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

FAA Sponsored Project Information

- PI & Researchers
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- Students
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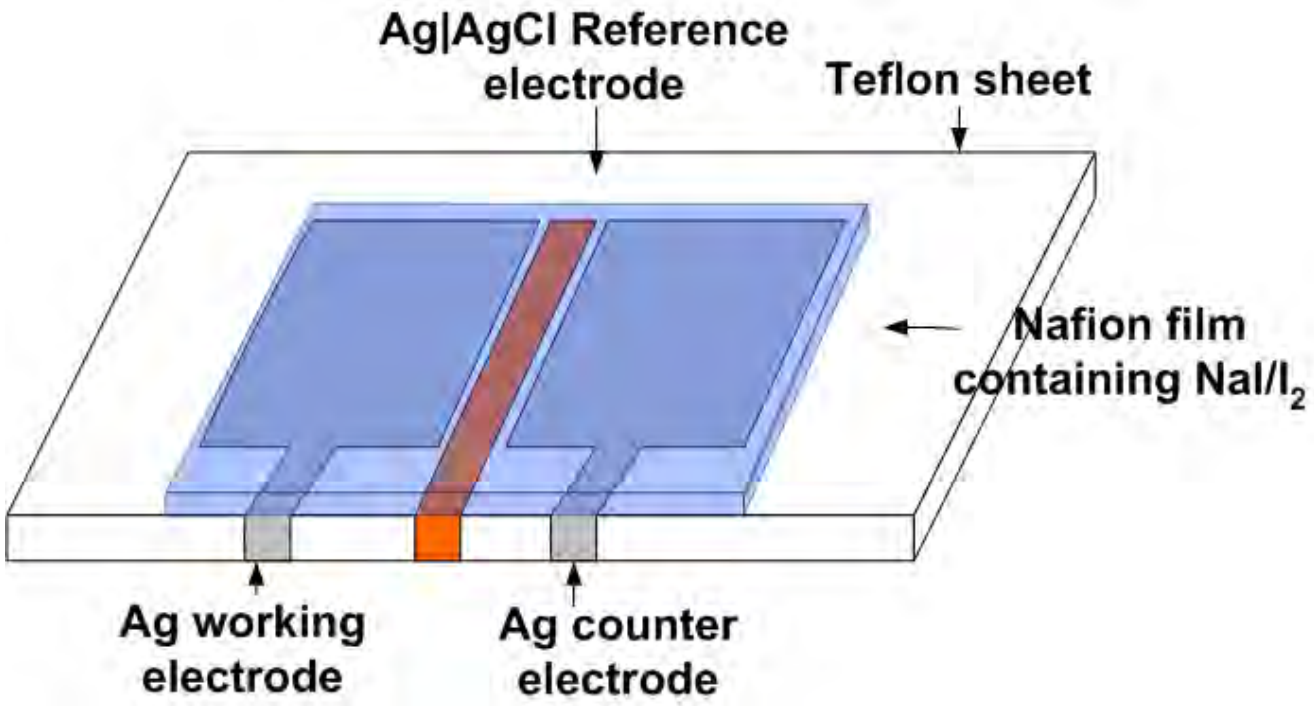
- FAA Technical Monitor
  - David Westlund, Curtis Davies
- Industry Participation
  - Exponent, Bombardier

