Handheld Characterization Probe for Catalytic Assessments of Electrodes and MEAs

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Problem Background

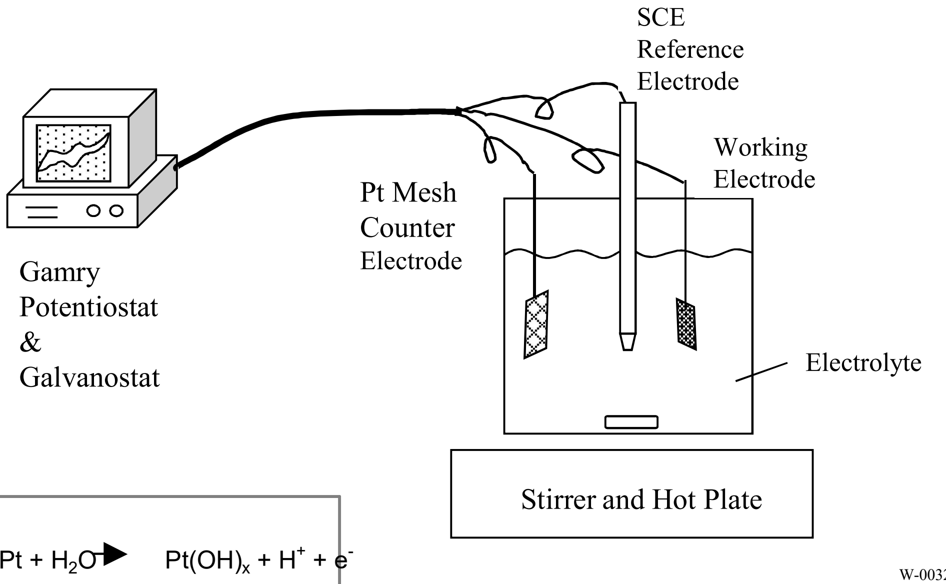
- Reactive or catalytic surfaces are abundant in many products including
  - Biotechnology (biomimetric membranes), biocatalytic coatings
  - Batteries, fuel cell (PEM, methanol, AFC, SOFC), electrolyzers
  - Photocatalytic and photobiocatalytic
  - Industrial catalysis
- In these reactive surfaces or films, there is often a catalyst that is needed to facilitate a reaction
- A fundamental question to ask is “how will this catalytically coated material perform in its application before it is processed further into a higher value product?”
  - This question is relevant for both research and manufacturing environments

