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

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FAA Sponsored Project Information

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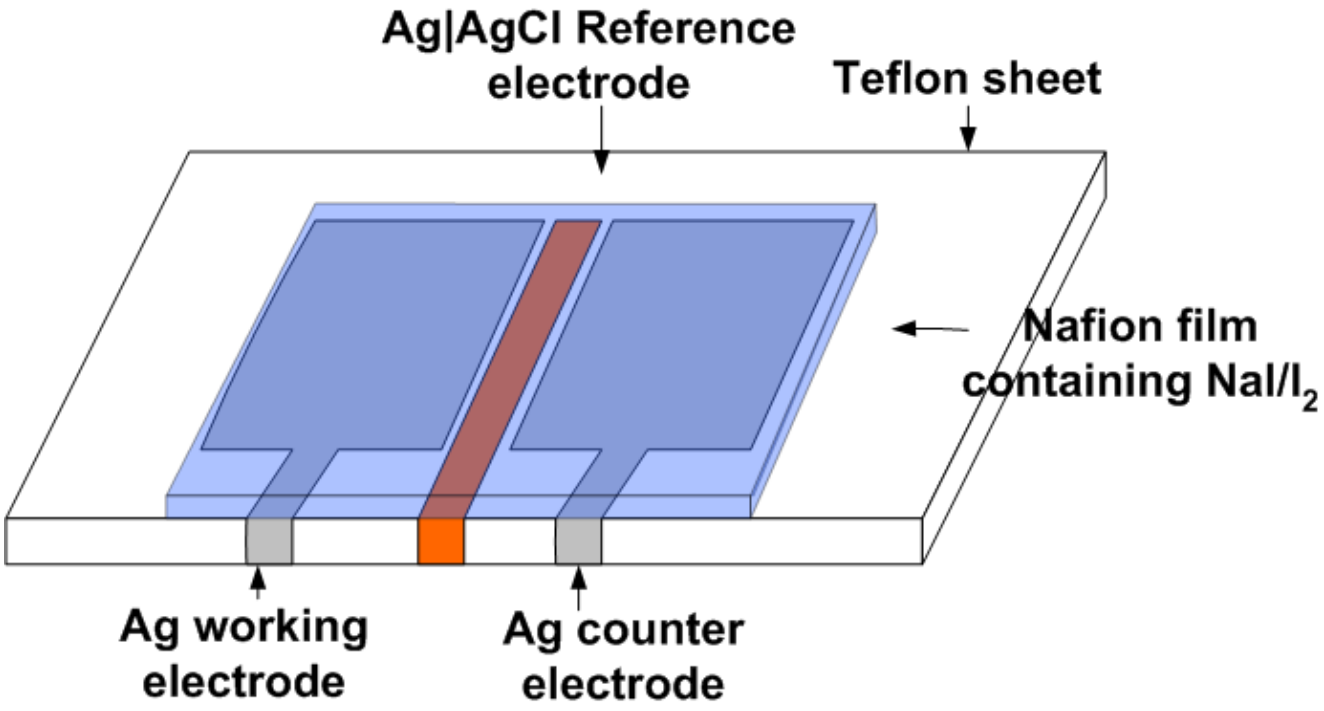
- FAA Technical Monitor
  - David Westlund, Curtis Davies
- Industry Participation
  - Exponent, Bombardier, DME, Avborne, AeroMatrix

