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

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The Joint Advanced Materials and Structures Center of Excellence

Introduction

- Motivation and Key Issues
  - Adhesive bonding has been used in the manufacture and repair as a direct competition to mechanical fastening.
  - Adherend surface preparation is a critical issue to the structural integrity and durability of bonded structures.
- Objective
  - benchmark surface preparation quality assurance methods
  - identify and validate definitive analytical chemistry methods to provide sufficient in-field quality assurance.
- Approach
  - Literature review and analysis
  - Surface chemistry analysis
  - Electrochemical sensor development
  - Experimental validation

FAA Sponsored Project Information

- PI & Researchers
  - Richard Burton, Rajiv Srivastava, Weihua Chang, Dwayne McDaniel, Wongbon Choi, Xiangyang Zhou
- Students
  - Sam Hill, Yao Ge, Shejie Tang, Ling Wang
- FAA Technical Monitor
  - Drs. Jim White & Curtis Davies
- Industry Participation
  - DME, Avborne, AeroMatrix

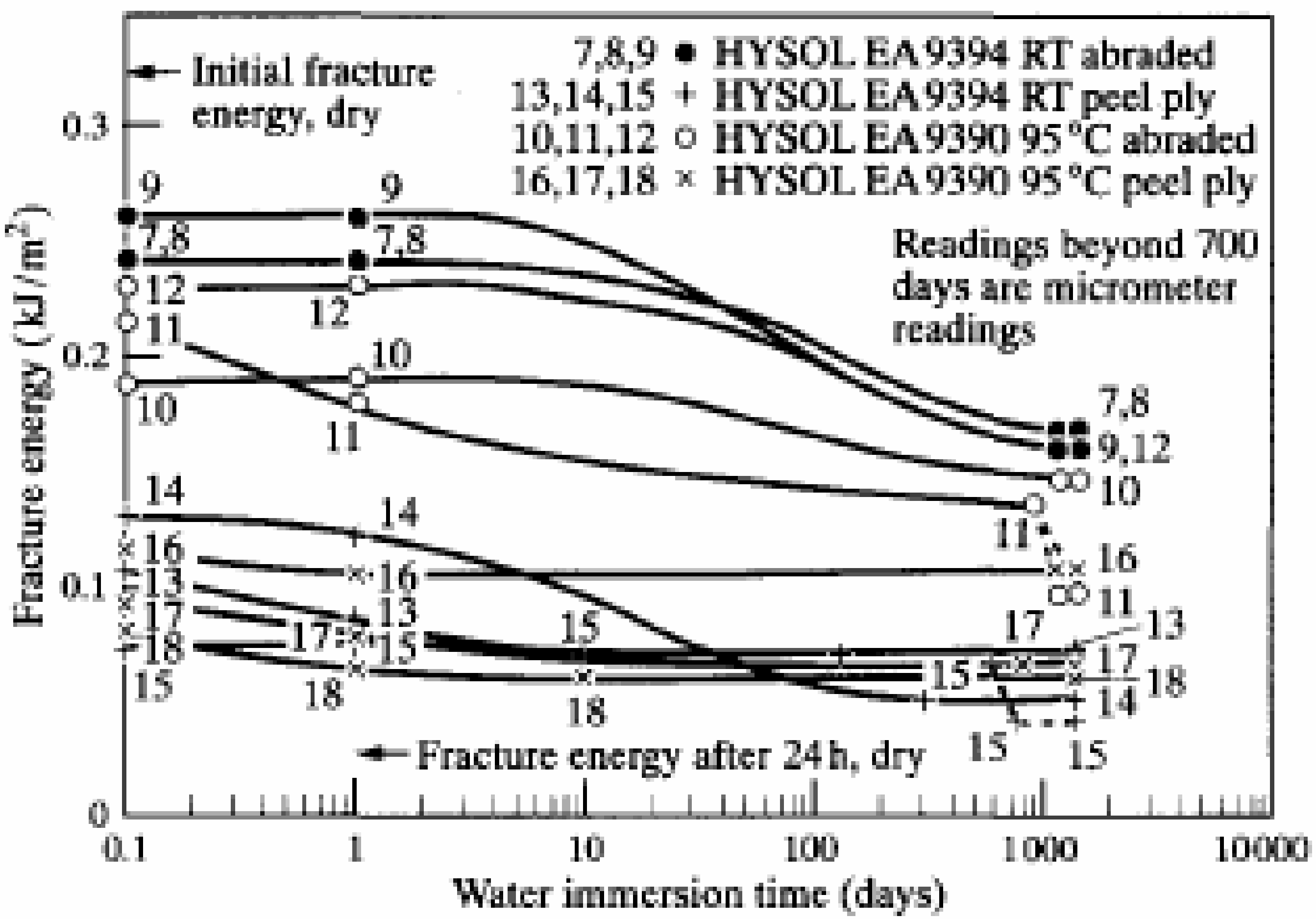
Main Results

- Literature database, complete
- Summary of literature review
  - Surface treatment, complete
  - Surface chemistry analyses, complete
- An electrochemical sensor for surface chemistry analysis, testing in progress
- Carbon nano-tube sensor for humidity sensing, testing in progress
- AFM/SEM study of surface-contamination (peel-plies, etc),testing in progress

Research Roadmap

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

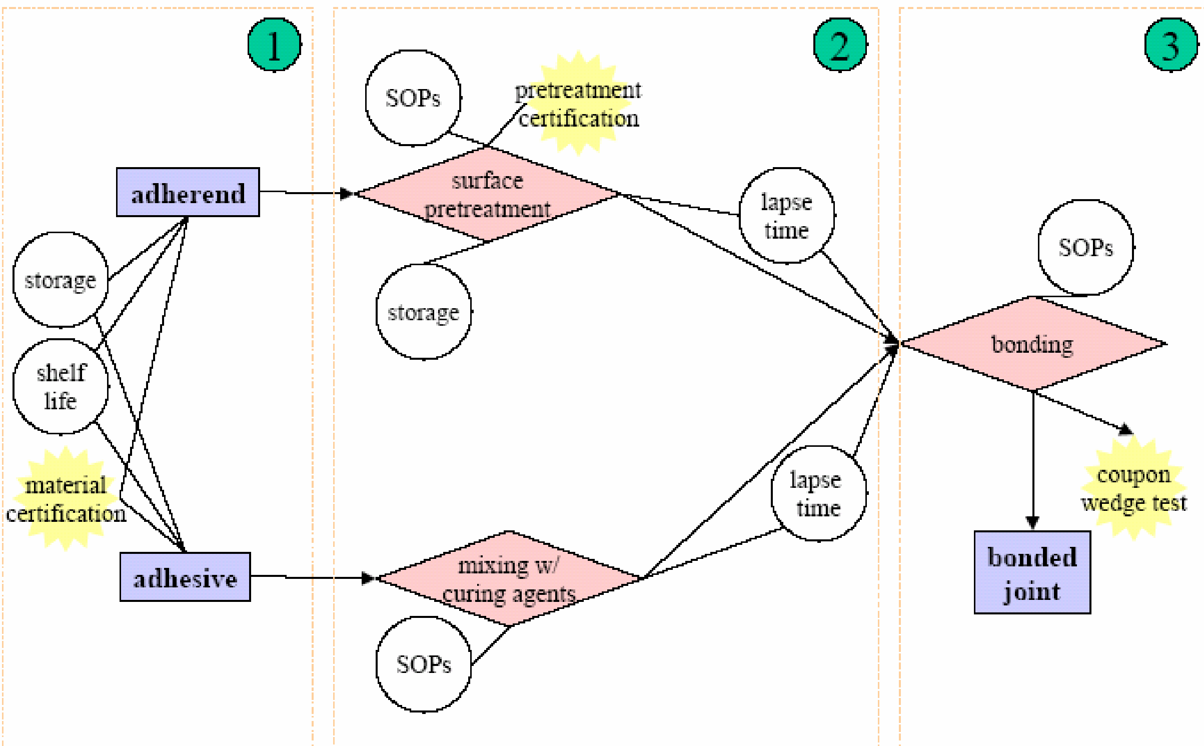
Literature Review: Effect of Various Surface Pretreatment Method



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

Quality Control

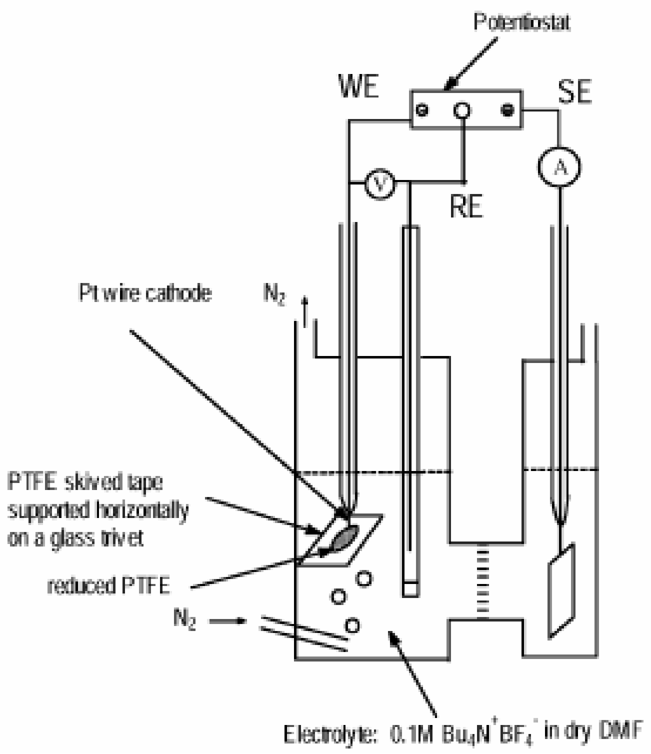


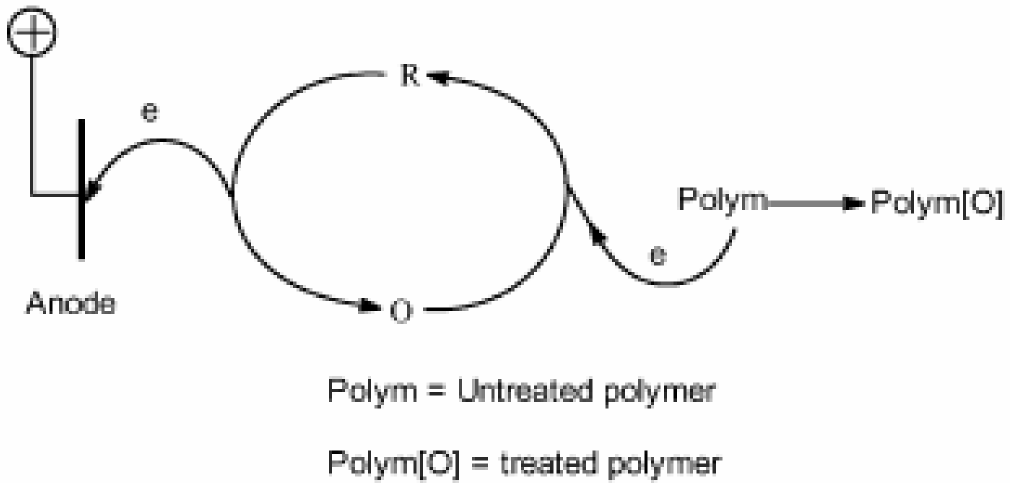
- Materials certification
- Pretreatment certification
- Adhesive application certification
- Bonding certification
- Technician certification
- Process flow management