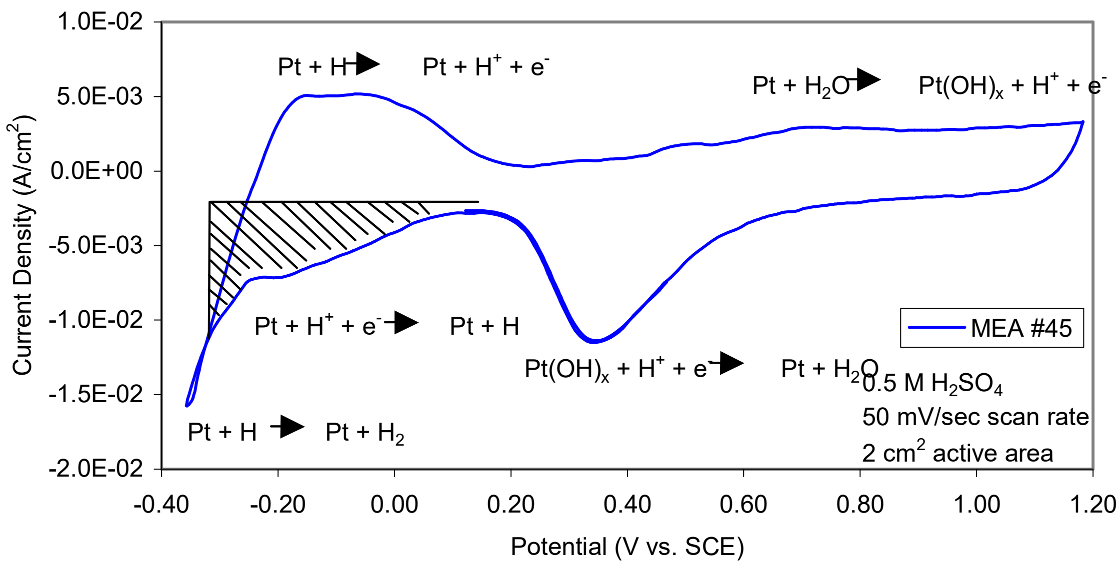
Current Technology

- Manufacturing sensor technologies are abundant for assessing certain types of film quality
- Optical and electrical metrology methods are often employed in practice to measure film thickness, surface roughness, porosity, and uniformity
- These are important variables that can affect how a catalytic film will perform, but the traditional optical and electrical measurement methods do not address the fundamental variable of interest – how chemically active is the coating?
