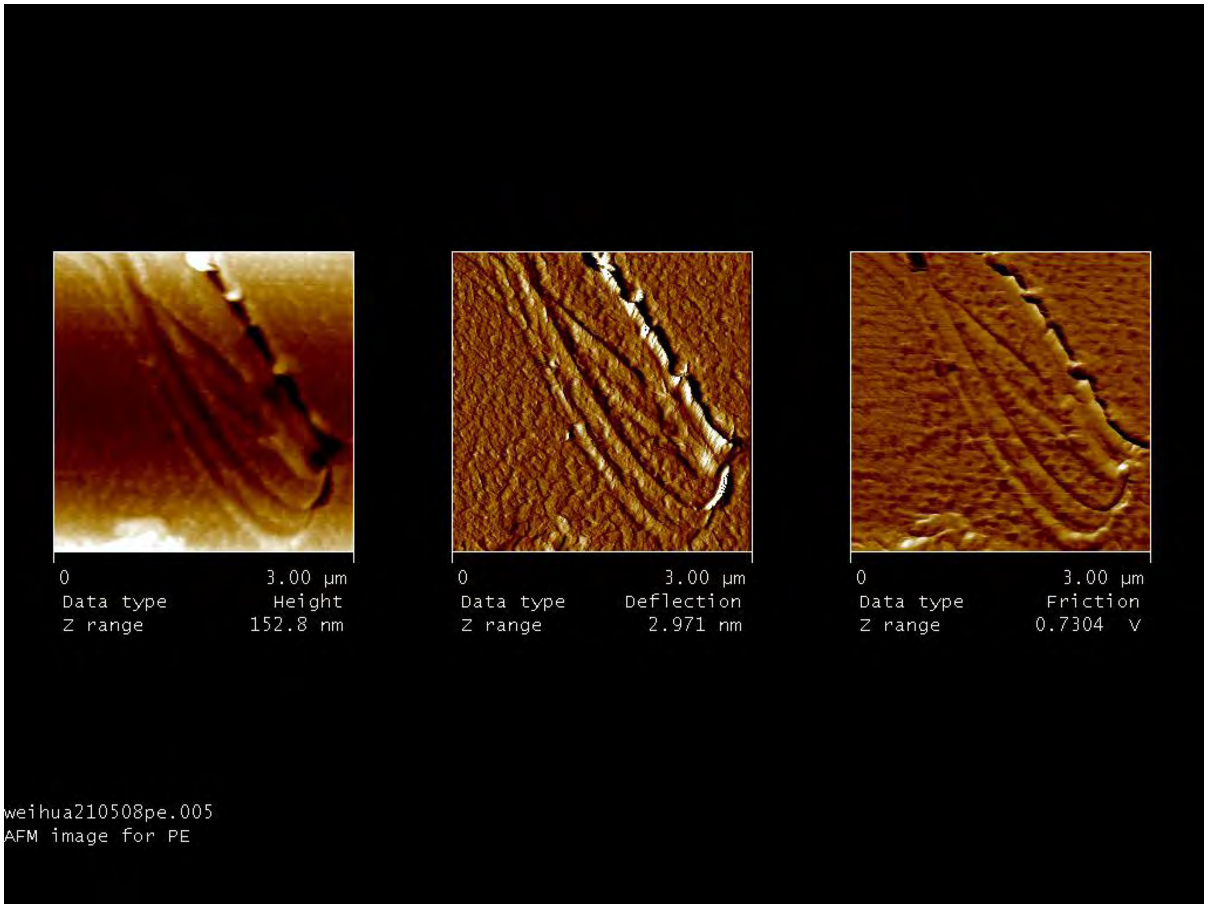


AFM Images of SRB Prepared