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

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

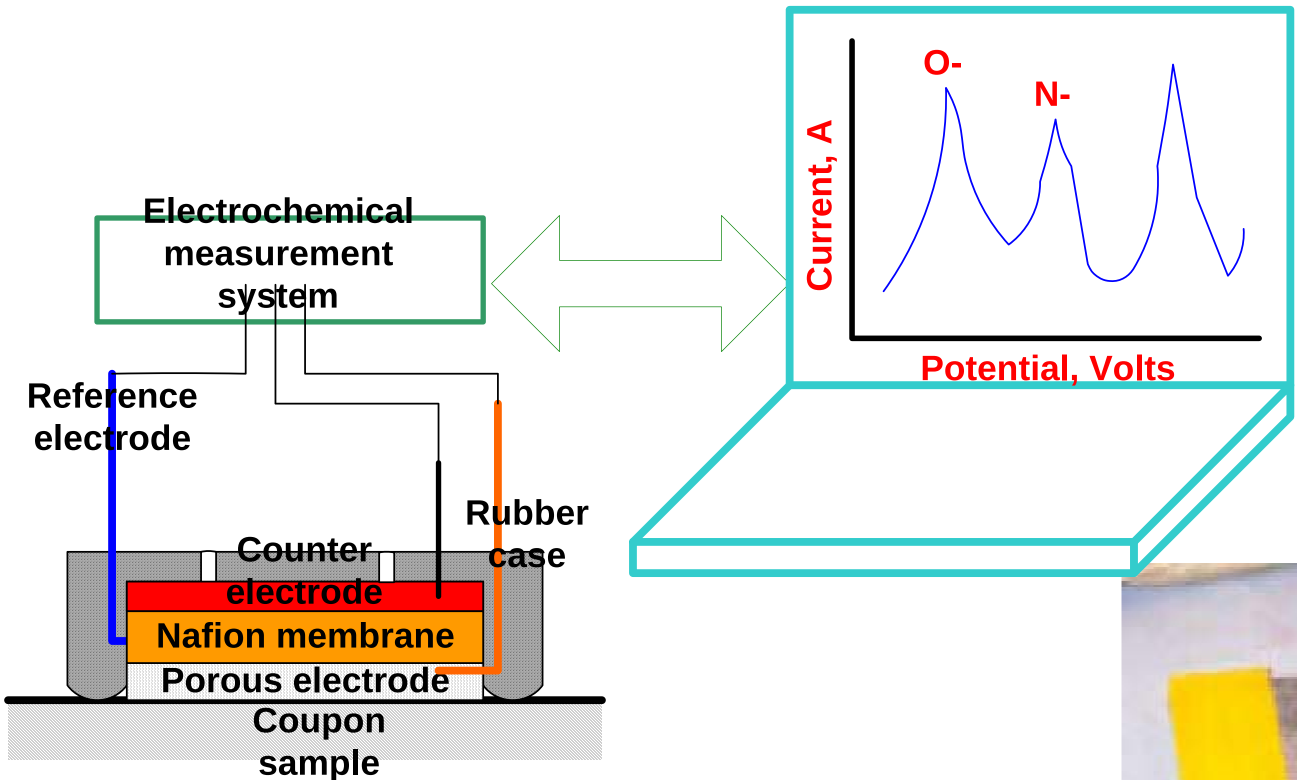
Electrochemical Sensor





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

Solid-State Electrochemical Sensor



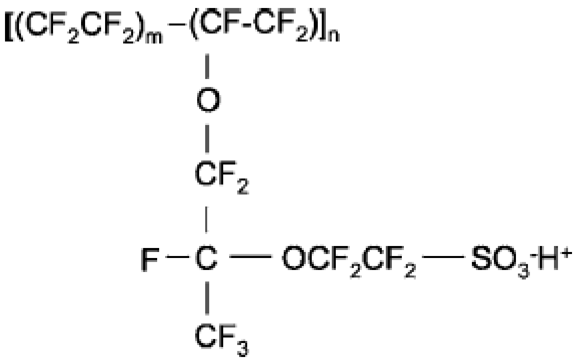
Candidate Mediator Couples

- Ag(II)/Ag(I) E^0=1.98 V
- Ag+/Ag E^0=0.8 V

- **Ce(IV)/Ce(III)** **E^0=1.72 V**
- **Co(III)/Co(II)** **E^0=1.83 V**
- **I_2/I^-** **E^0=0.54 V**
- **$Fe(CN)_6^{-4}/Fe(CN)_6^{-3}$** **$E^0$=0.36 V**
- **Fe^{+3}/Fe^{+2}** **E^0=0.77 V**

Solid-State Electrolyte

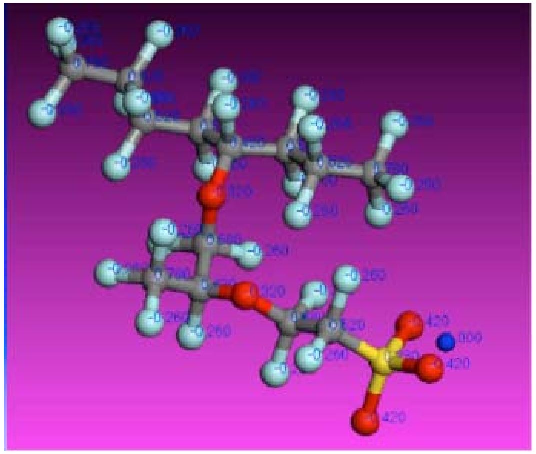
Nafion + Nafion Resin
(Sulfonated tetrafluorethylene copolymer)



Extremely resistant to chemical attack

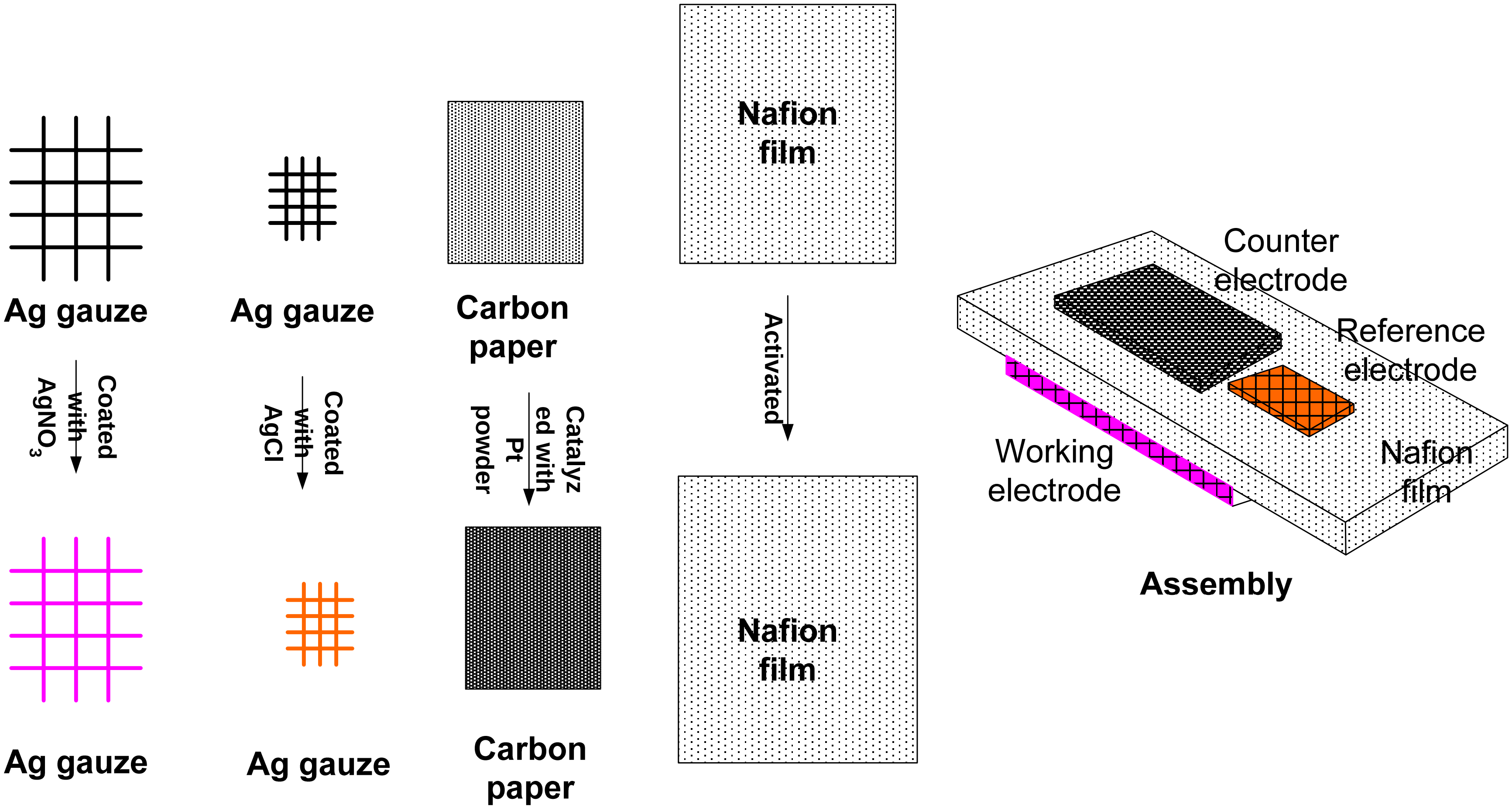
Proton conductor

Strong proton donor and free electron acceptor-superacid catalysts (neutral pH)