- An improved approach would be one that can assess the catalytic activity of the film in a non-destructive manner by actually performing a reaction on the film

Chemical Reactivity Assessment by Cyclic Voltammetry

- Applied voltage scans to impart reduction and oxidation behavior on the reactive surfaces
- Correlations needed to interpret response data to real world physical variables





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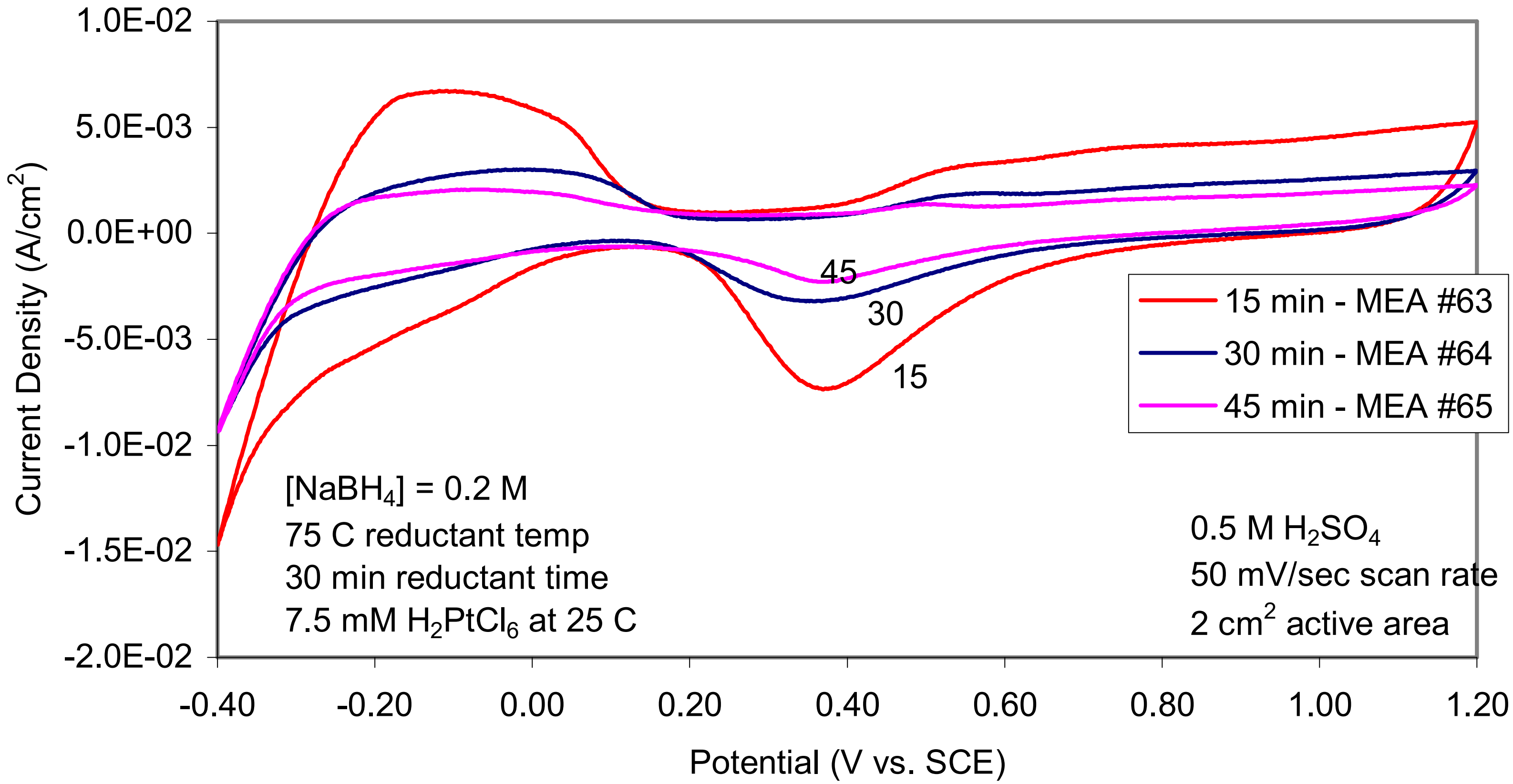
Variation in the Cyclic Voltammetric Behavior with Changes in the Reactive Surface Manufacturing Process