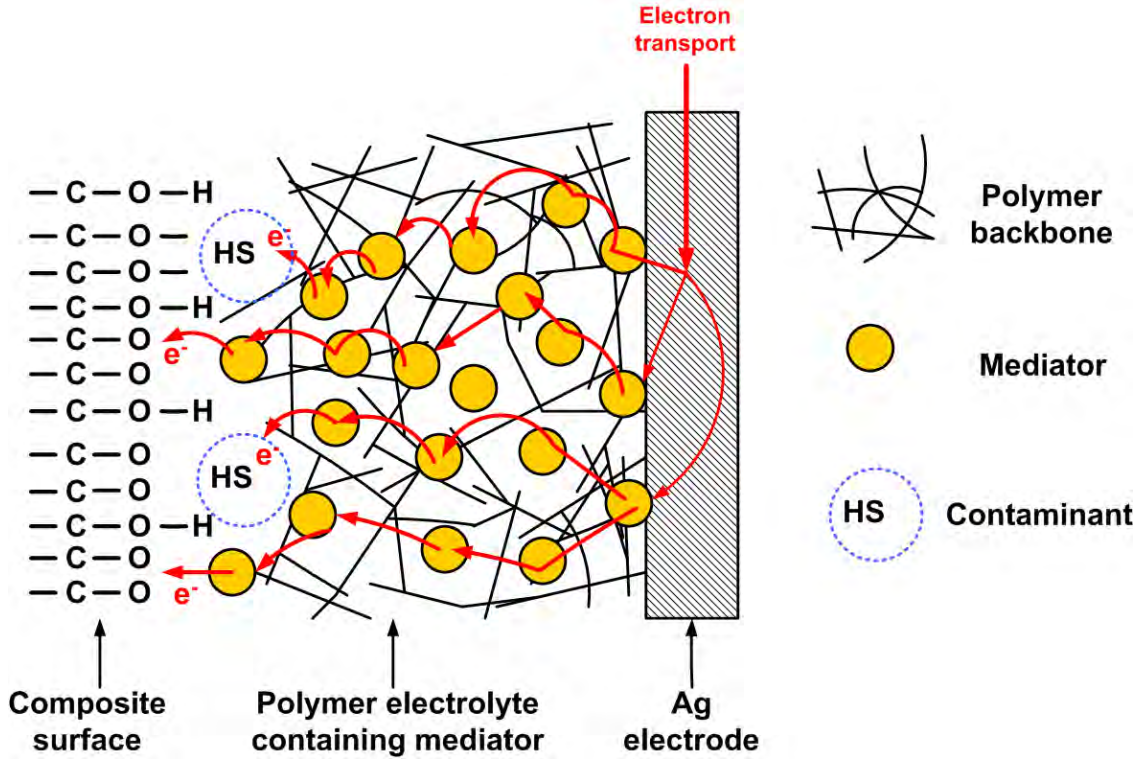
Introduction

- 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

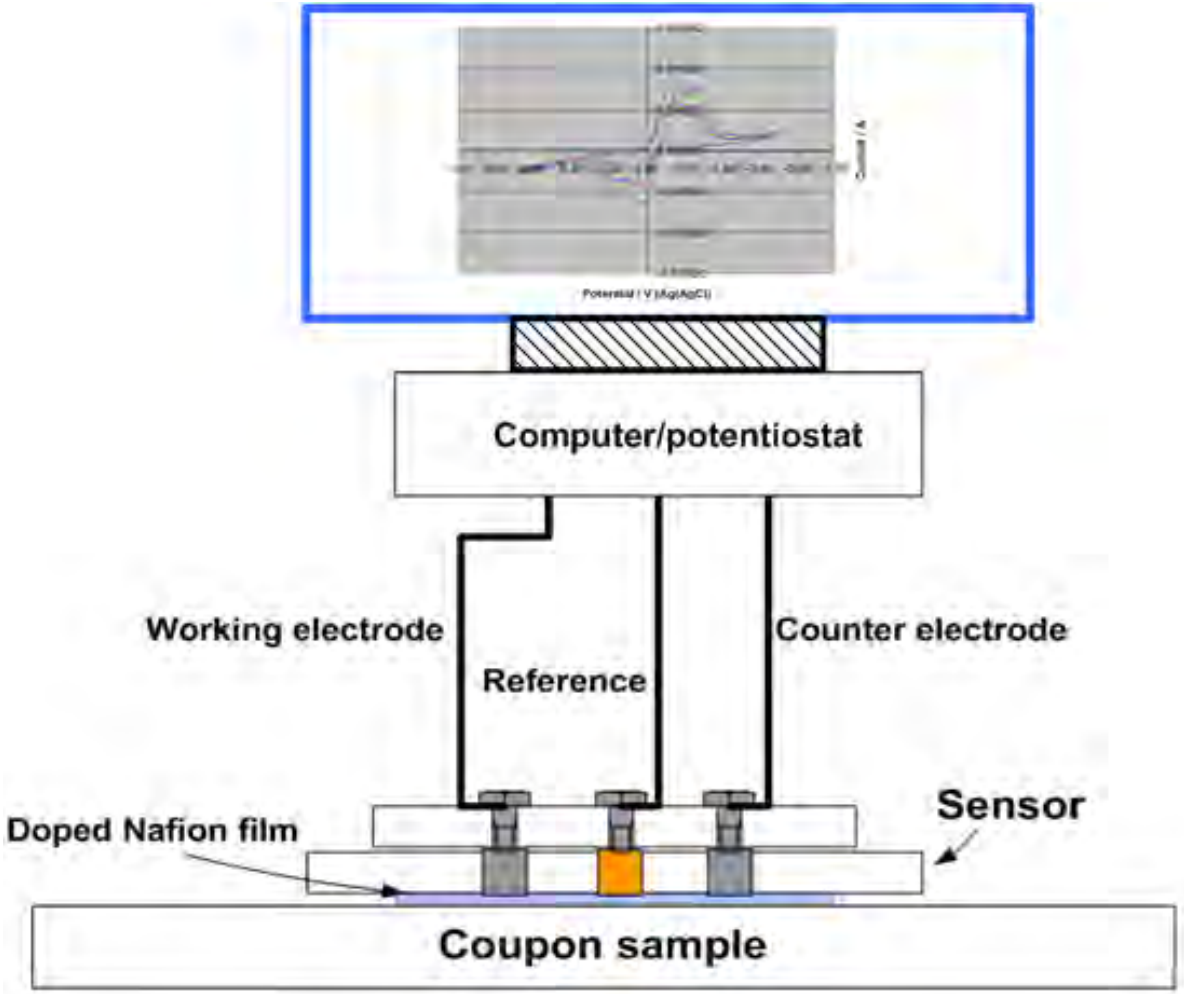


Working principle of the All Solid-state Electrochemical Sensor



The electrons that are given off at the reactions between mediator and the functional groups and/or contaminants are compensated by a current through the Ag electrode. The amount of the electrons that are given off is reflected by the current passing through the electrode.