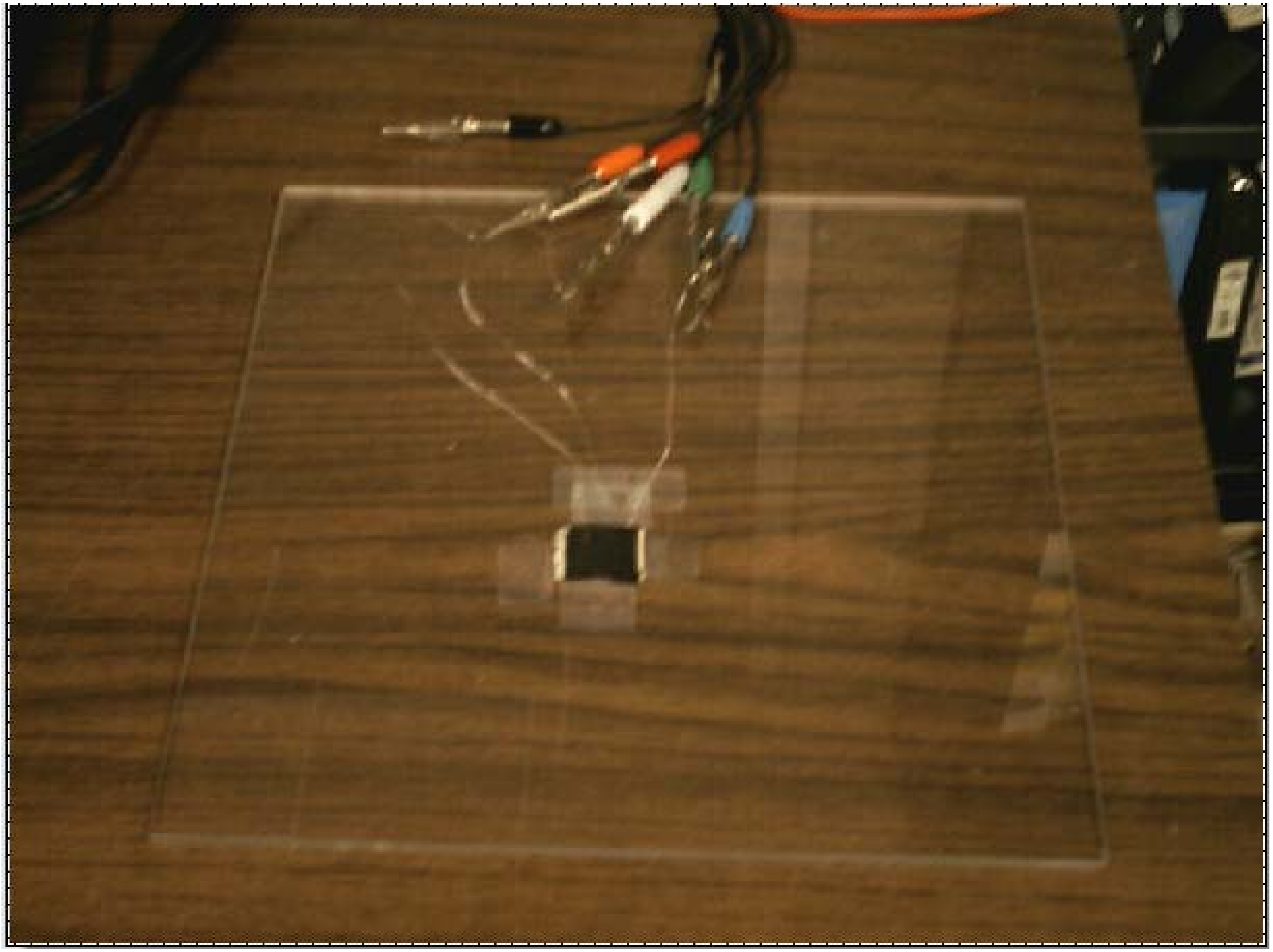


Minimum oxidation and reduction of water

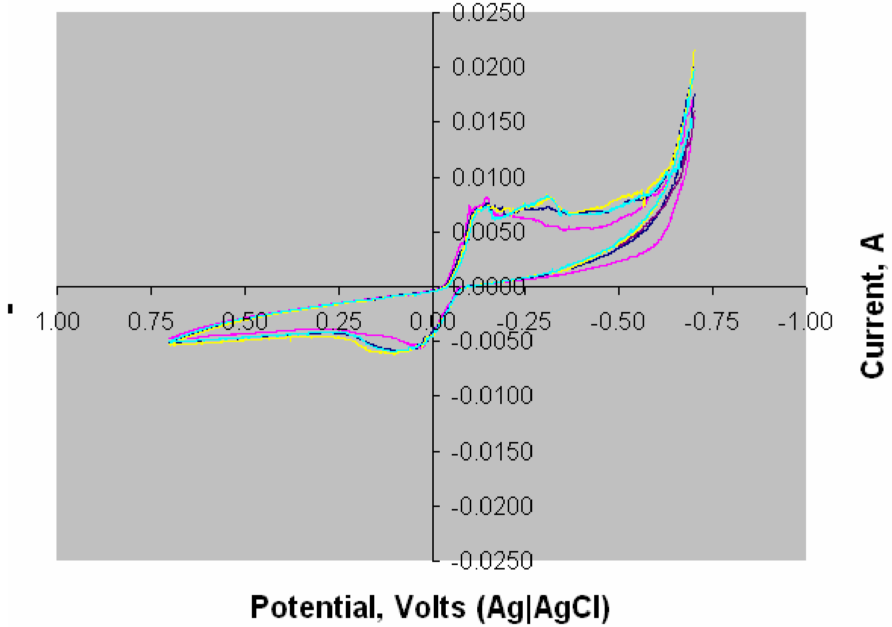
Fabrication of Electrochemical Sensor

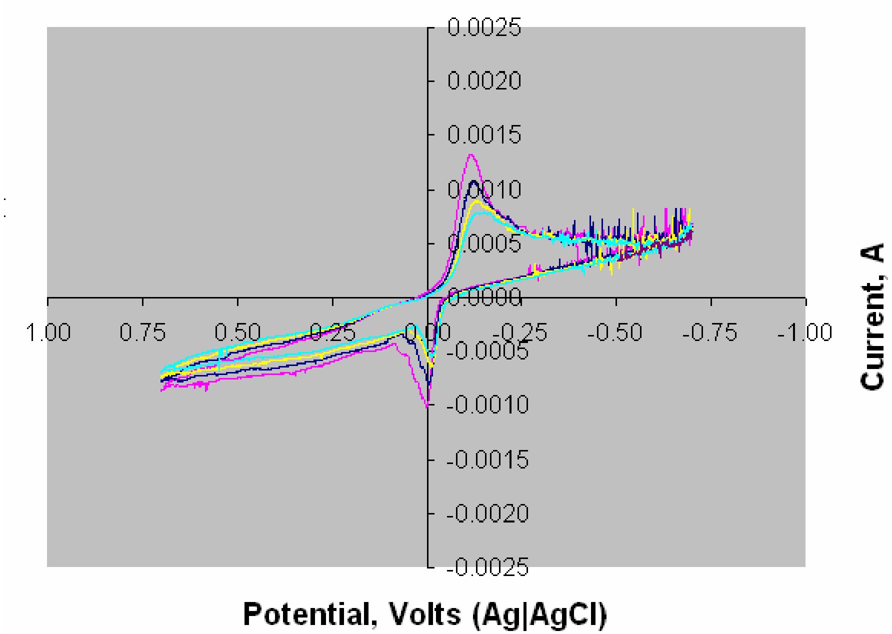


Solid-state Electrochemical Sensor

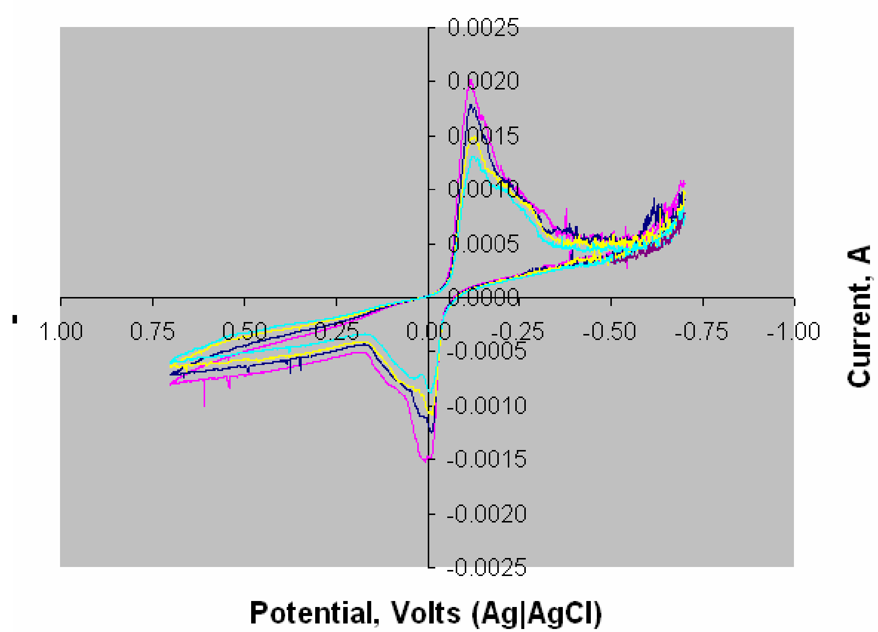


Treated with sulfuric acid





Original acrylic plastic surface

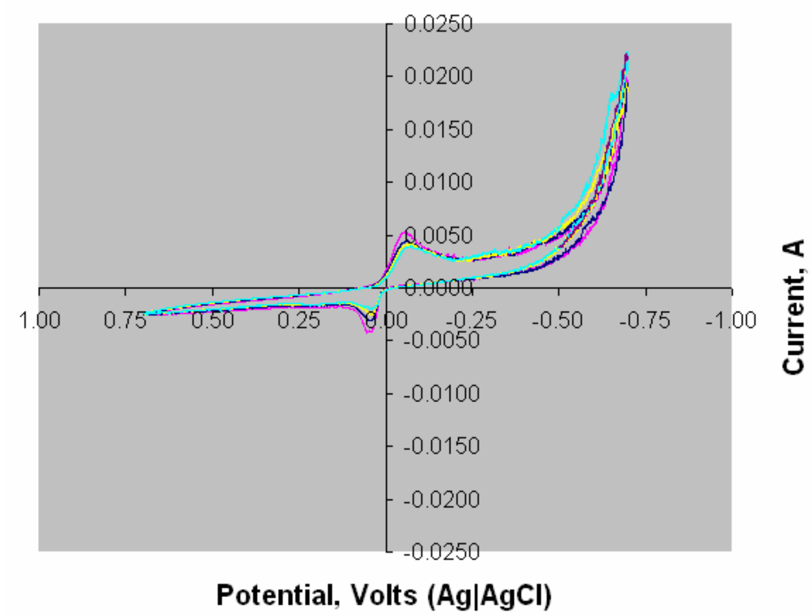


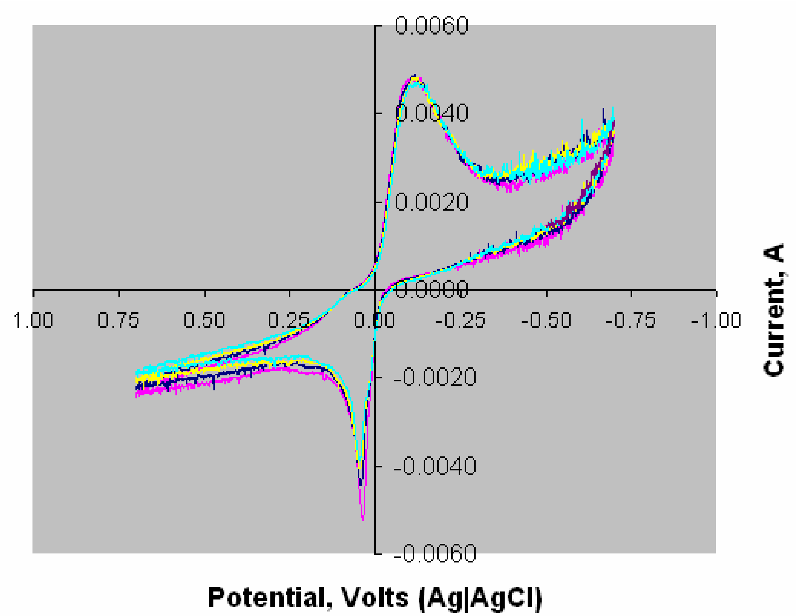
Polished acrylic plastic surface

$$2H^+(aq) + 2e^- \leftrightarrow H_2(g), \ 0 \text{ V}$$

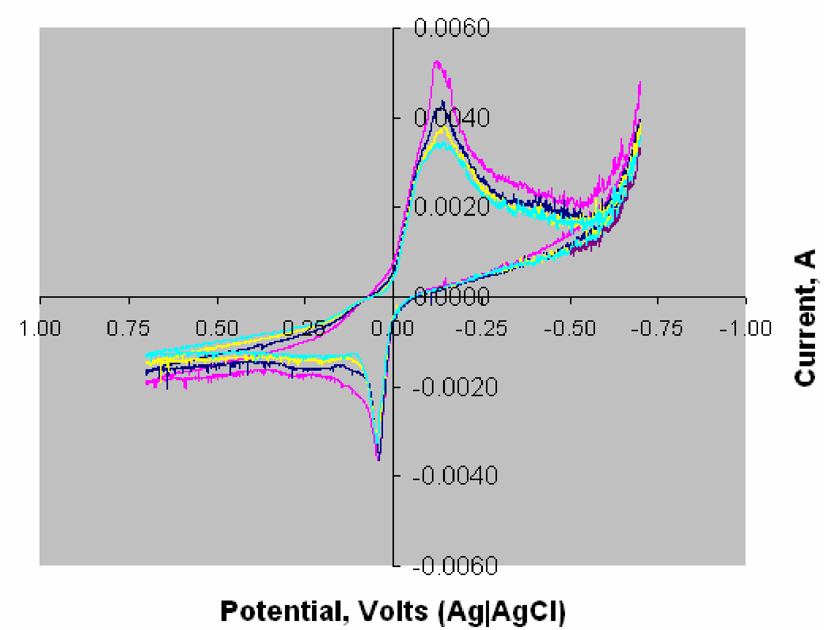