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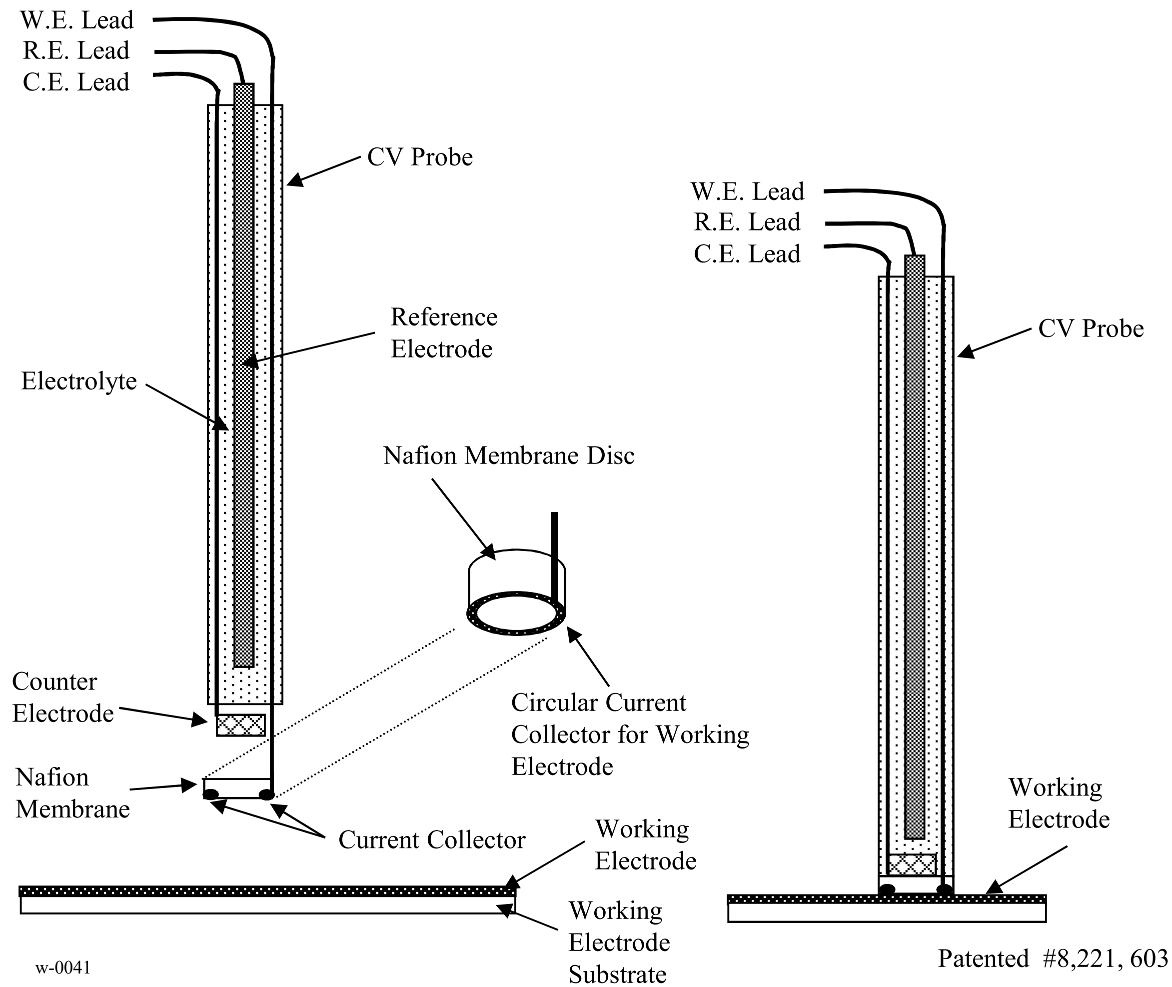
Technical Approach