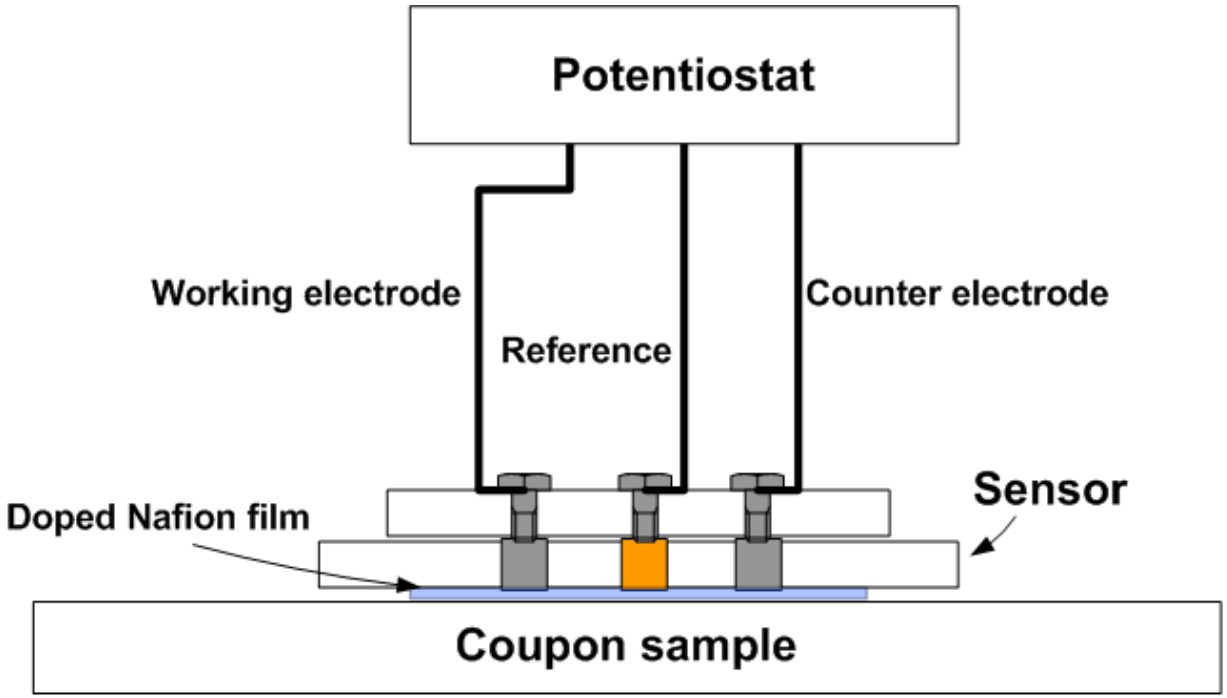
Introduction

- Motivation and Key Issues
  - Adhesive bonding is now used in manufacture and repair and 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

2nd Generation Electrochemical Sensor



2nd Generation Solid-state Electrochemical Sensor-Experimental Setup

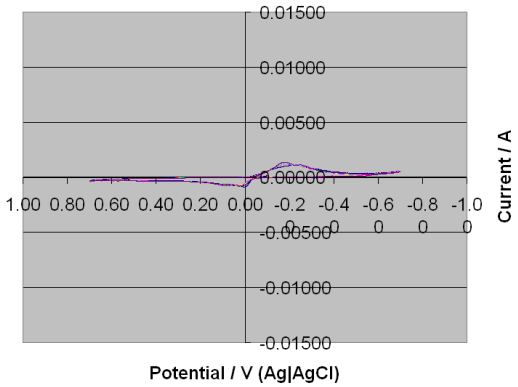


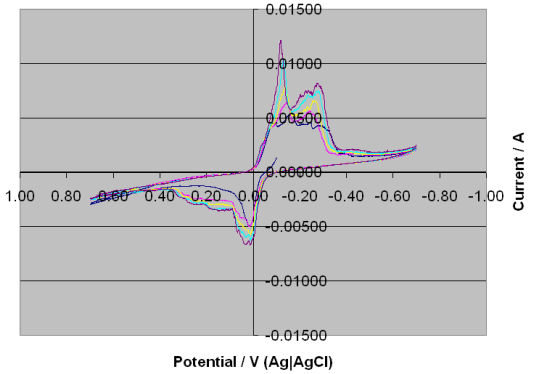
Tests on Polyester Peel Ply Samples

- Original /non-contaminated 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.