2nd Generation Solid-state Electrochemical Sensor-Experimental Setup

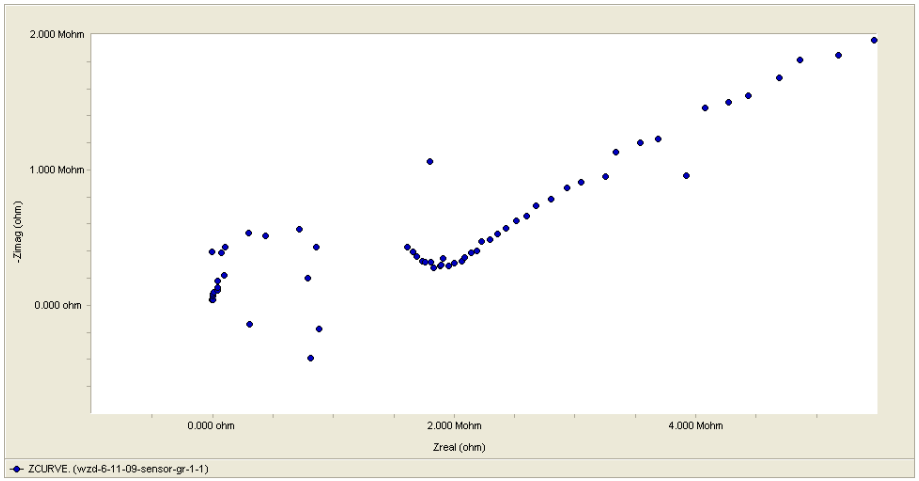


EIS Composite Samples

- EIS was conducted on composite samples supplied by Bombardier.
- The composite samples' surface conditions were varied. Contaminants included:

  Diestone HFP cleanser, UV dye, ultrasonic coupling gel, silicone glove residue, solution from marker, tape residue (no silicone, MTI RAE1000), soda, coffee and protective cream.

EIS Results

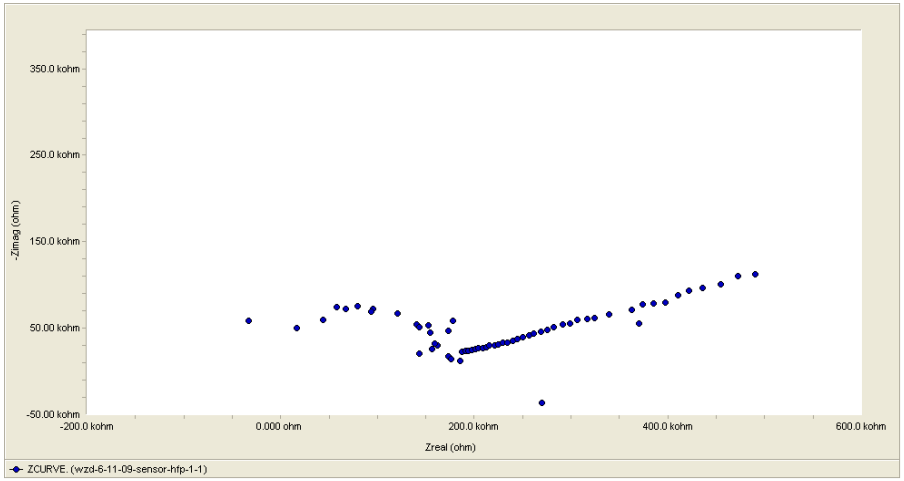


Pristine composite surface

Impedance - 2 x 10^6 ohm

Composite surface with cleanser (Diestone HFP) residue

Impedance - 1.8 x 10^5 ohm

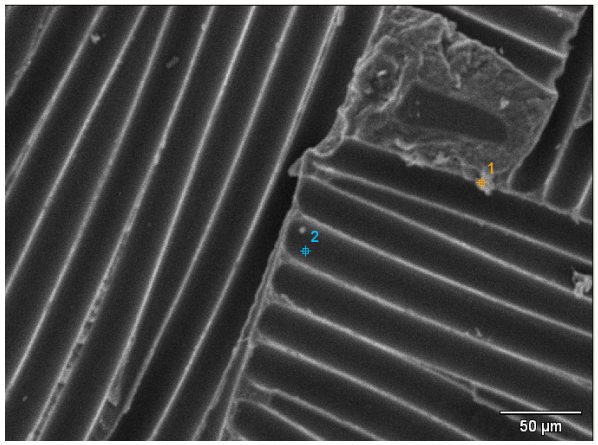


Electrical Impedance Spectroscopy Results

Sample	Polarization Impedance (ohm)
Pristine	2.0×10^6
Cleanser (Diestone HFP) residue	1.8×10^5
UV dye	6.0×10^5
Ultrasonic coupling gel	6.0×10^5
Silicone rubber glove residue	1.8×10^6
Solution from a marker	8.0×10^5
Tape Residue no silicone (MTI RAE1000)	1.7×10^6
Soda	6.5×10^5
Coffee	6.0×10^5
Protective cream	1.2×10^3

SEM/EDAX Results

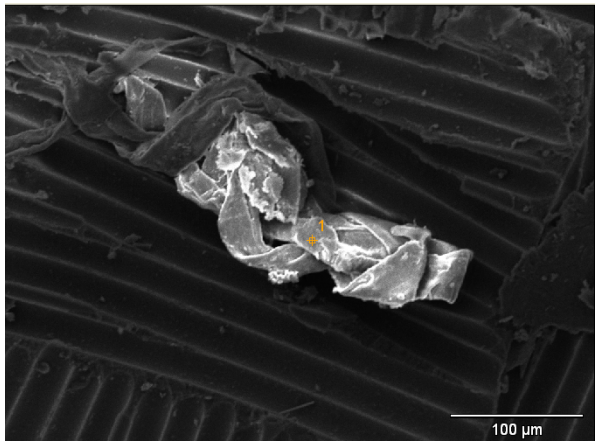
Pristine Surface



Element Line	Weight %	Weight % Error
C K	92.38	+/- 1.49
O K	3.41	+/- 1.03
Al K	4.21	+/- 0.35
S K	0	
S L	---	
K K	0	
K L	---	
Total	100.00	