- Our approach is to package a cyclic voltammetric sensor into a hand-held probe that can be placed against a reactive surface
  - Use an ion-exchange membrane as a solid electrolyte separator that can be touched up against a reactive surface to probe its chemical activity
  - Package a counter electrode, a reference electrode, and a liquid electrolyte within the hand held sensor probe
  - Place a current collector on the outer membrane surface to touch the reactive surface
- With this probe approach, we obtain a three-electrode arrangement necessary to conduct a cyclic voltammogram (or an AC impedance scan as well) where the reactive surface remains intact and dry.
- Thus, the reactive surface article under test:
  - is not destroyed,
  - is assessed for its chemical activity,
  - is capable of having more regions analyzed for statistical comparison,
  - is capable of being assessed in a continuous manufacturing line, and
  - is usable in its final product application

Handheld Electrochemical Probe Design

- Classic wet-electrochemistry components packaged into a hand-held probe
- Material challenges
  - Working electrode current collector
  - Membrane transducer
  - Electrolyte
  - Housing
- Mechanical challenges
  - Packaging
  - Ergonomics
  - Seals
  - Membrane transducer tightness and flatness



Patented #8,221, 603

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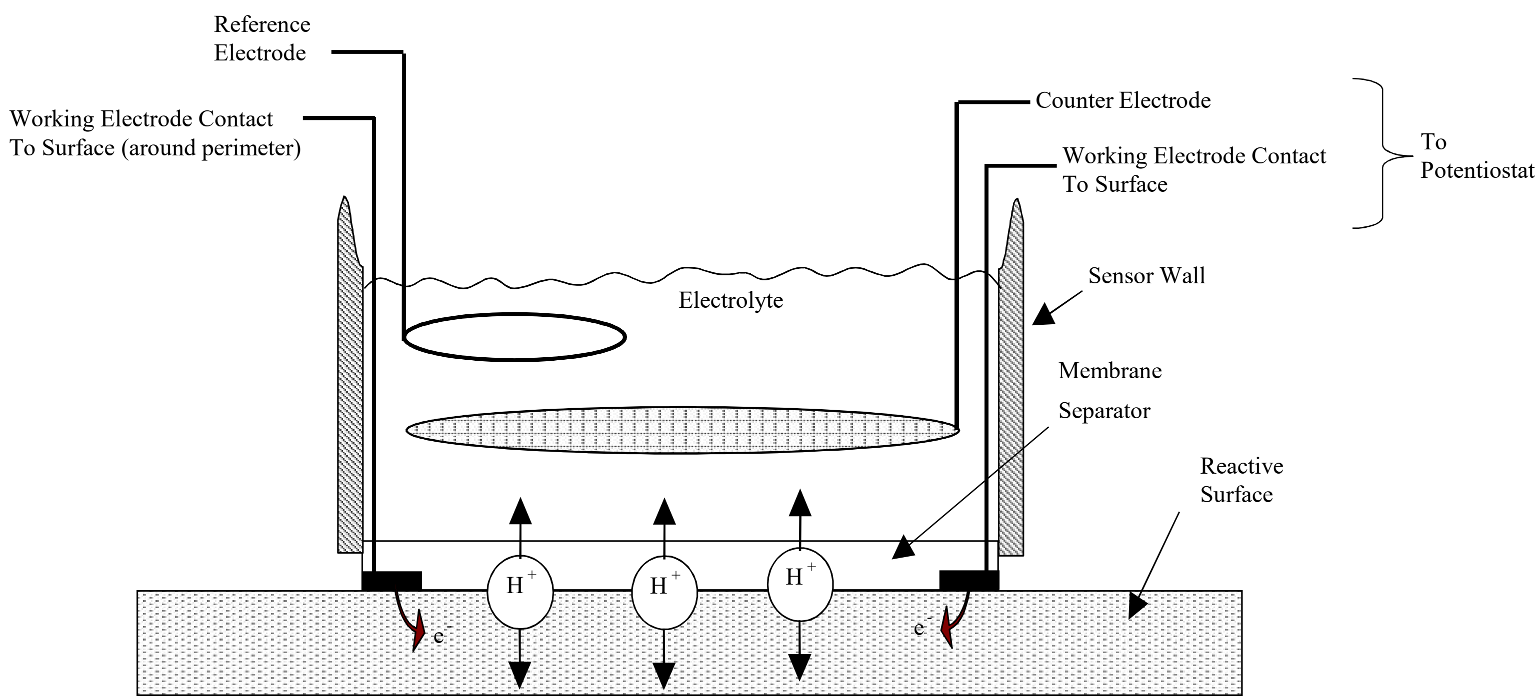
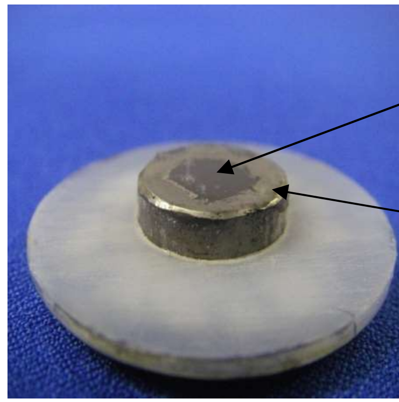
Sensor Operation