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad -0.83$$

Treated with sulfuric acid





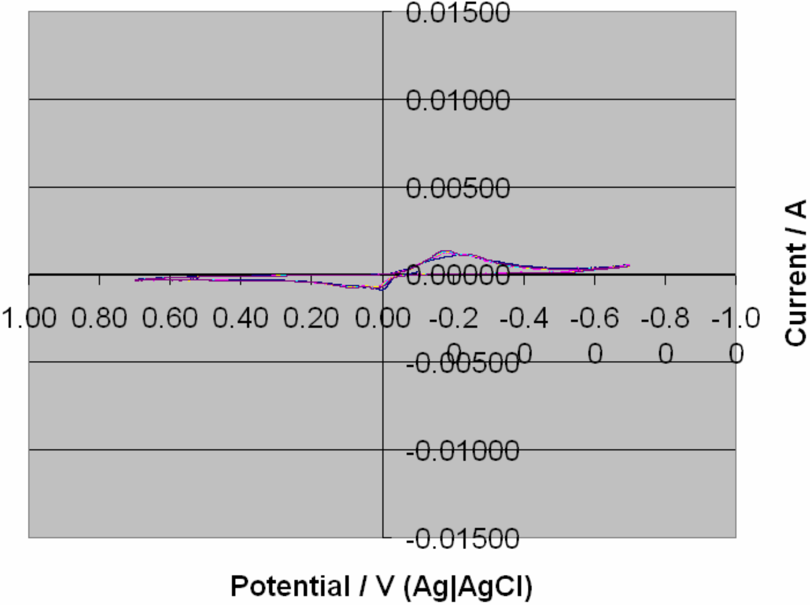
Original acrylic plastic surface



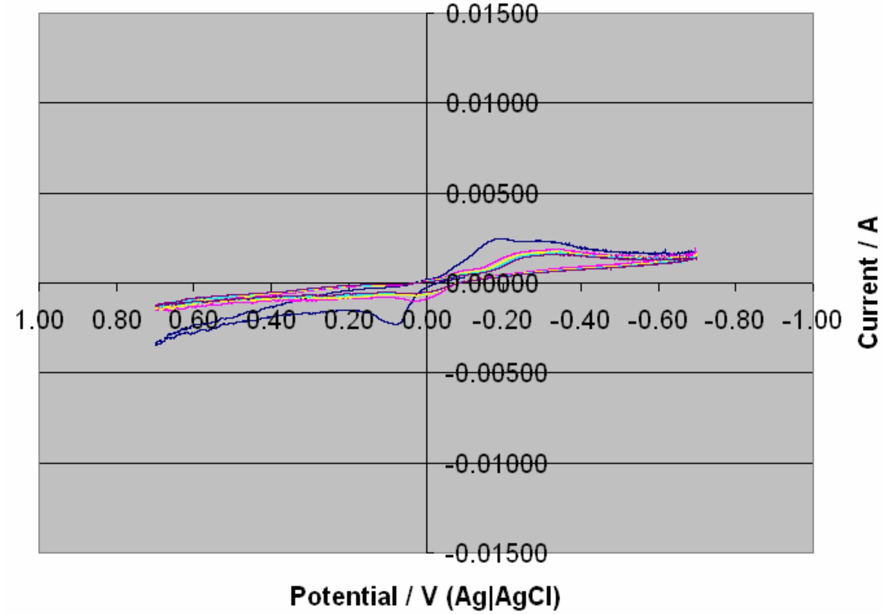
Polished acrylic plastic surface

Tests on Polyester Peel Ply Samples

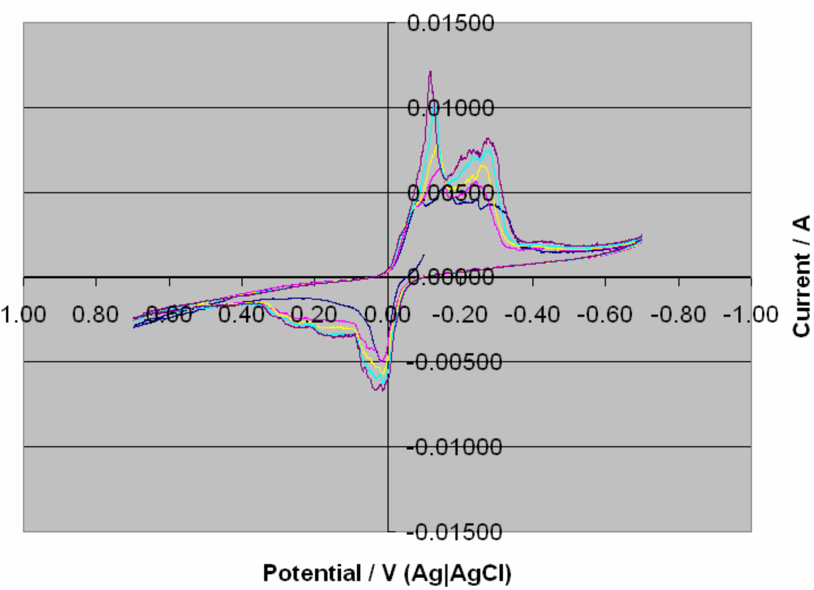
- Original surface: after removing peel ply
- Polished surface: polished using polishing paper (#600), and wiped with paper.
- Sulfuric acid etched: immersed in 50% sulfuric acid for 1-2 seconds, washed with DI water, and dried.