Note: scan area is 0.3 cm^2

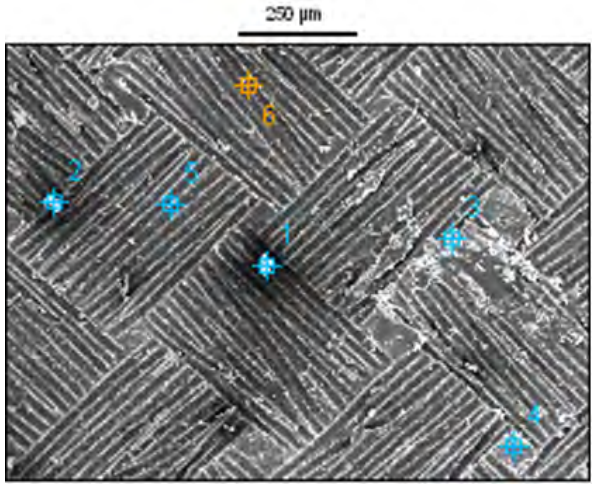
Surface Contaminated with Ultrasonic Coupling Gel



Element Line	Weight %	Weight % Error
C K	70.52	+/- 1.21
O K	21.15	+/- 1.36
Al K	4.36	+/- 0.29
S K	1.83	+/- 0.25
S L	---	---
K K	2.15	+/- 0.21
K L	---	---
Total	100.00	

SEM/EDAX Results

Surface Contaminated with Protective Cream

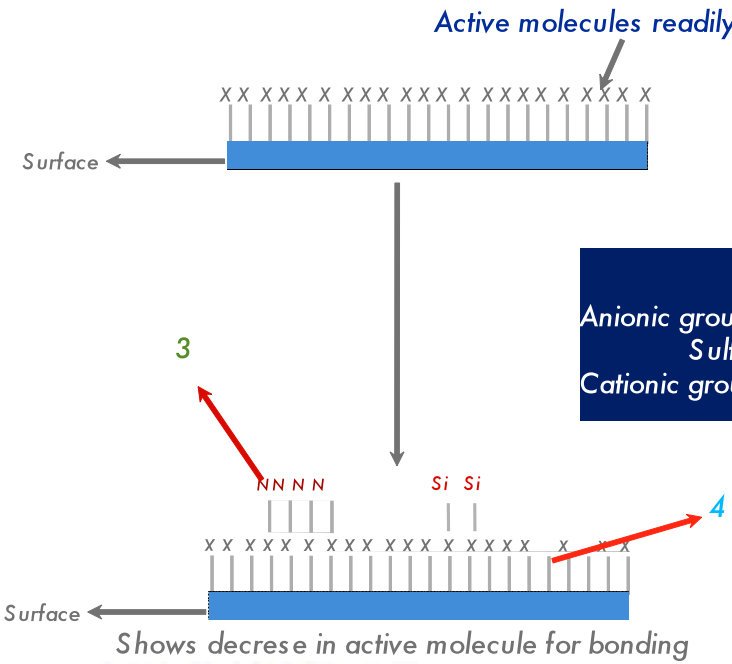


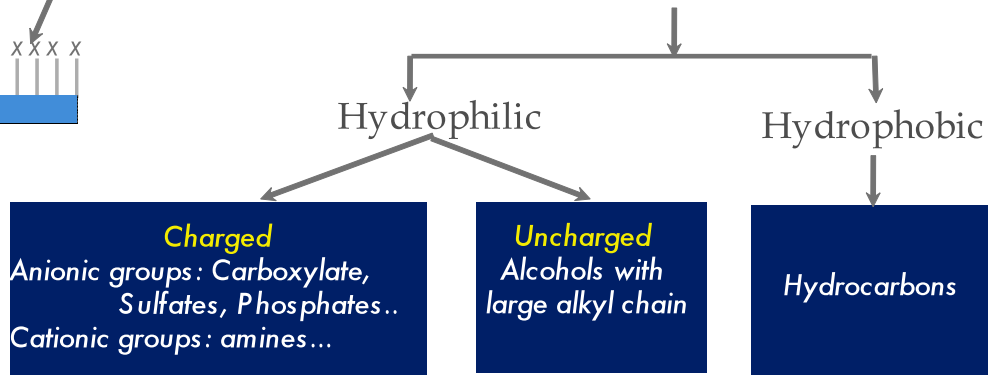
	C-K	O-K	Na-K	Al-K	Si-K	S-K	Cl-K	K-K	Ca-K	Ti-K	Fe-K	Cu-K	Zn-K	Ag-L	Ce-L
P1	39.7	24.2	0.27	0.06	0.22	0.00	0.00	0.00	0.00	0.00	34.1	0.00	0.13	0.00	1.10
P2	75.5	13.5	1.45	1.07	0.48	0.00	0.66	0.83	0.54	0.00	1.07	0.00	4.69	0.00	0.04
p3	34.2	1.09	0.32	2.24	1.67	0.00	0.44	1.37	1.56	46.9	0.49	5.24	1.94	2.43	0.00
P4	83.9	7.8	0.64	4.41	0.78	0.23	1.23	0.21	0.04	0.18	0.00	0.51	0.00	0.00	0.00
P5	81.2	7.7	1.71	0.73	0.28	0.00	0.09	0.08	0.06	0.00	0.00	0.11	7.94	0.00	0.07
P6	90.8	6.2	0.92	0.13	0.01	0.00	0.06	0.07	0.08	0.00	0.07	0.11	1.38	0.00	0.00