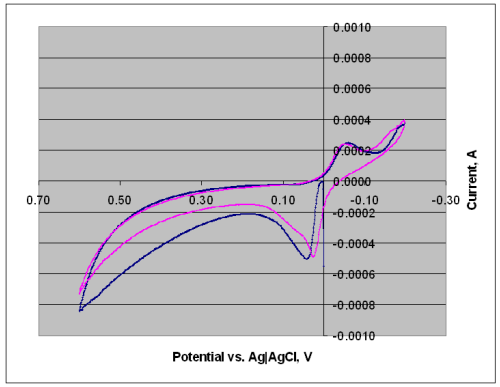
Various Mediators

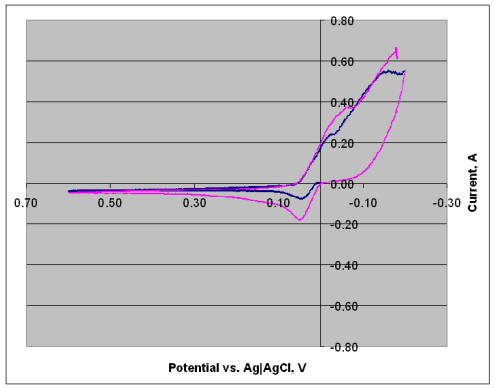
Ag(I)/Ag(II) Mediator





Mn(II)/Mn(III) Mediator

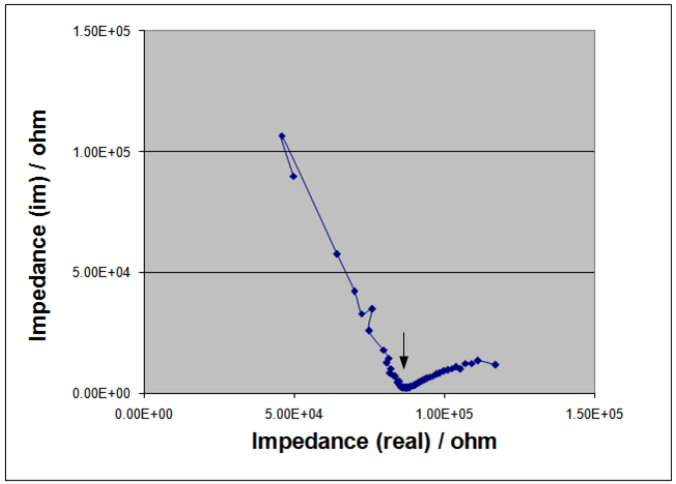


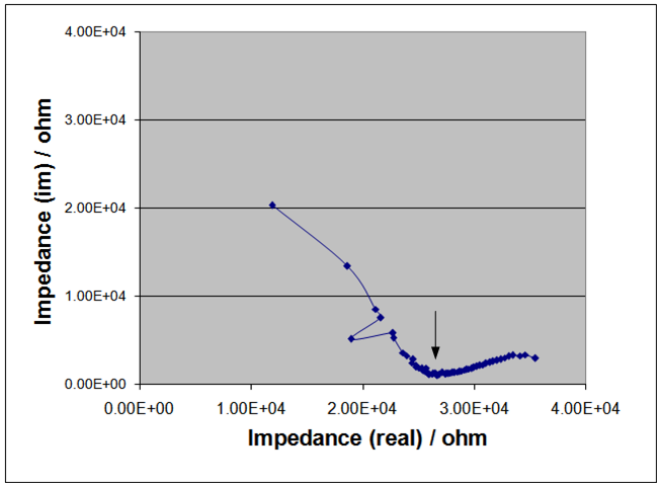


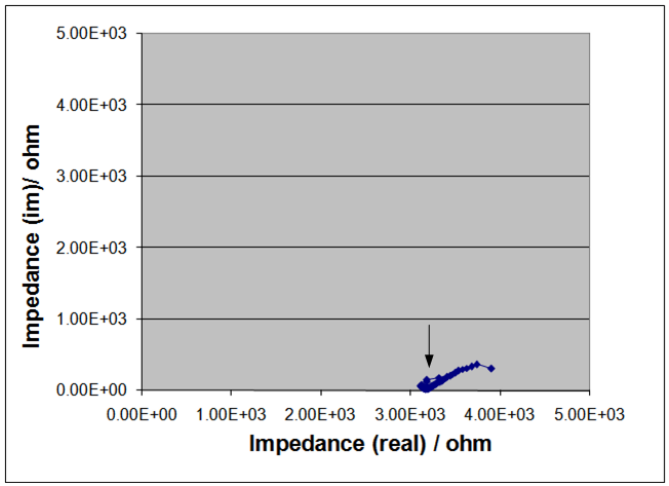
Original sample

Sulfuric acid treated sample

EIS Results : 2nd Generation Sensor

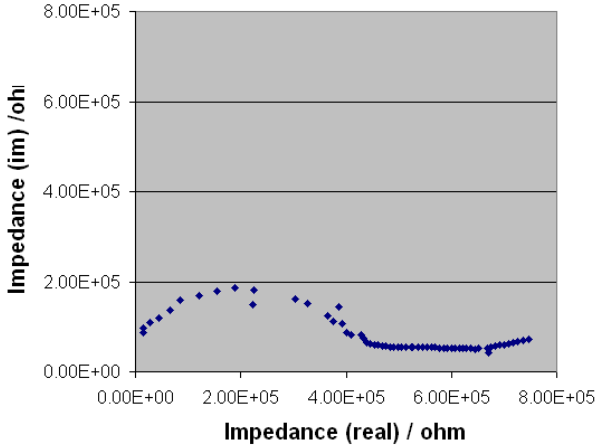


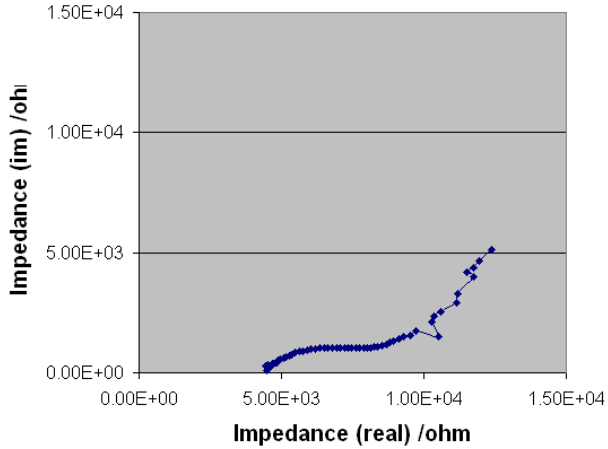




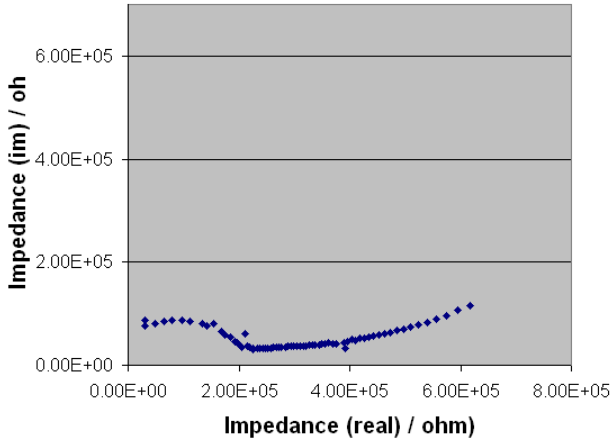
EIS Results

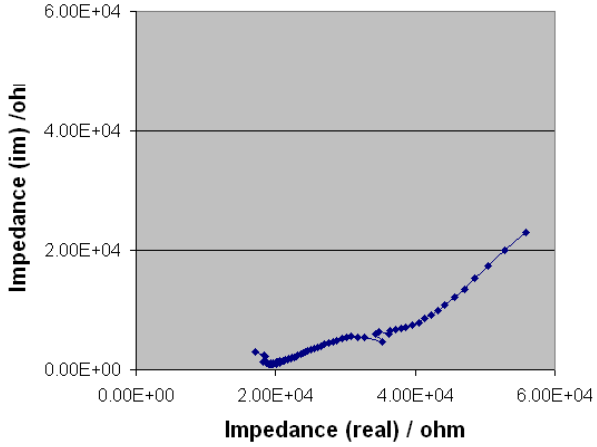
2nd Sensor



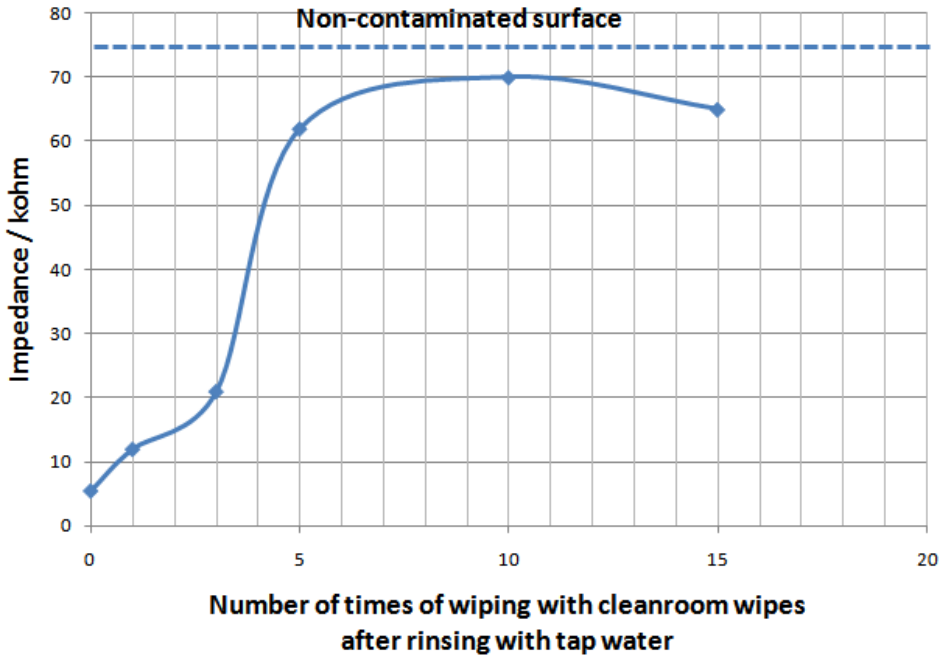