Sensor Manufacturing Process

Platinized
Nafion film



Nafion
Film

Platinum
Current
Collector

Enlarged view of flat membrane
surface

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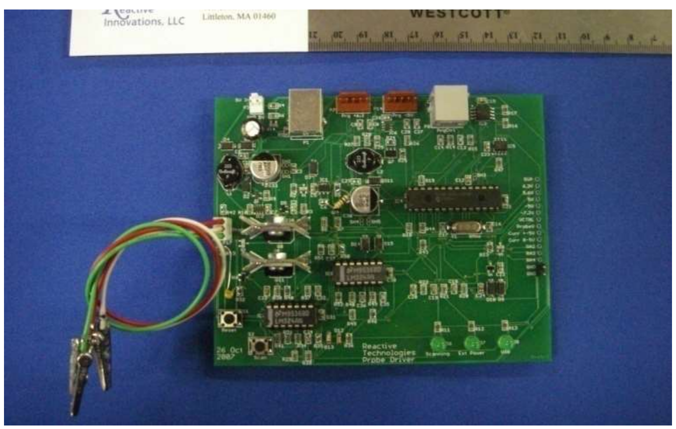
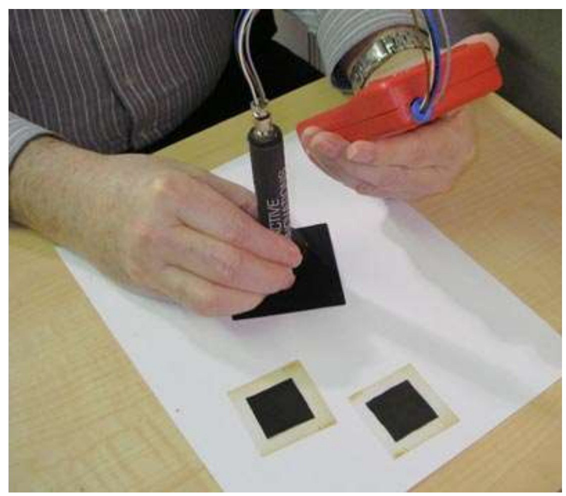




Membrane Transducer Film

- Membrane film must remain flat, even when wetted on one side, to contact the reactive surface
  - Electron transfer through the current collector ring
  - Ionic transfer through the membrane film
- Need to maintain low ohmic resistance through the membrane to maximize the reactive film signal

Case	**Trial Number**	**Resistance (ohms)**	
		Solvent Expansion	