EDAX/EIS Results

Sample	[O], wt%	[Al], wt%	[K], wt%	[Si], wt%	[Na], wt%	[S], wt%	[Zn] Wt%	Polarization Impedance (ohm)
Pristine	3.41	4.21	0	0	0	0	0	2.0×10^6
Cleanser	18.63	4.51	0	0	0	1.63	0	1.8×10^5
UV dye	17.19	4.03	0	0	0	2.55	0	6.0×10^5
Ultrasonic coupling gel	21.15	4.36	2.15	0	0	1.83	0	6.0×10^5
Silicone rubber glove residue	18.15	4.46	0	0	0	2.09	0	1.8×10^6
Solution from a marker	17.69	3.64	0	0	0	2.63	0	8.0×10^5
Tape Residue	16.02	4.55	0	0	0	2.85	0	1.7×10^6
Soda	25.12	3.77	0	0	0	1.07	0	6.5×10^5
Coffee	15.07	4.57	0	0.75	0	2.37	0	6.0×10^5
Protective cream	9.31	0.88	0	0.10	0.58	0	2.75	1.2×10^3

CFM Principles

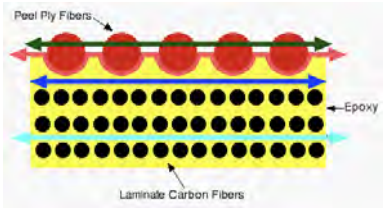




Laminate Surface Composition

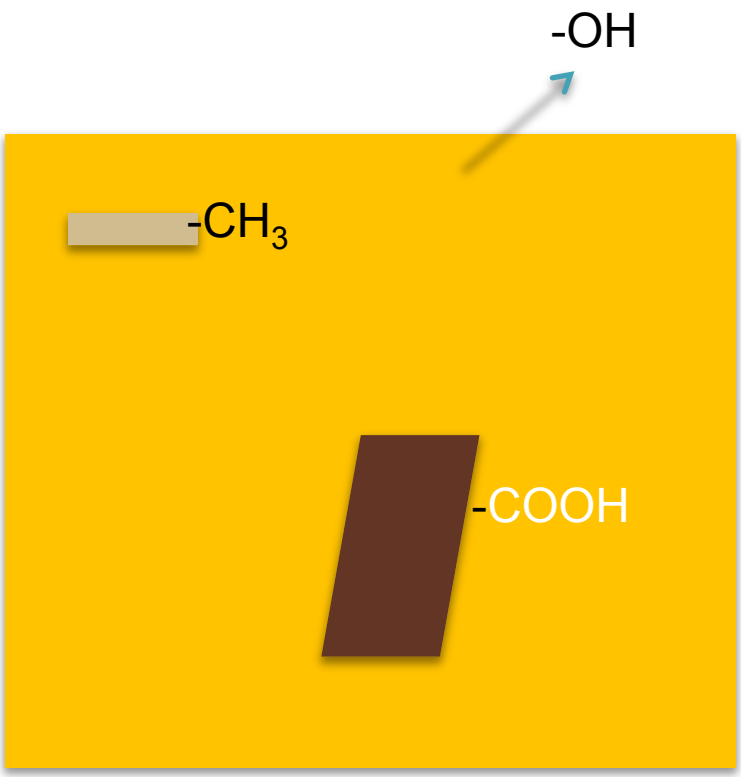
Peel Ply	%C	%O	%N	%Si
Nylon	77.5	12.6	9.8	Tr.
Polyester	75.5	21.6	1.9	1.0
SRB	68	24.2	0.9	6.9

XPS results - UW

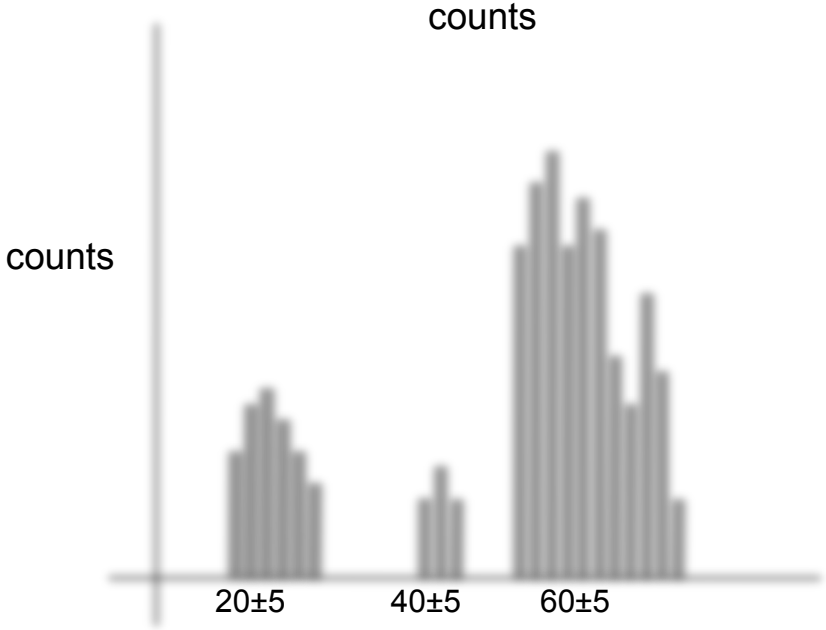


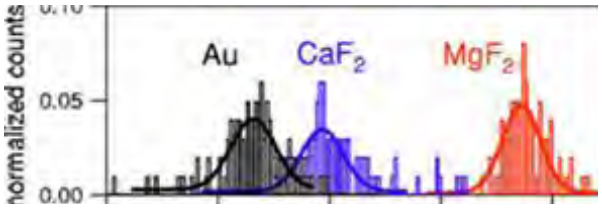
Fracture of the epoxy between peel ply and carbon fibers(1)
Interfacial fracture between the peel ply fabric fibers and the epoxy matrix (2)
Peel ply fiber fracture(3)
Interlaminar failure(4)