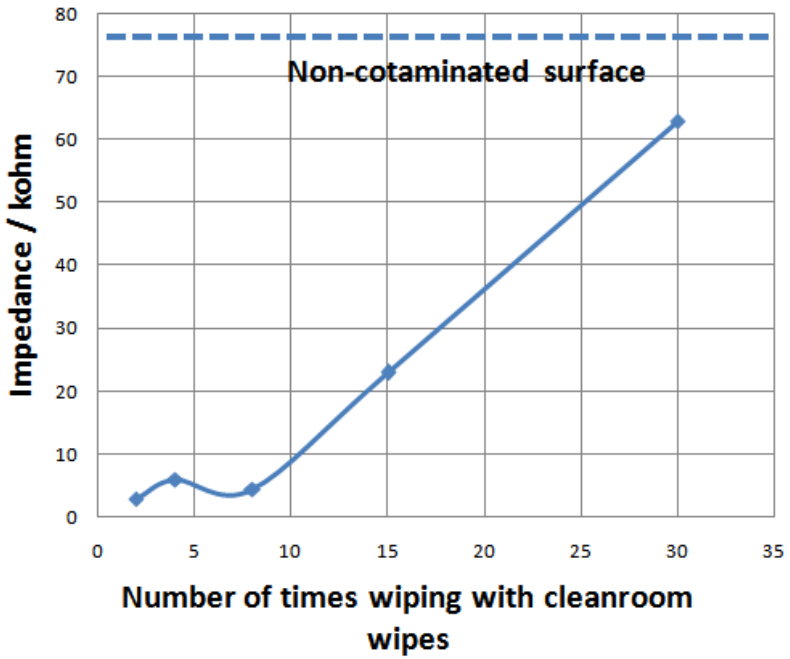
3rd Sensor





Electrochemical Impedance Spectroscopy

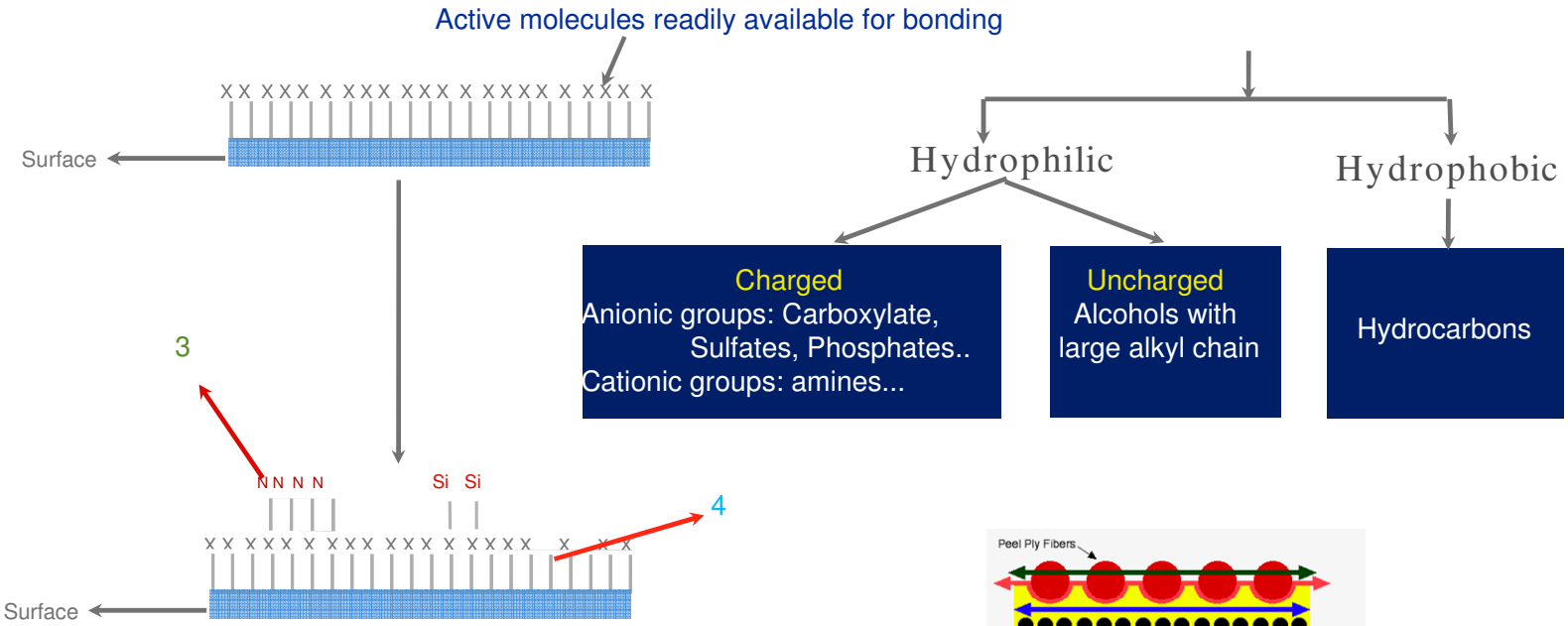




Reaction Mechanisms

- Treatment with sulfuric acid produces
  - Hydroxyl, carbonyl, carboxylic acid, phenol, and sulfonated groups, ions, or fragments that may be unstable and can be readily reduced or oxidized at certain potentials.
- The surface chemistry can be analyzed using XPS and FTIR.
- The electrochemical sensor can sense the presence of these groups, ions, or fragments on the surfaces.

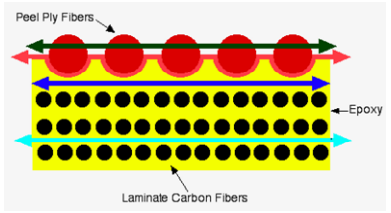
CFM Principles



Laminate Surface Composition