Laminate Surfaces

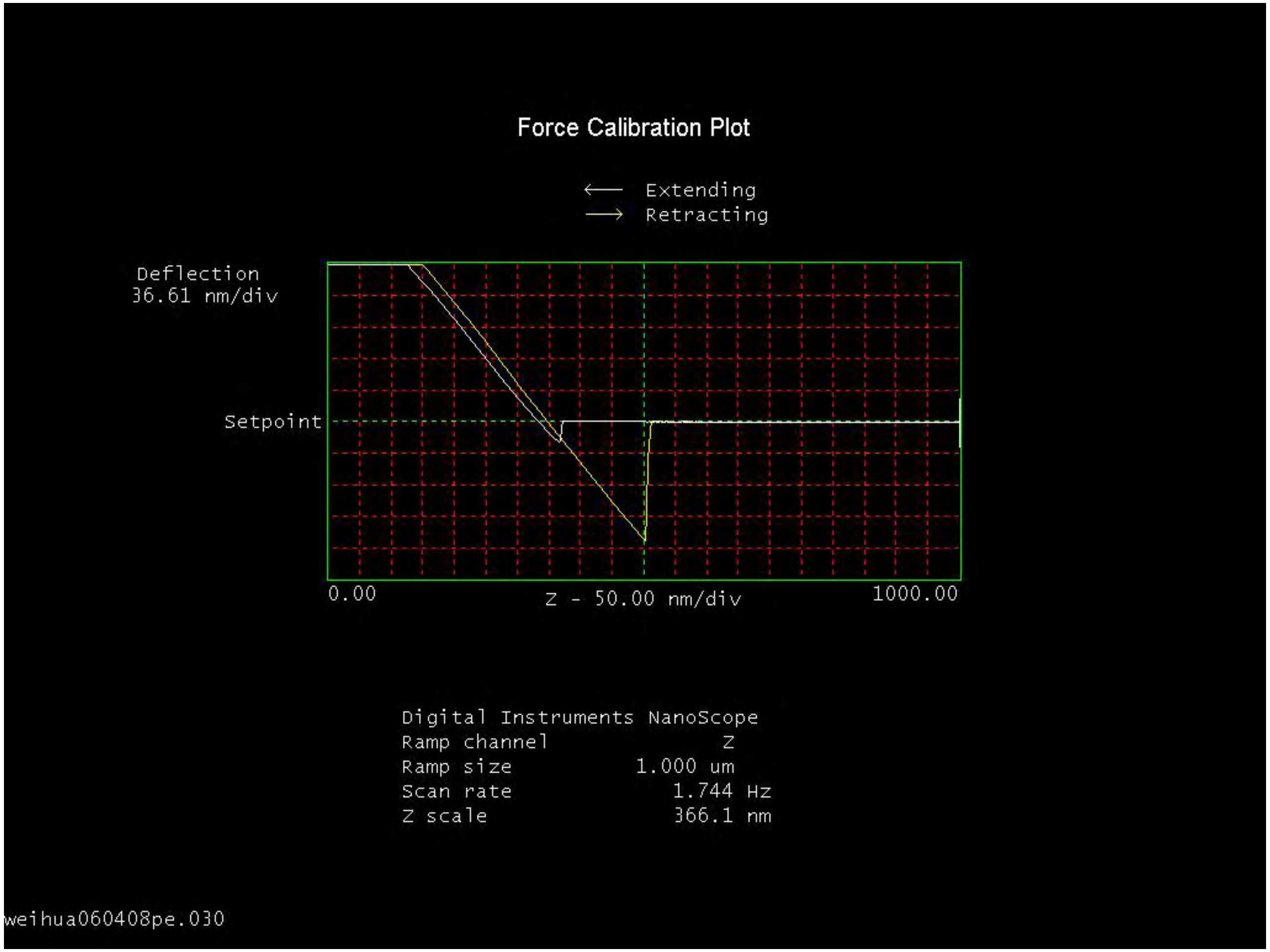