		Water	**MeOH**
Membrane Transducer Dried Out	1	5527	3407
	2	5000	1193
	3		2000
	Avg	5264	2200
	Stdev	373	1120
Membrane Transducer Re-Wetted, 25 C	1	2.975	2.415
	2	2.736	2.970
	3	2.959	2.961
	Avg	2.890	2.782
	Stdev	0.134	0.318
Membrane Transducer Boiled	1	2.596	2.710
	2	2.520	3.016
	3	2.489	2.727
	Avg	2.535	2.818
	Stdev	0.055	0.172

Correction for Platinized Current Collector Contact Ring

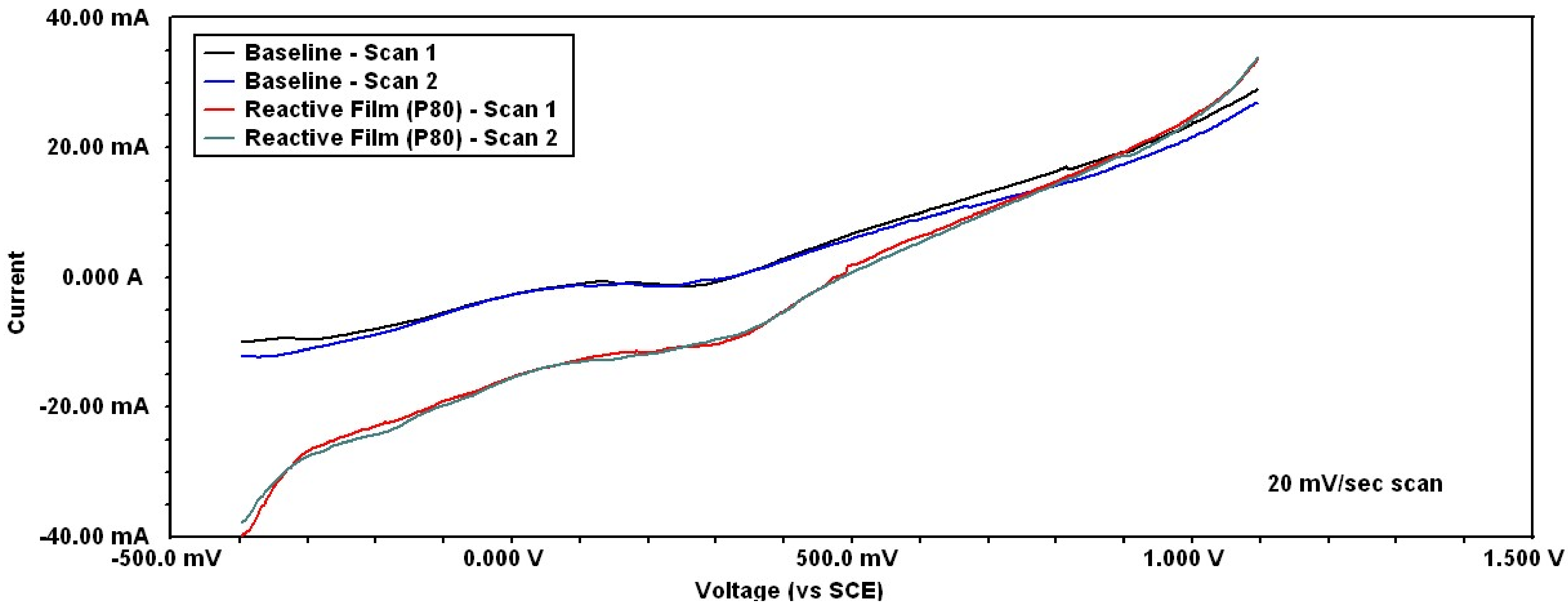
Probe 3I		Pt Area by H2 charge	
From CV probe		at 0.0 to -0.4 V	
Physical area		cm2	0.71
Sample charge dens		C/cm2	6.67E-02
Baseline charge dens		C/cm2	6.39E-02
Corrected charge dens		C/cm2	2.80E-03
Real area/geom area		ratio	13