Peel Ply	%C	%O	%N	%Si
Nylon	77.5	12.6	9.8	Tr.
Polyester	75.5	21.6	1.9	1.0
SRB	68	24.2	0.9	6.9

XPS results - UW



Fracture of the epoxy between peel ply and carbon fibers(1)
Interfacial fracture between the peel ply fabric fibers and the epoxy matrix (2)
Peel ply fiber fracture(3)
Interlaminar failure(4)

CFM Principles

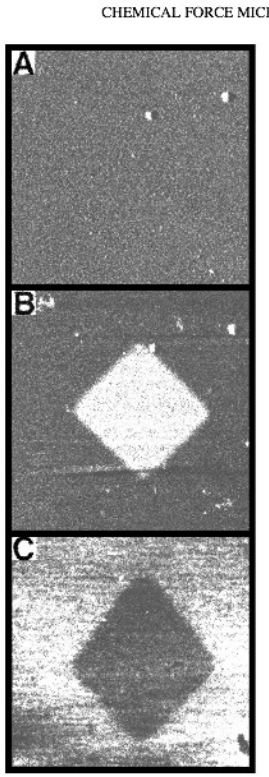


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Figure 16 Force microscopy images of a photopatterned SAM sample. The 10 × 10 μm square region terminates in COOH, and the surrounding region terminates in CH_3. The images are of (*A*) topography, (*B*) friction force using a tip modified with a COOH-terminated SAM, and (*C*) friction force using a tip modified with a CH_3-terminated SAM. Light regions in (*B*) and (*C*) indicate high friction; dark regions indicate low friction (reproduced from Reference 33).

Force microscopy images of a photopatterned SAM sample. The 10 × 10 μm square region terminates in COOH, and the surrounding region terminates in CH3.

(A) Topography,

(B) friction force using a tip modified with a COOH-terminated SAM,

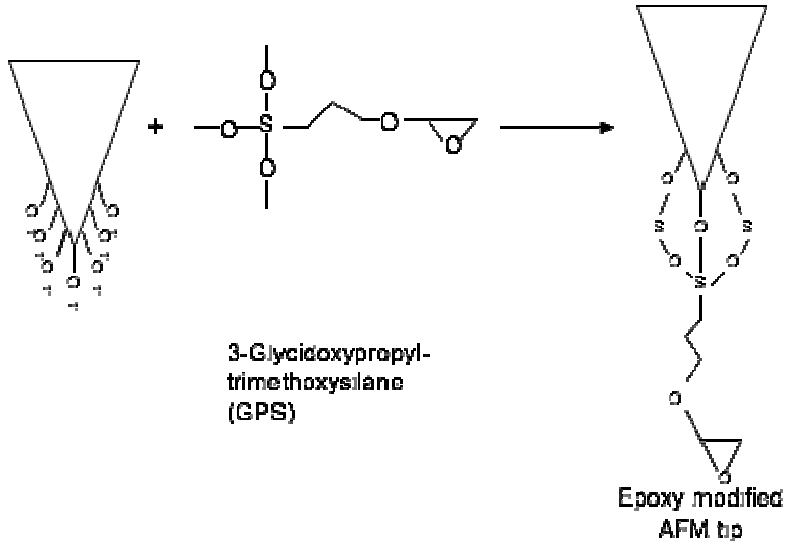
(C) friction force using a tip modified with a CH3-terminated SAM.