Mapping Laminate Surface Using Force Spectroscopy



Plot b/w adhesion forces and counts



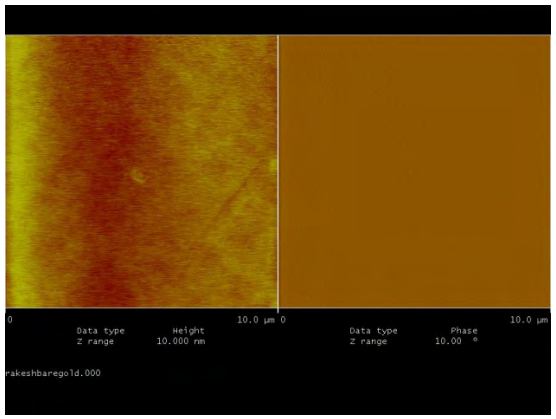


Note: Adhesion force is between the epoxy and the surface functional groups

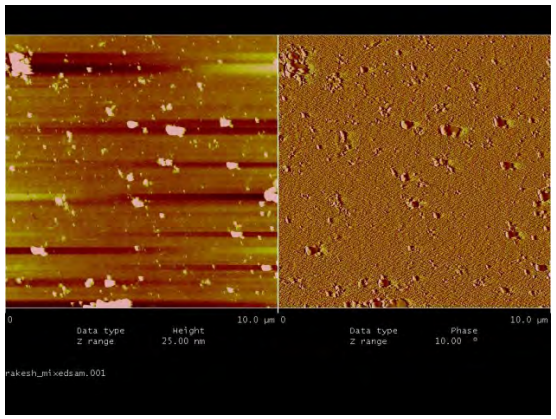
Results – Unmodified Probe vs. Epoxy Probe

Results on Gold-Coated Silicon Wafers

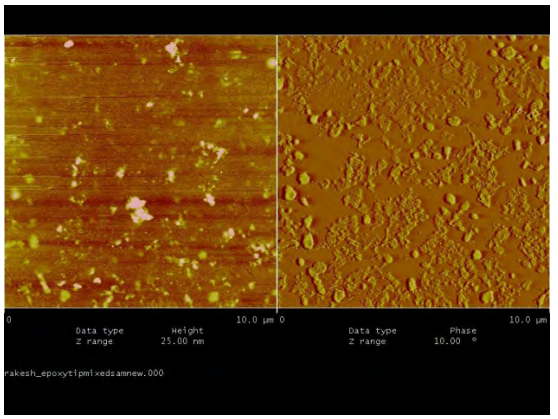
Topography Image Phase Image



Unmodified surface - unmodified probe



Modified surface - unmodified probe



Modified surface - Modified probe

Modified surface is mixed with hydrophobic and hydrophilic domains

Results on Clean Mica Wafers

Probe	Adhesion Force (nN)	SD
Epoxy	65.36	1.85
Unmodified	2.66	0.194

AFM – Environmental Effects

Day 1

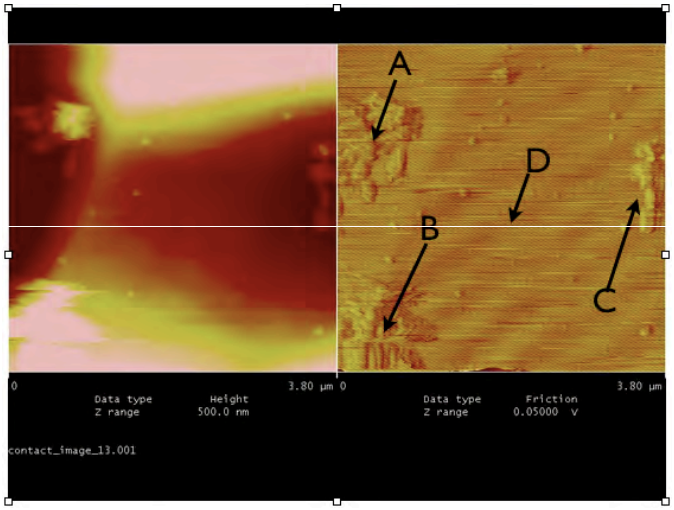
Humidity	Temperature (C)	Tip No.	Mean of 50 adhesion force	S.D
52.2	22.5	1	10.997	1.7966
50.4	23.4	2	32.803	0.97307
50.3	23.5	3	19.967	1.3857
49.6	23.7	4	13.714	2.2984
49.0	23.8	5	18.056	6.0413