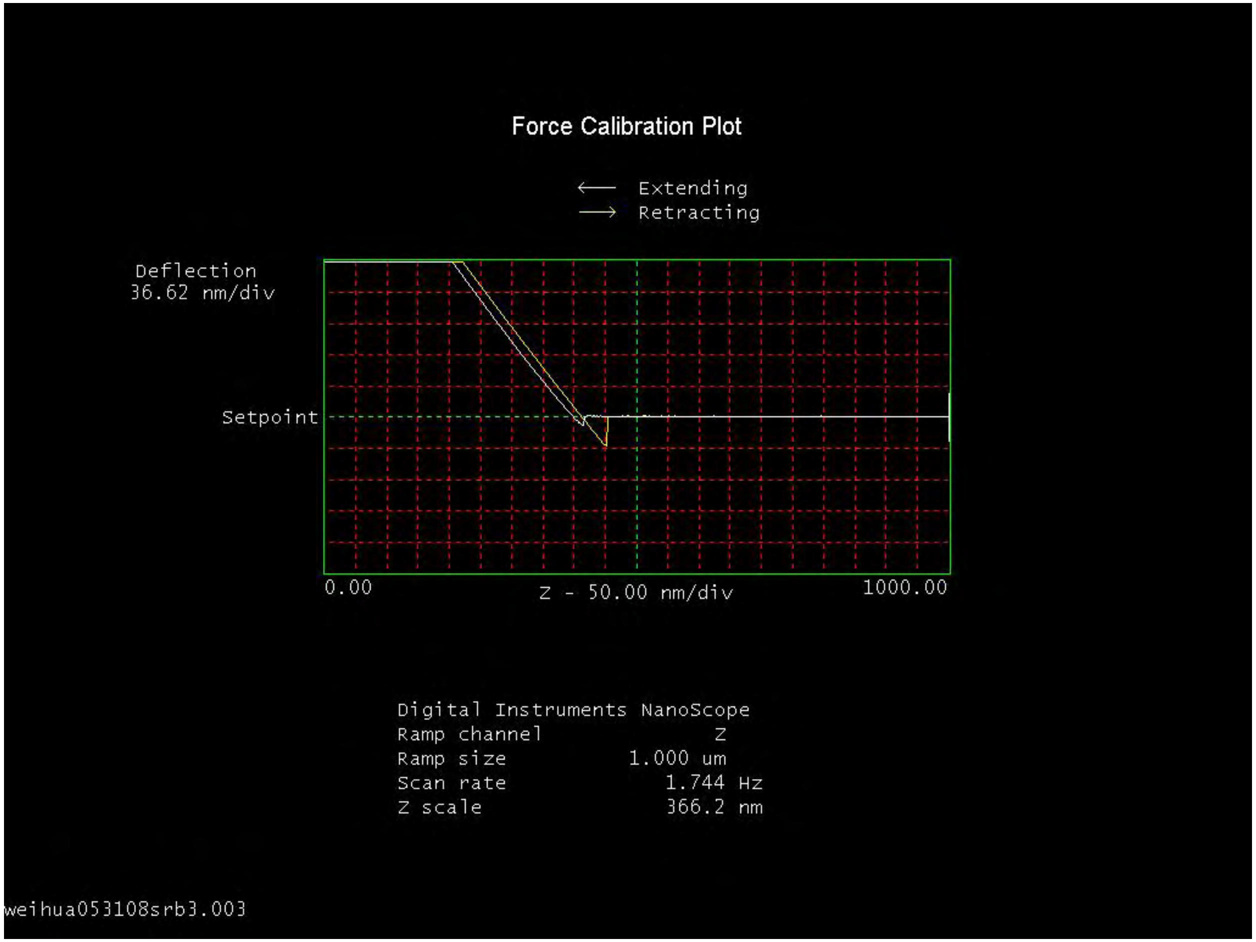
AFM Images of PE Prepared Laminate Surfaces