NOTE: Light regions in (B) and (C) indicate high friction; dark regions indicate low friction.

Design of Epoxy Probe

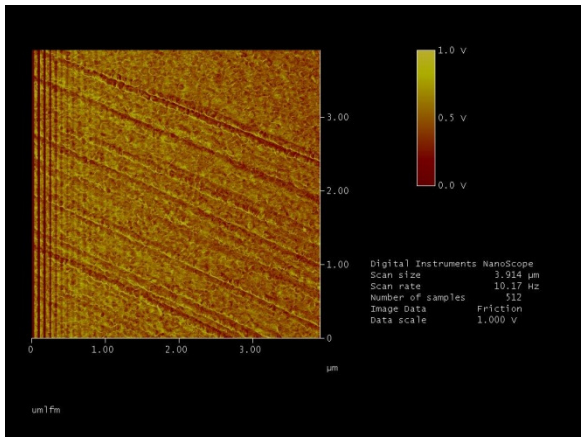
Protocol

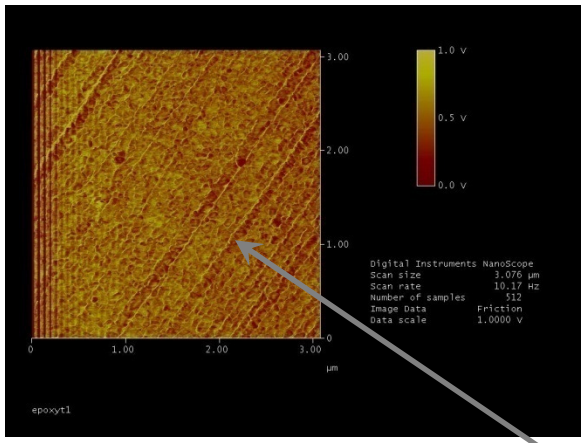
- Clean silicon or silicon nitride tips with ethanol for 5 minutes followed by rinsing with milli-Q water for 5 minutes.
- Treat with a freshly prepared acidic mixture (H_2SO_4:H_2O_2) ratio 7:3 v/v for 15 minutes, followed by rinsing with milli-Q water for 5 minutes.
- Dry in vacuum for 10 minutes to remove the water layer on the surface.
- Treat with 2 % 3-Glycidoxypropyltrimethoxysilane (GPS) in dry toluene for 2 hrs.
- Rinse with toluene, ethanol and milli-Q water for 3 minutes each.
- Dry in vacuum for 1 hr and store in desiccators until use.