Day 2

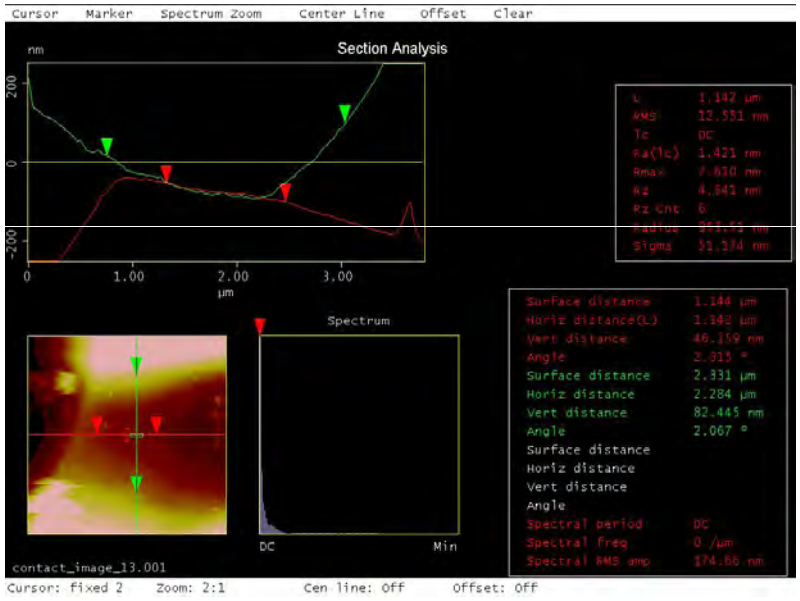
Humidity	Temperature (C)	Tip No.	Mean of 50 adhesion force	S.D
56.7	22.2	1	17.036	1.1987
55.2	22.5	2	7.7828	0.71156
55.6	22.6	3	9.7174	1.1738
54.7	22.6	4	6.0493	0.61482
54.2	22.8	5	7.7124	0.8806

Trials were conducted with unmodified tips on a freshly cleaved mica wafer

CFM Images and Adhesion Force Values



CFM contact mode: height and friction image of nylon peel-ply sample

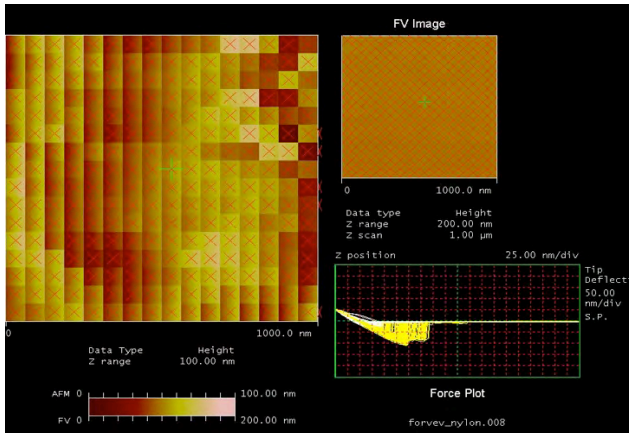


Sectional analysis of composite laminate

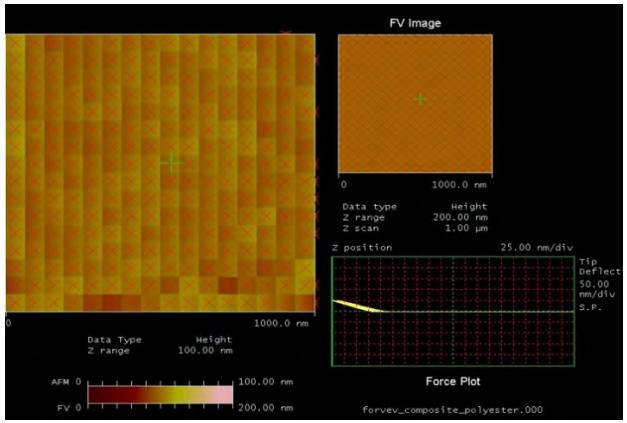
Points	Mean Adhesion Force (nN)	SD
A	0.772	0.01
B	0.215	0.013
C	0.023	0.015
D (background)	0.579	0.013