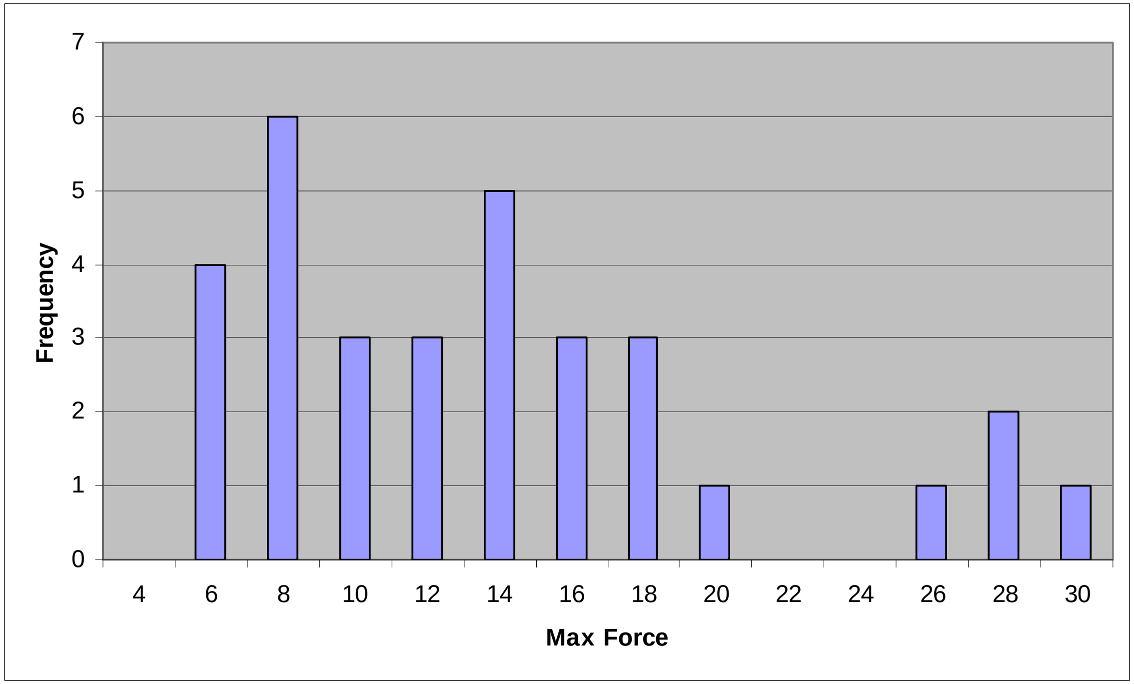
Typical Force Spectroscopy for PE



Typical Force Spectroscopy for SRB



Force Spectroscopy Statistics PE Prepared Surfaces



Average Force: 11.4 nN

Std. Deviation: 7.5 nN**

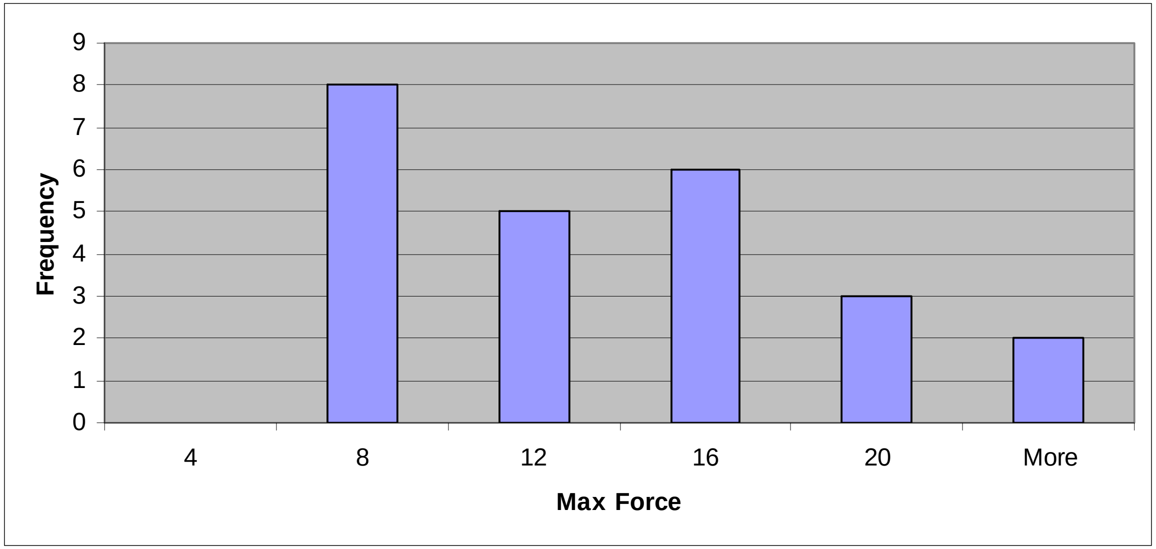
Skew: 0.6

(8 scanned areas)