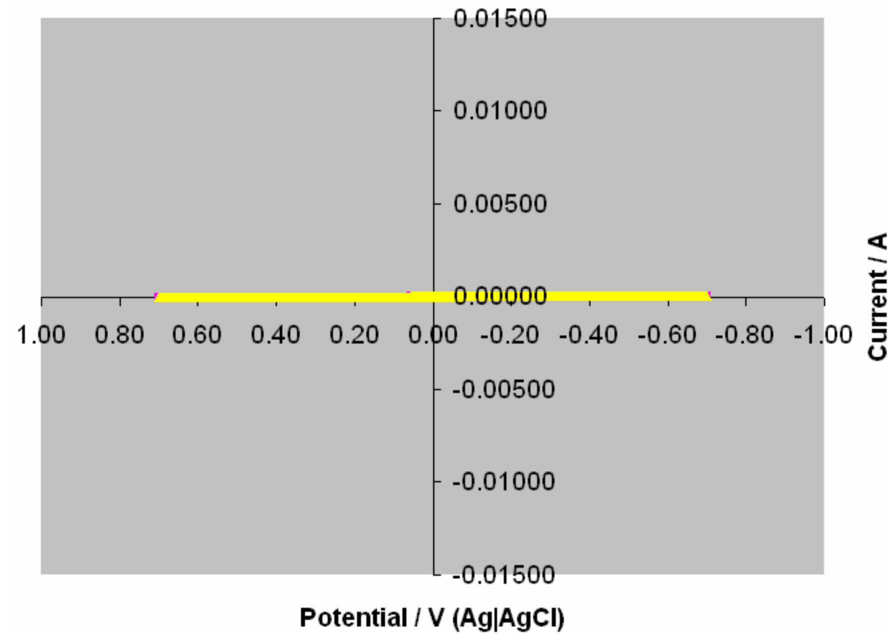
Original peel ply sample



Polished sample

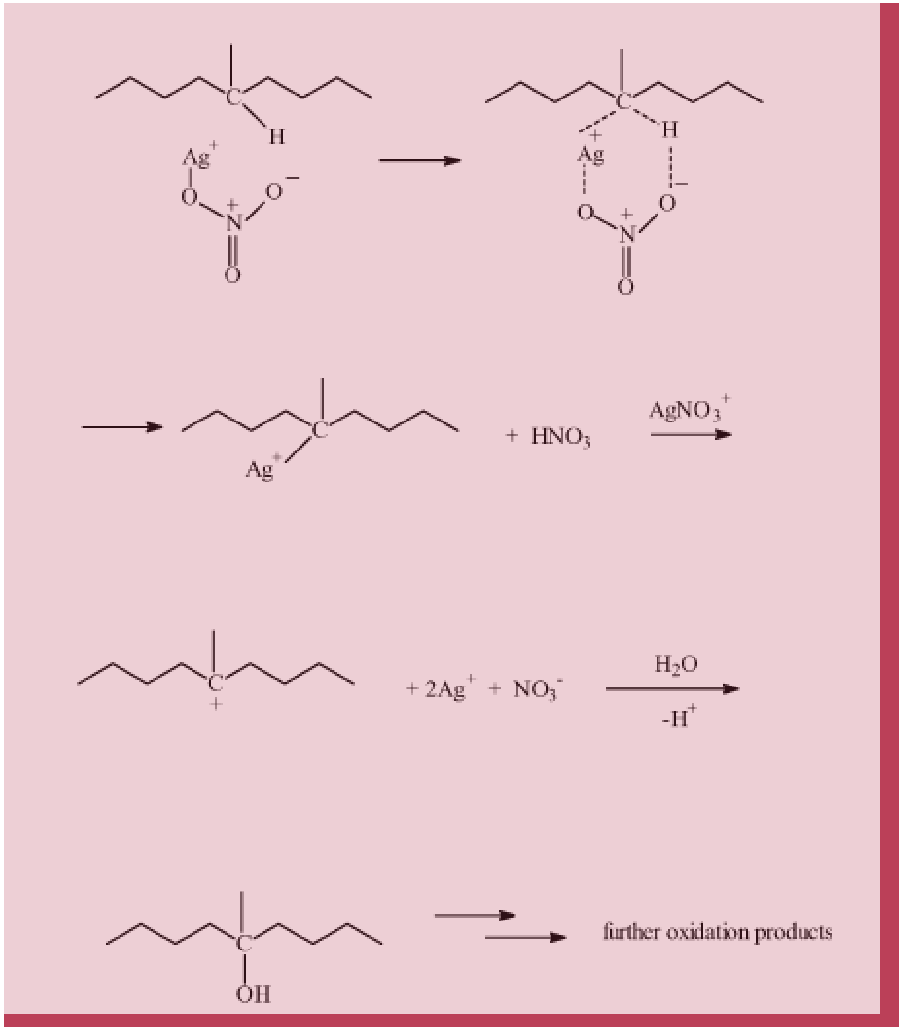


Sulfuric acid treated sample



In air

Reaction Mechanisms



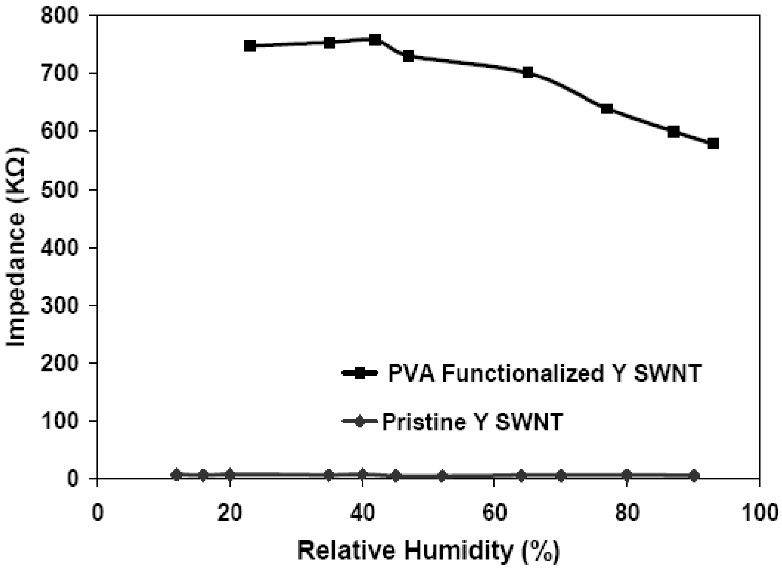
Reaction Mechanisms

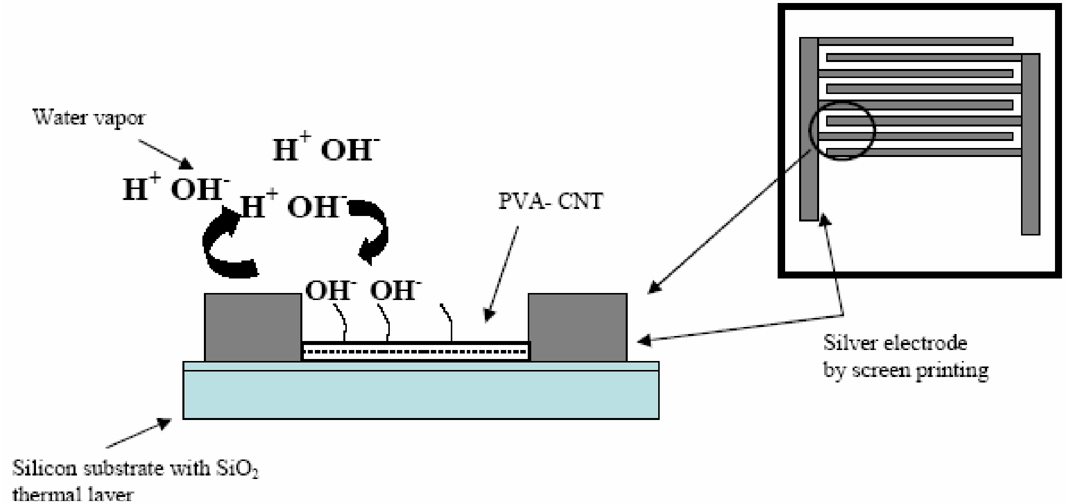
Treatment with sulfuric acid produces

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.

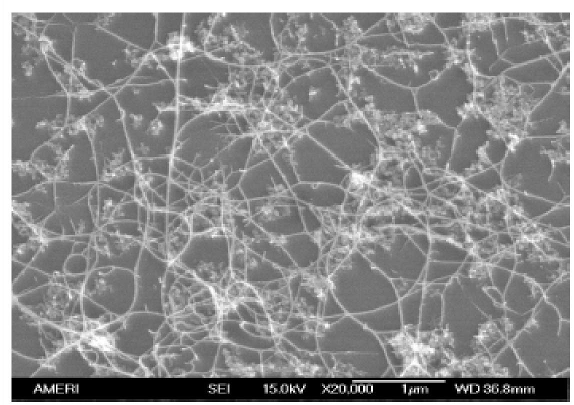
The electrochemical sensor can detect these groups, ions, or fragments on the surfaces.

Carbon Nanotube Based Humidity Sensor

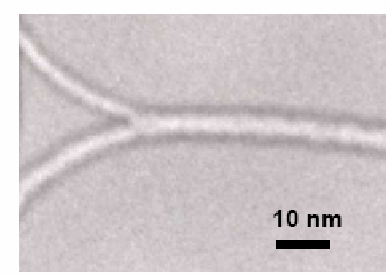




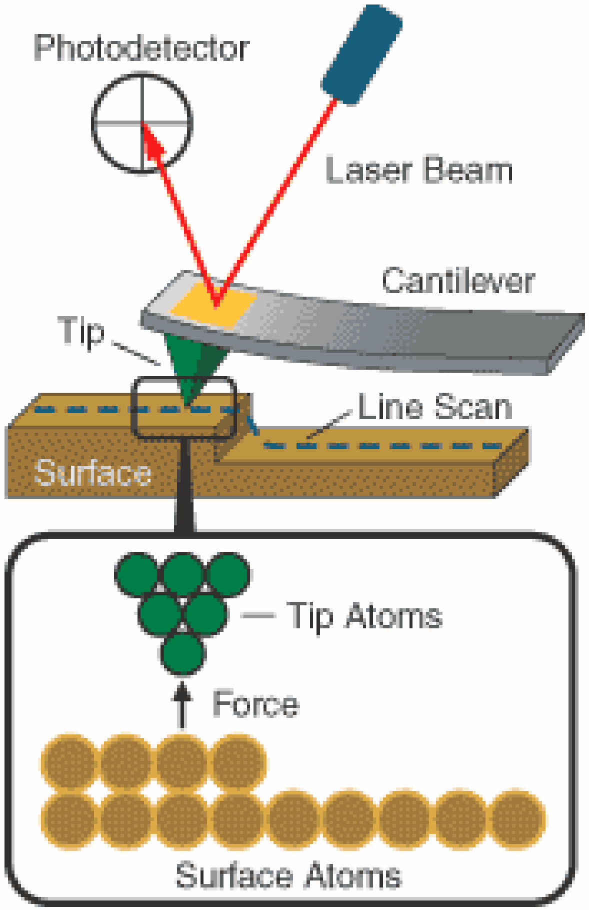
(c)



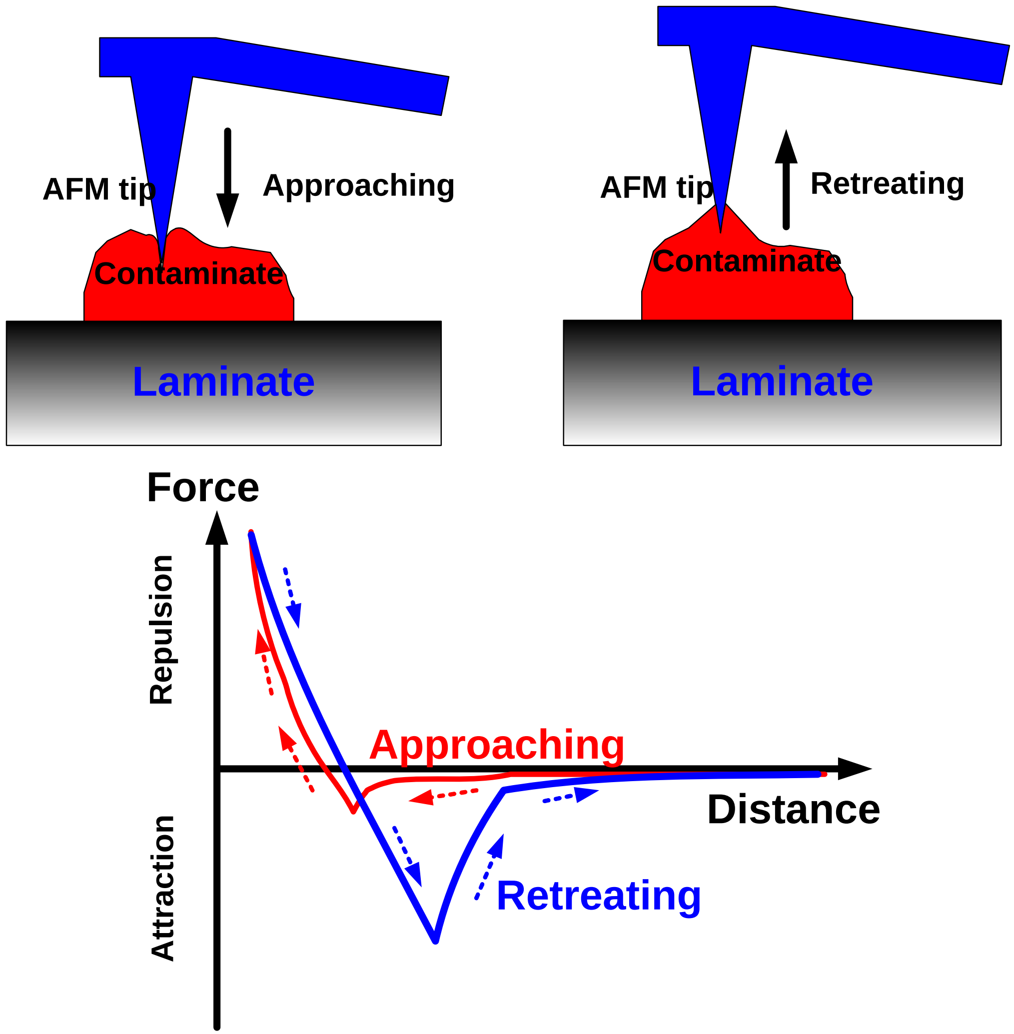
(d)