Force curves on nylon peel-ply sample

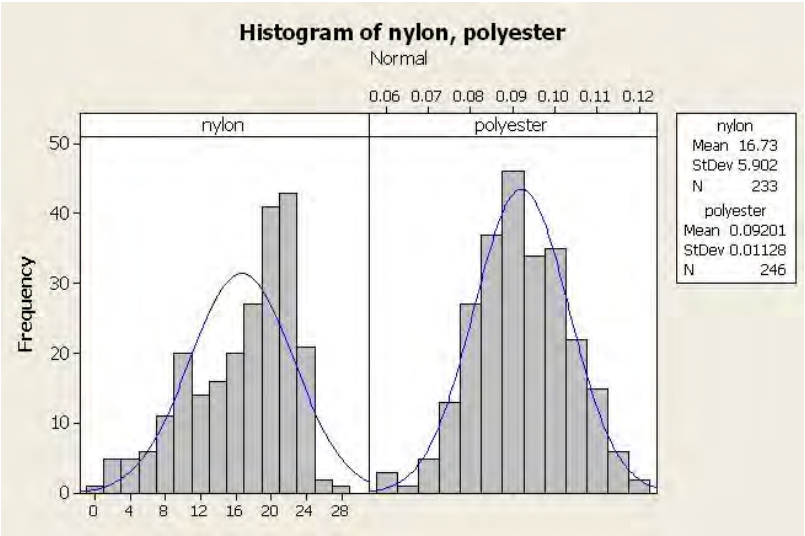
Force Volume – Unmodified Probe



Nylon prepared peel-ply sample surface



Polyester prepared peel-ply sample surface



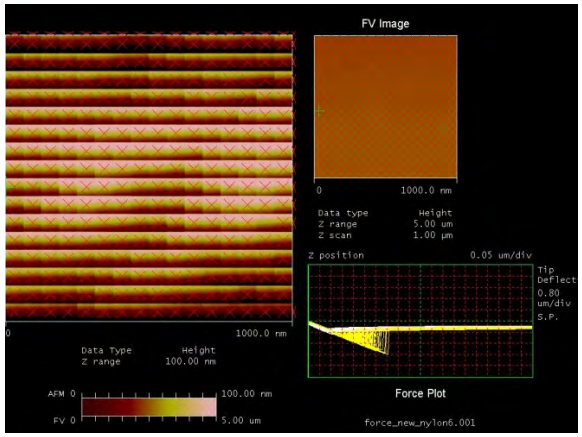
Mean Adhesion Force

Nylon: 16.73 nN
Polyester: 92.01 pN

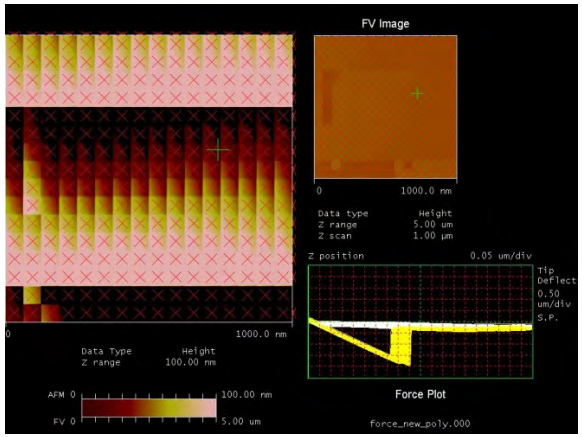
Water contact angle

Nylon ply: 75°
Polyester ply: 130°

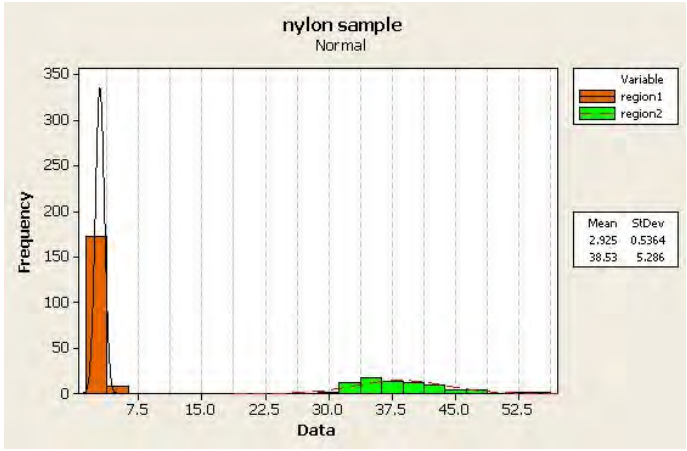
Force Volume – Epoxy Probe



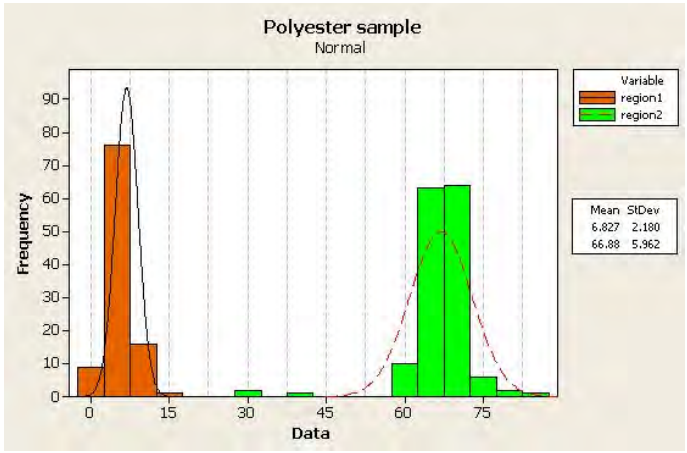
Nylon prepared peel-ply sample surface



Polyester prepared peel-ply sample surface



Histogram shows two different regions of adhesion Indicating the epoxy probe is sensitive to surface contamination.



The adhesion values are higher for polyester when compared with nylon, demonstrating the hydrophobic (epoxy probe) and hydrophilic (nylon surface) nature of the materials.

Conclusions

- The all solid-state electrochemical sensor can differentiate the pristine and a variety of contaminated laminate surfaces. The simple designs, fabrication protocols, and testing setup allow implementation of an online and in-field technology for pre-bonding inspection of the laminate surface.
- EIS results show that a specific mediator or redox pair may be sensitive to certain compounds but insensitive to others. The sensitivity of other mediators or redox pairs needs to be examined.
- SEM/EDAX analyses confirm that the surface of the pristine sample has a simplest composition and hence may be used as a baseline for the EIS measurements. More analyses are needed to establish a correlation between surface chemistry and polarization impedance.
- The epoxy probe is shown to be more sensitive than the unmodified probe.
- As expected, humidity can dramatically influence the AFM adhesion force results.
- CFM can be used to discriminate between various function groups on composite surfaces prepared with nylon and polyester peel-plies.
- Force volume is a promising technique for systematically quantifying the surface activity using force spectroscopy.