**** Std. Dev. was significantly less for individual scans**

Slope Information

Force Spectroscopy Statistics
SRB Prepared Surfaces



Average Force: 12.0 nN

Std. Deviation: 6.8 nN**

Skew: 1.5

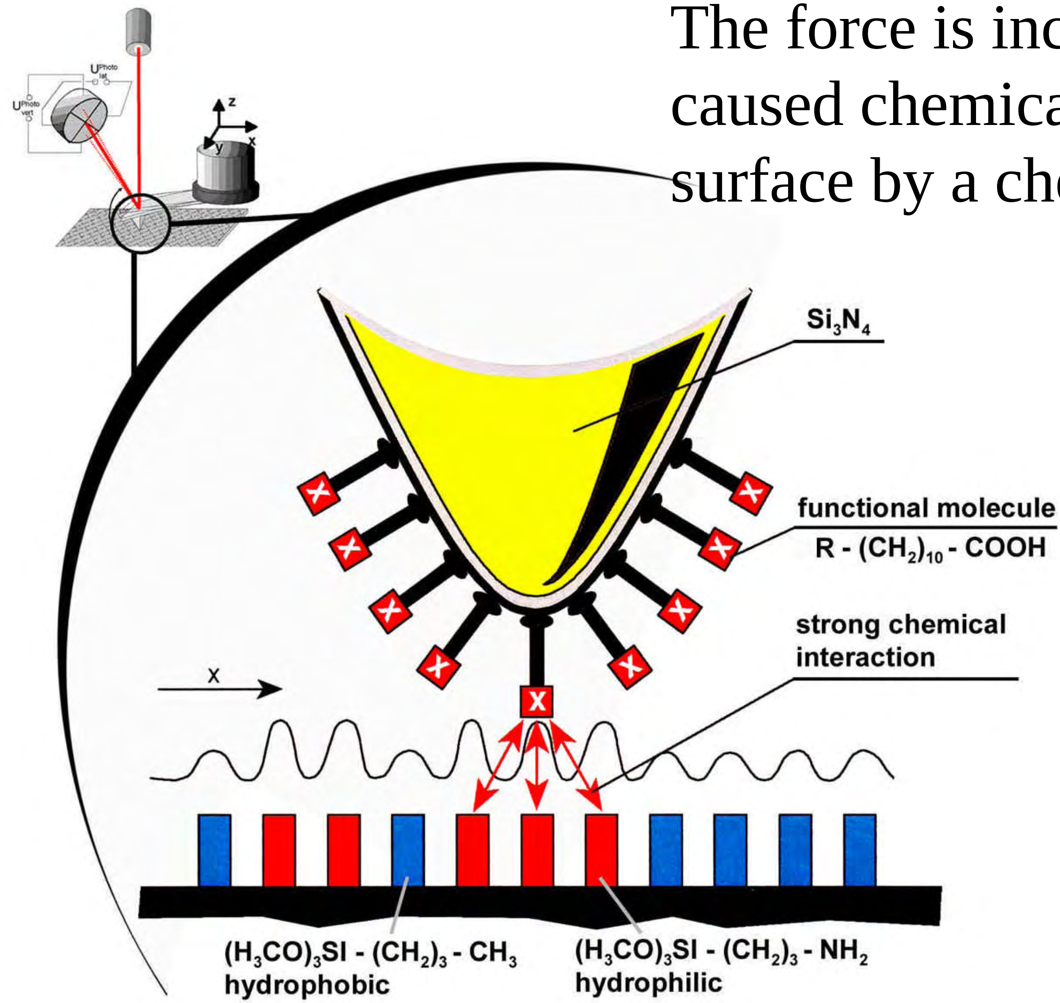
(6 scanned areas)