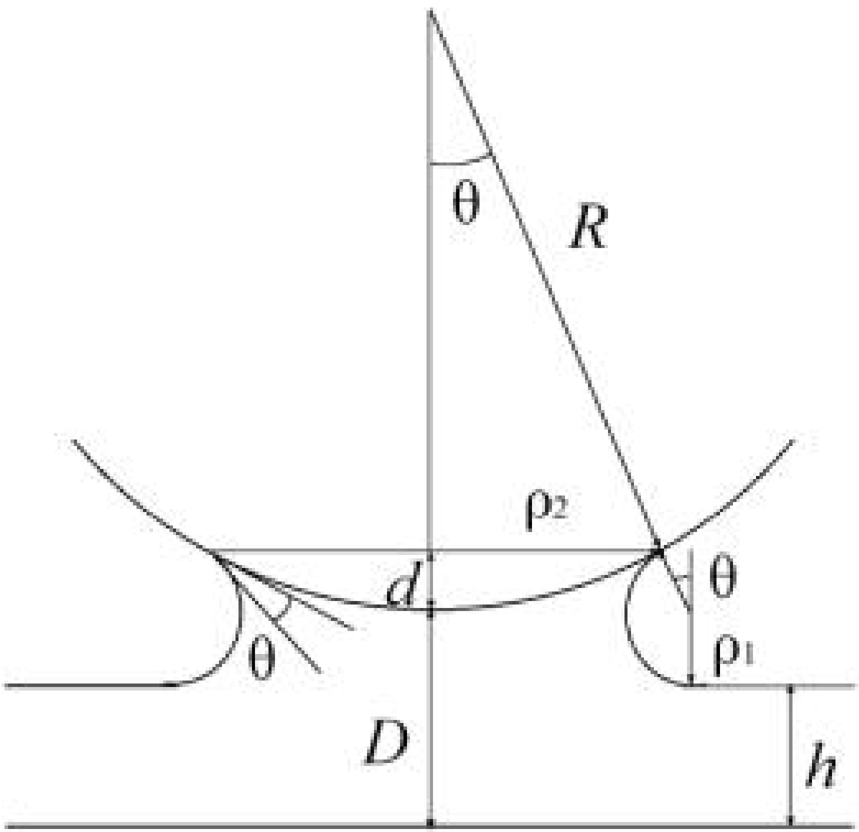
Atomic Force Microscopy (AFM) Study



AFM Force Spectroscopy



Evaluation of Surface Adhesion

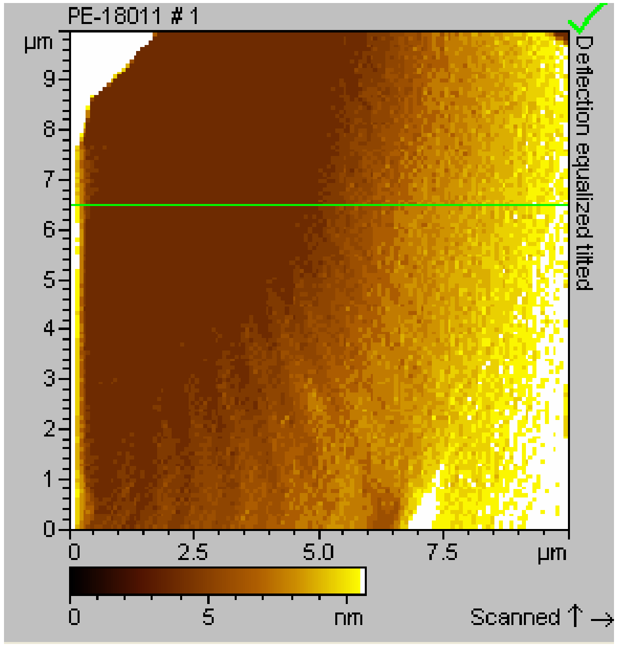


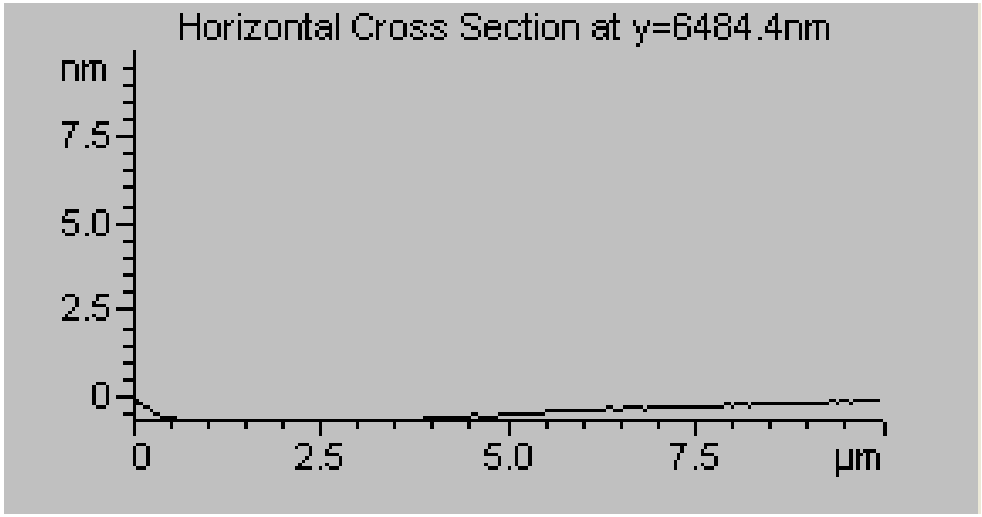
$$\sigma = \frac{F_{\max.attraction}}{4\pi R\cos\theta}$$

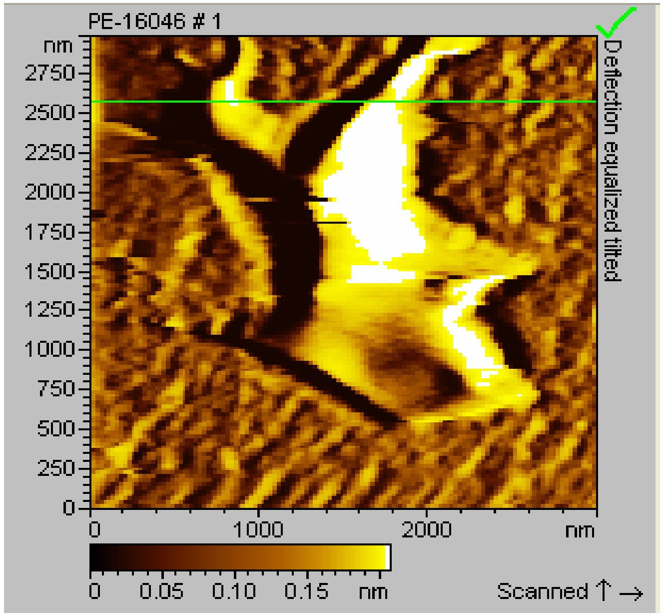
Previous SEM and XPS Results on Peel Ply Surfaces

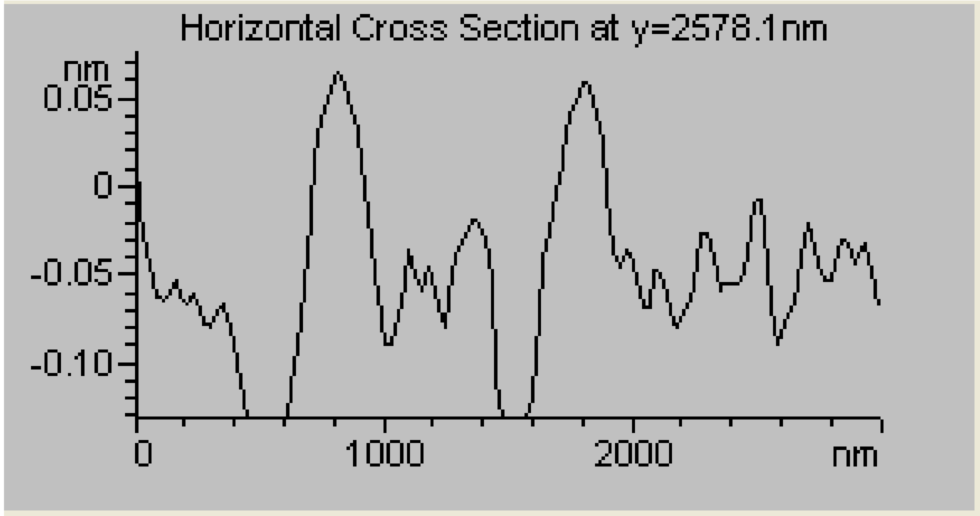
- **Polyester (PF 60001): No transfer, strong bonds**
- **SRB (PF 60001): Siloxane coating transfer, weak bonds**
- **Nylon (PF 52006): Fiber transfer, bond strength depends on adhesive**