Probe Images

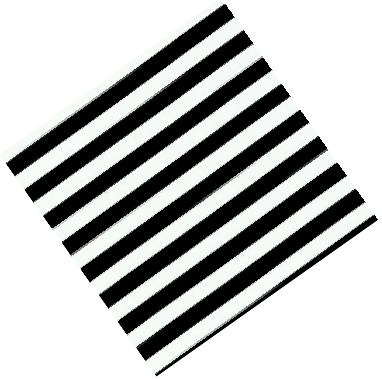
Unmodified Probe



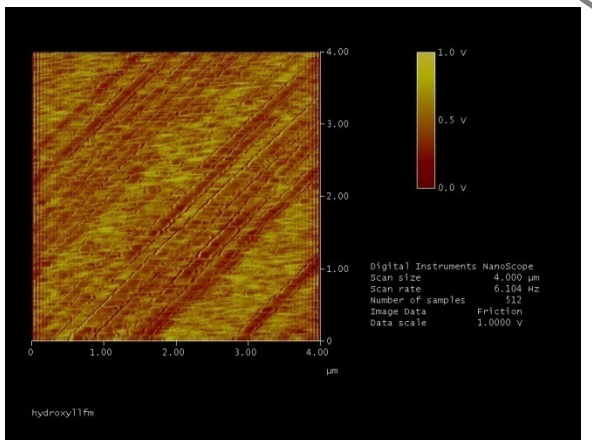


Epoxy Probe

Dark bands are low friction regions/hydrophilic



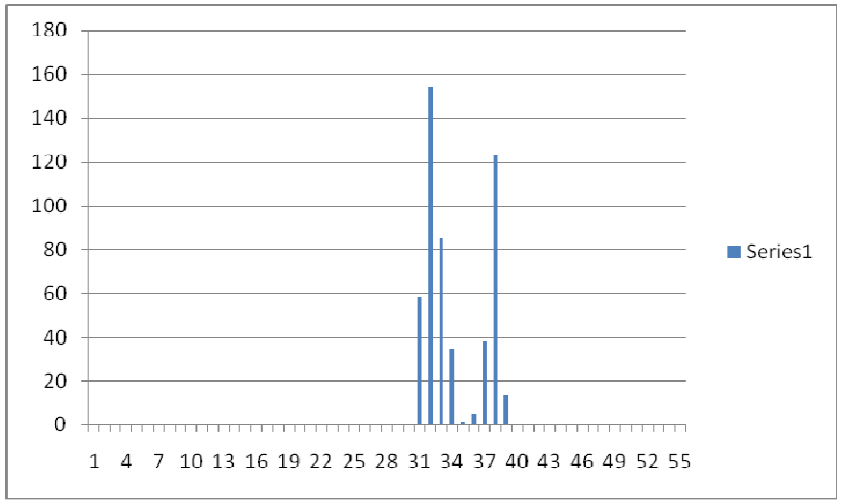
Patterned gold surface - alternative hydrophobic (ODT) and hydrophilic (gold surface)



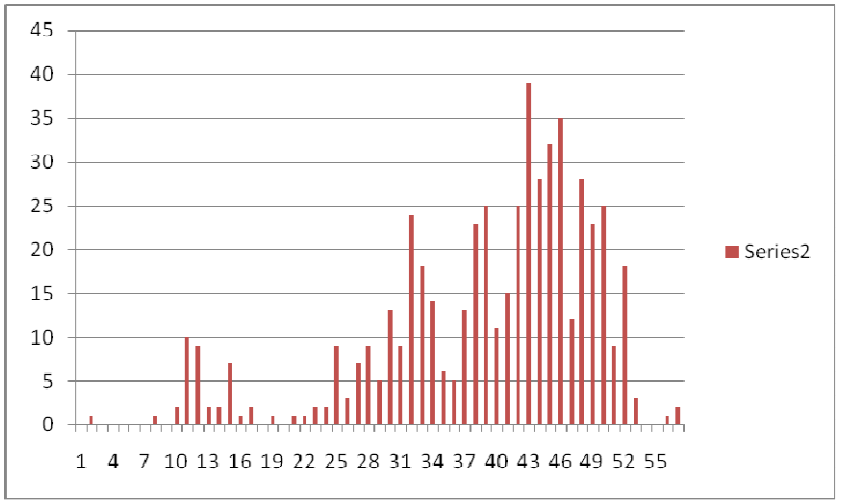
Hydroxyl Probe

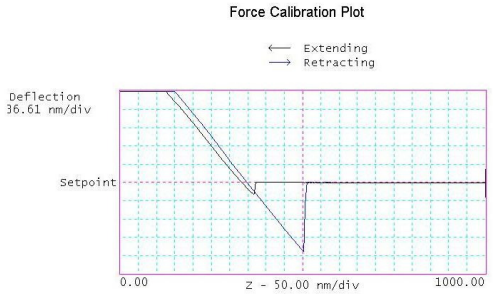
Force Spectroscopy

Unmodified Probe



Epoxy Probe





500 force curves at 5 locations on gold coated surface

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 NaI/I_2, Ag(I)/Ag(II), both Mn(II)/Mn(III) and Cu(I)/Cu(II) are effective mediators for electrochemical sensors.
- In addition to cyclic voltammetry, electrochemical impedance spectroscopy can be a good method for surface inspection.
- The sensitivity and reproducibility are improved with the new design of the sensor.
- A procedure to modify AFM tip probes with the epoxy function group has been achieved and validated with SEM and force spectroscopy.
- Friction force images indicate that contrast between hydrophilic and hydrophobic domains are similar for the epoxy modified tip, hydroxyl modified tip and for the unmodified tip.
- Force spectroscopy results show that the epoxy probe has a higher sensitivity to chemical variations than the unmodified tip probe. The larger adhesion force variation is likely due to the probes ability to detect surface contamination.

A Look Forward

- Establish a calibration protocol using a reference laminate surface.
- Integrate the sensor and a micro-potentiostat to make into a handhold measurement device
- Validate the technology with an industrial partner.
- Validate the force spectroscopy data analysis approach with the probe tips on pre-patterned samples.
- Use CFM/force spectroscopy on various peel ply prepared composite surfaces.