** **Std. Dev. was significantly less for individual scans**

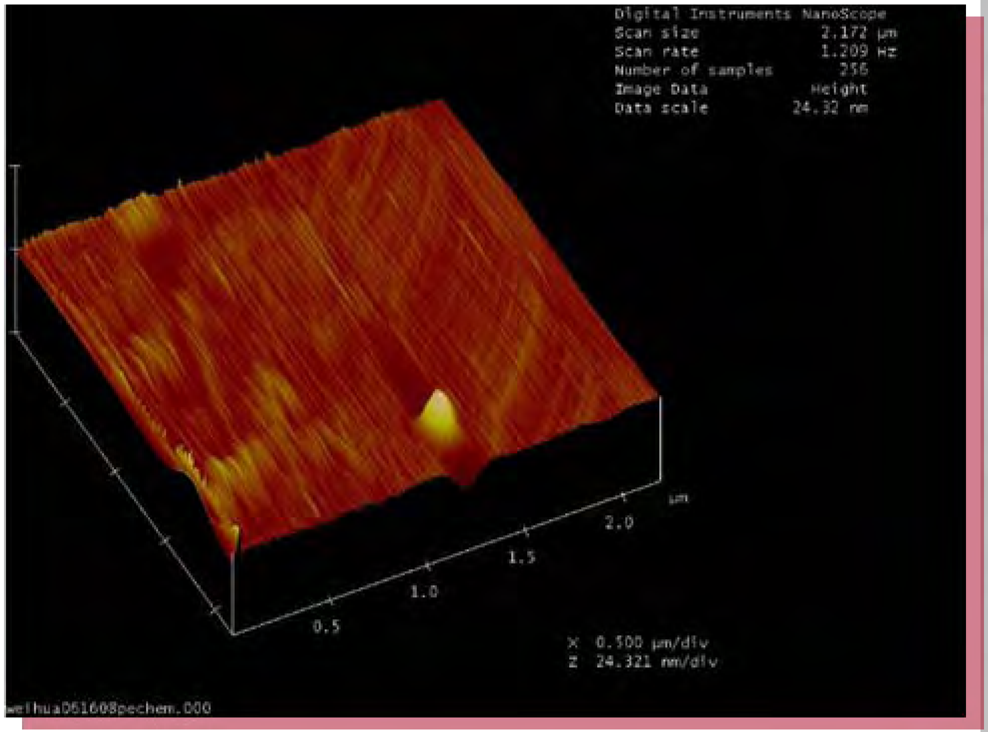
Slope Information

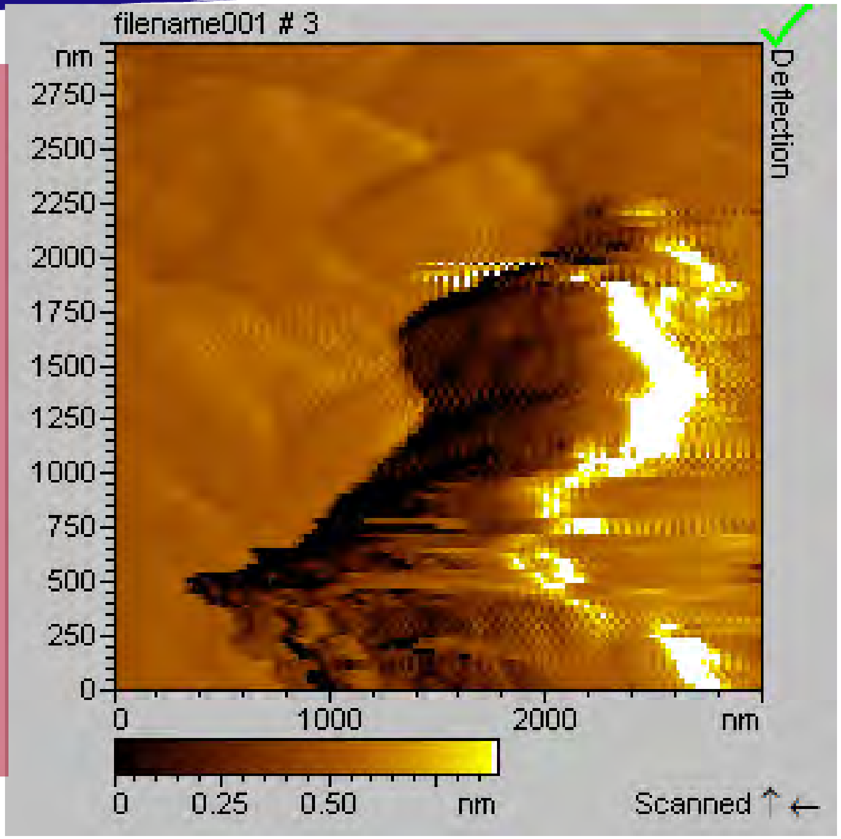
CFM Principles

The force is increased by the locally caused chemical reaction to the surface by a chemical component



CFM Image





- 3-D topographic Image
- PE prepared surface
- Hydroxyl group modified probe

- Deflection Image
- SRB prepared surface
- Hydroxyl group modified probe

Conclusions

- Solid-state electrochemical sensor can detect contamination on peel ply surfaces and is a promising technology for in-field surface chemistry analysis.
- In addition to Ag(I)/Ag(II), both Mn(II)/Mn(III) and Cu(I)/Cu(II) are effective mediators for electrochemical sensors.
- In addition to cyclic voltametry, electrochemical impedance spectroscopy can be a good method for surface inspection.

Conclusions

- AFM force spectroscopy can evaluate adhesion of the surfaces prepared with peel plies. The maximum adhesion of laminate surfaces prepared with PE peel plies is greater than that of the surface prepared with SRB peel ply, correlating with bond strength and contamination level.
- CFM images in combination with force spectroscopy can potentially provide useful information for surface activity.

A Look Forward

- Benefit to Aviation
  - Better understanding of the pre-bond surface preparation methods
  - Better understanding of bond strength and durability versus surface preparation
  - Practical in-field, online certification and assurance technology for surface preparation
  - Reduced costs for surface preparation and adhesive bonding processes
- Future needs
  - In-field, online analytical detection and monitoring technologies for manufacture, chemical, environmental, and energy industries.
- Path
  - Continue Candidate sensor evaluation – 1. Voltametry, 2. Impedance (Conductance)
  - Sensor prototype assessment and evaluation
  - XPS/FTIR verification
  - Continue AFM/CFM series experimentation - alternate modes.