Polyester Peel Ply Surface

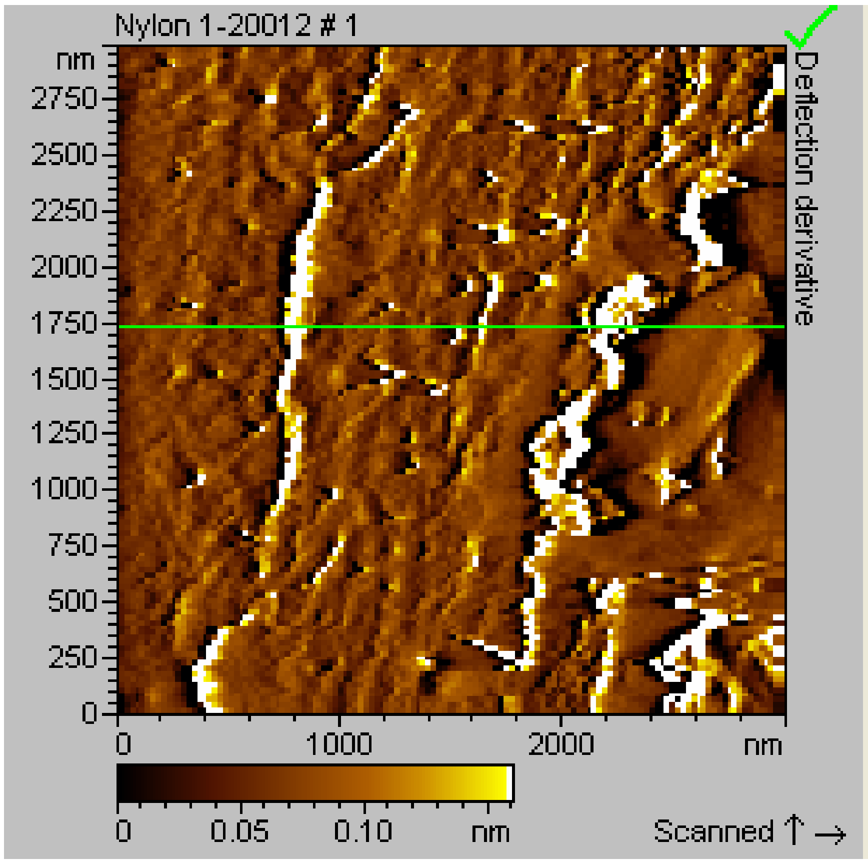


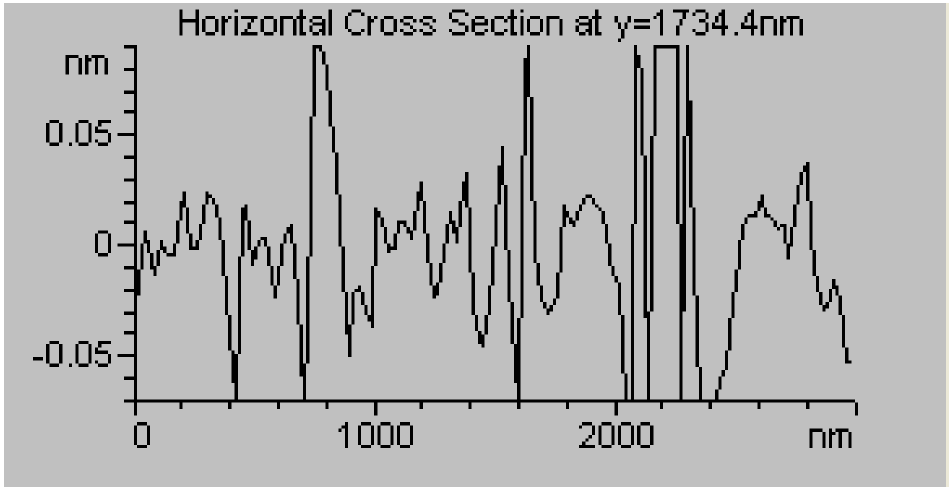




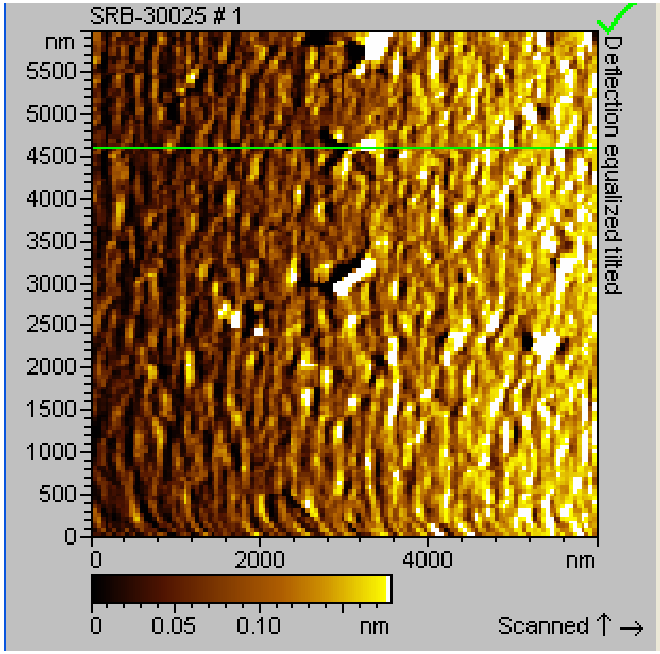


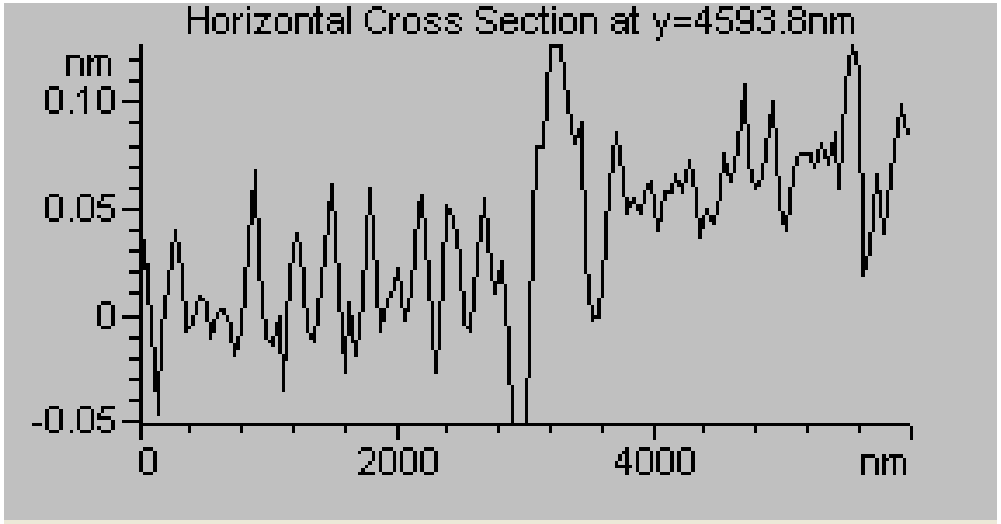
Nylon Peel Ply Surface

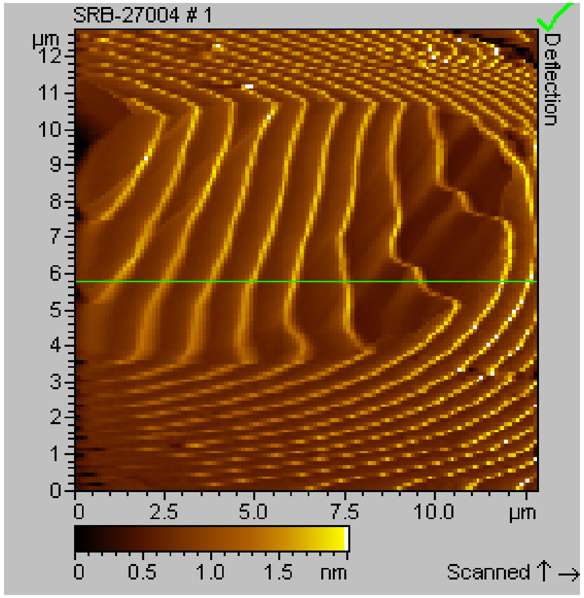


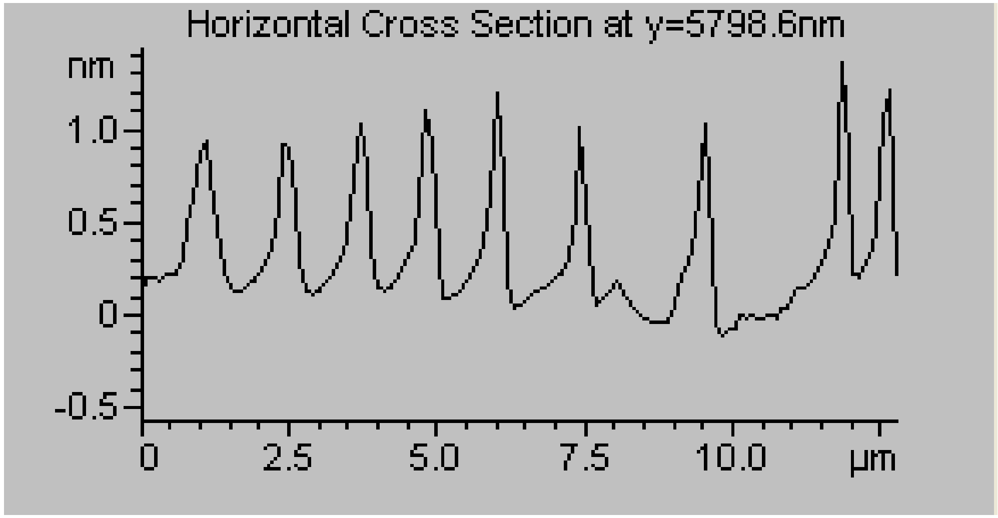


SRB Peel Ply Surface

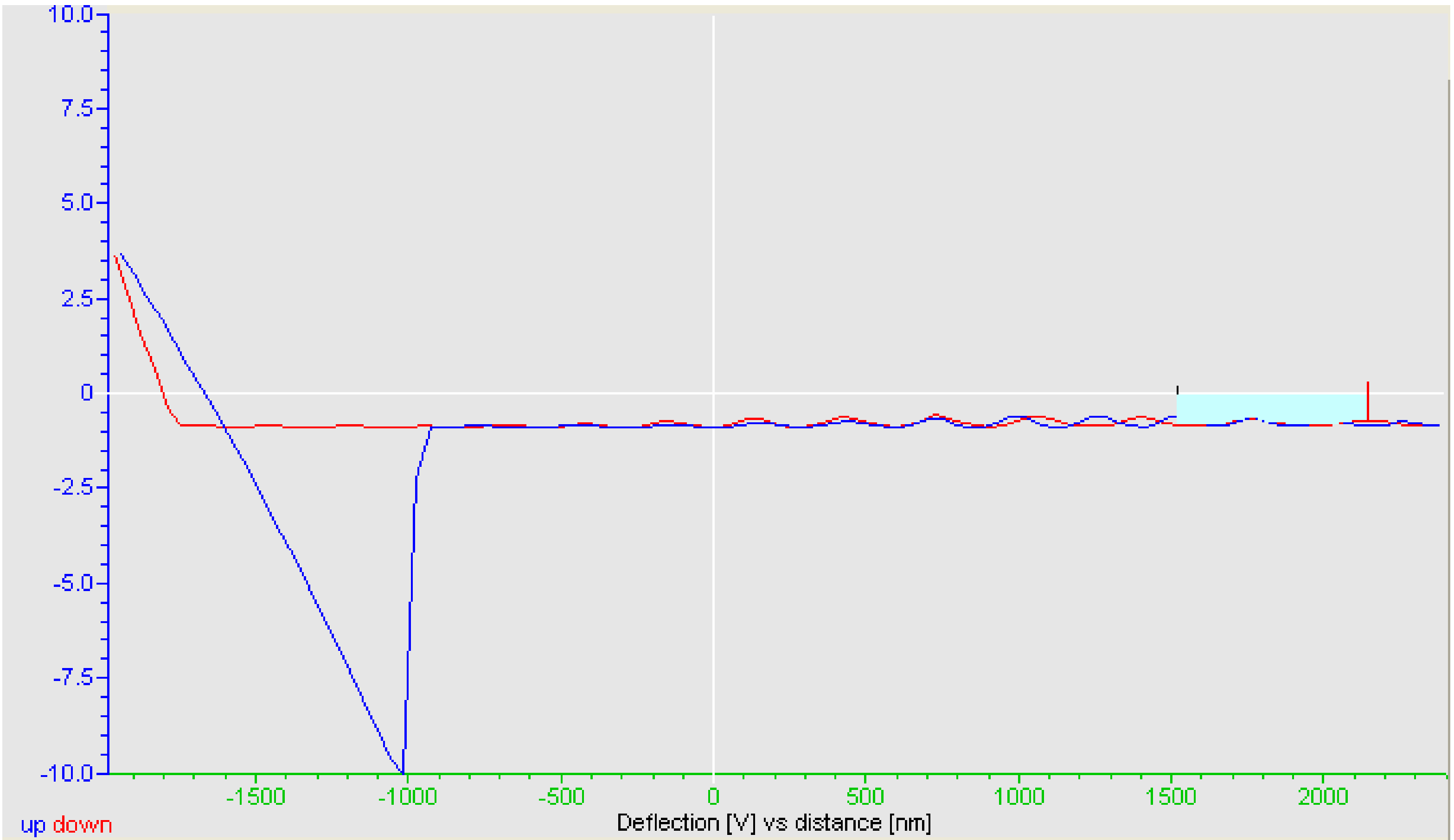




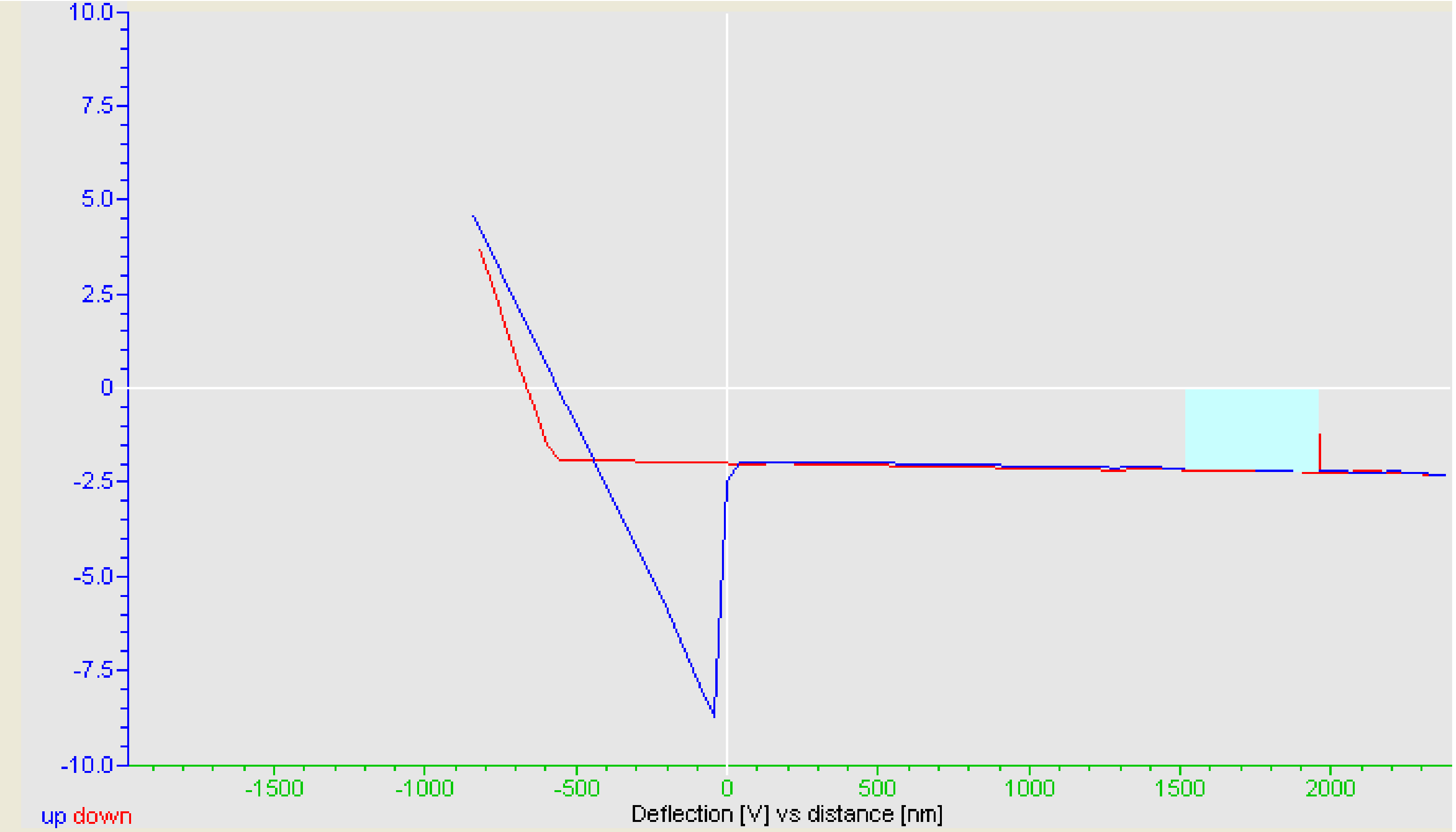




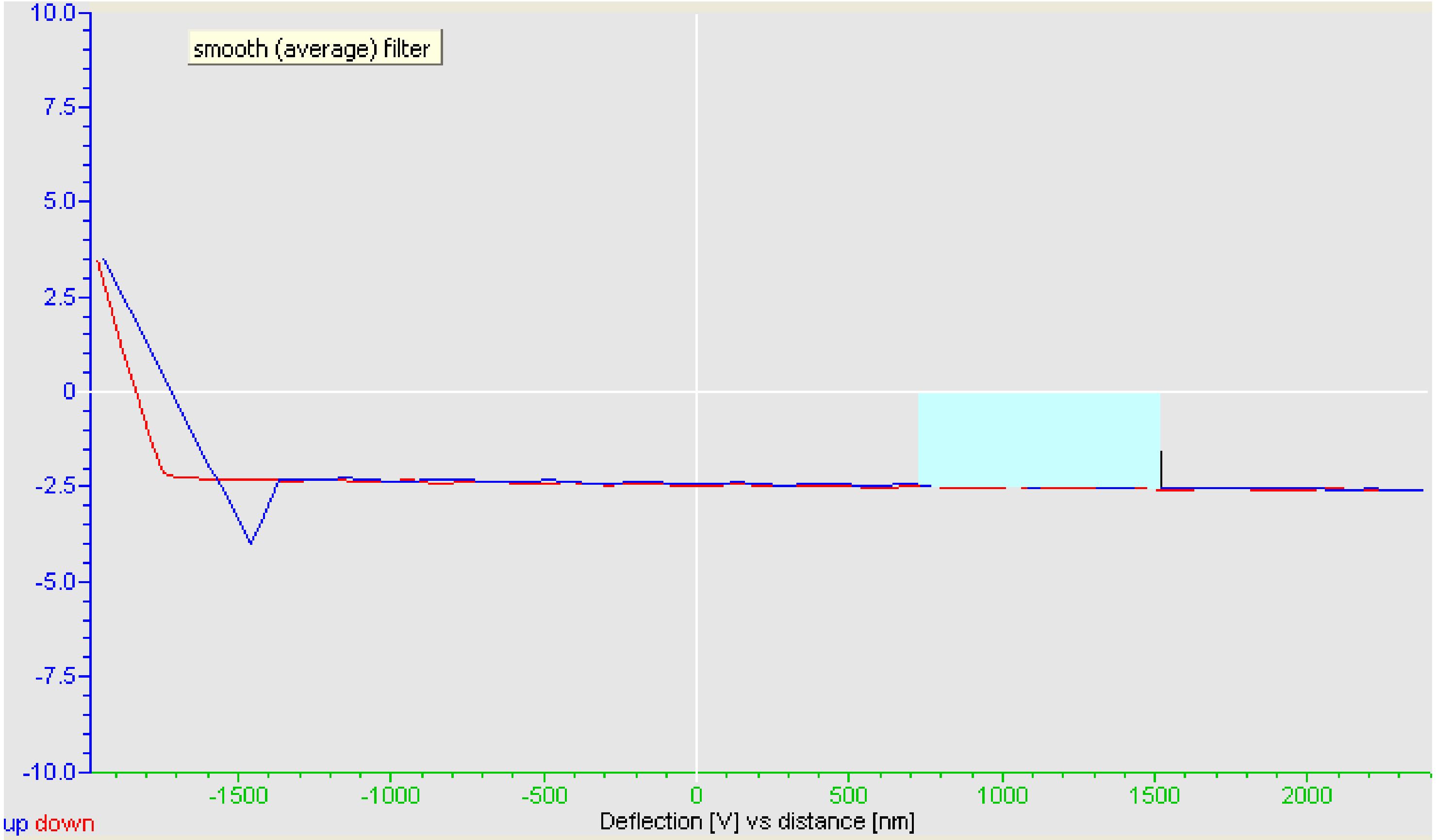
Typical Force vs. Distance For PE Peel Ply Prepared Surface



Typical Force vs. Distance For Nylon Peel Ply Prepared Surface



Typical Force vs. Distance For SRB Peel Ply Prepared Surface



Conclusions

- Certification of pre-bond surface preparation quality requires implementation of effective surface chemistry inspection technologies for each and every step of the surface preparation procedure to ensure the strength and durability of the bonded aviation structures.
- Solid-state electrochemical sensor can detect contamination on peel ply surfaces and is a promising technology for in-field surface chemistry analysis.

Conclusions

- AFM can evaluate the contamination and damage of the laminates surfaces prepared with peel plies.
- AFM force spectroscopy can evaluate adhesion of the surfaces prepared with peel plies. The adhesion of laminate surfaces prepared with PE and nylon peel plies is greater than that of the surface prepared with SRB peel ply, correlating with bond strength and contamination level.

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
  - Novel 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.