Inherent surface area of the Pt contact ring

MEA A	Pt/C	Tested dry using probe 3I					
		C urrDens @ --0.4V				Pt Area by H2 charge	
From CV probe				From CV probe		at 0.0 to -0.4 V	
Background corrected		i/cm2	0.0051	Physical area		cm2	7.10E-01
				Sample charge		C/cm2	1.38E-01
				Baseline charge		C/cm2	9.56E-02
				Corrected charge dens		C/cm2	4.25E-02
				Real area/geom area		ratio	202
Wet electrochemistry				Wet electrochemistry			
Wet electrochemistry		i/cm2	0.0094	Physical area		cm2	6.45E+00
				charge density		C/cm2	4.27E-02
				Corrected charge dens		C/cm2	2.75E-01
			54	Real area/geom area		ratio	203

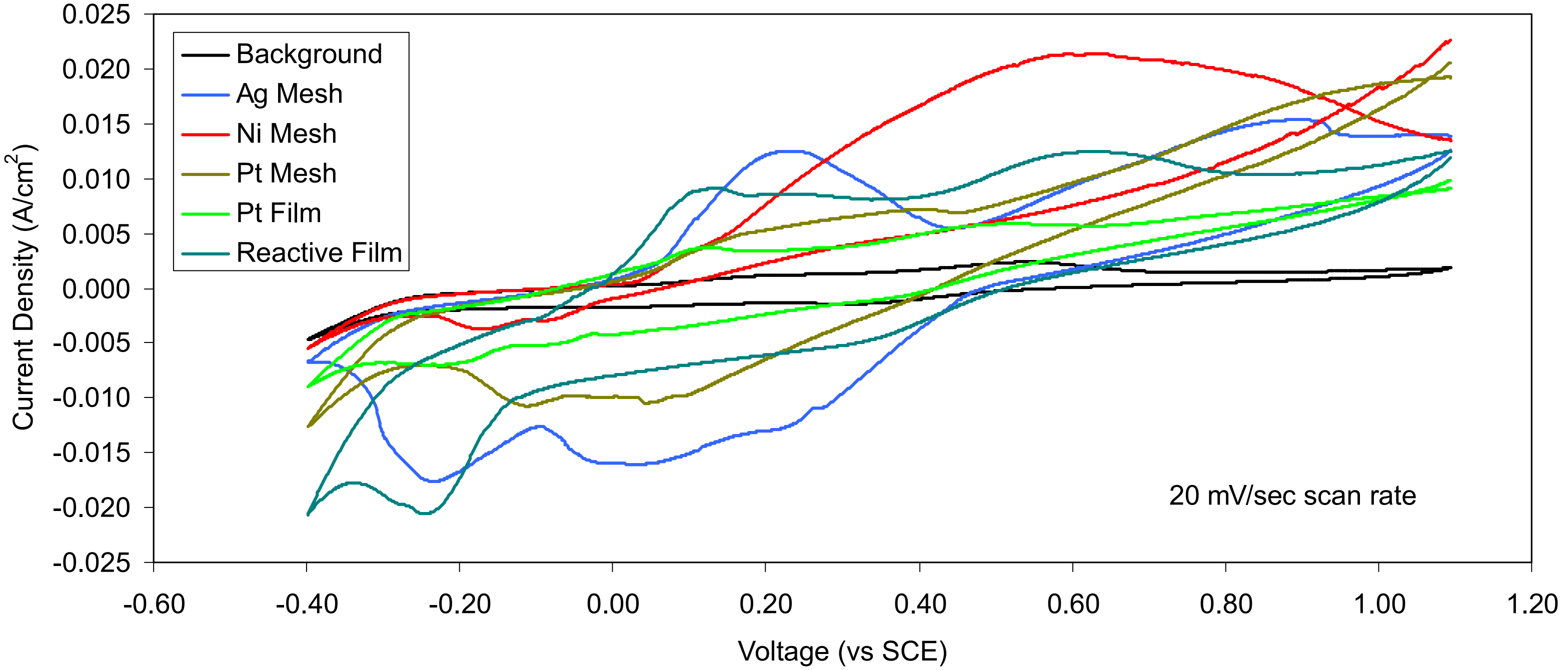
Comparable specific areas measured via both methods

Reproducible Behavior Obtained With the Reactive Surface Probe



At –0.4 volts, the classic "wet-electrochemistry" method gives a current density of 41 mA/cm^2 whereas the sensor probe gives a current density of 39.8 mA/cm^2, a 2.9% deviation!

Hand-Held CV Probe Gives Distinctive Responses on Various Catalytic Surfaces



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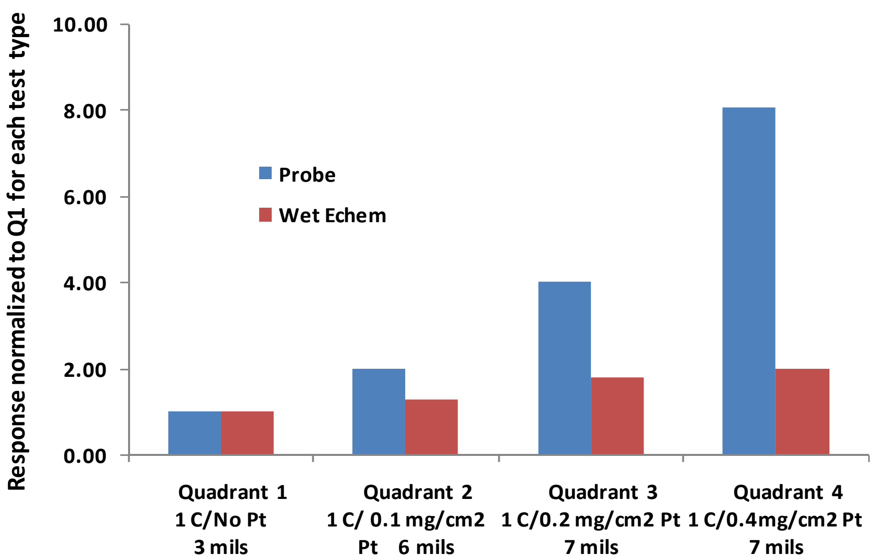
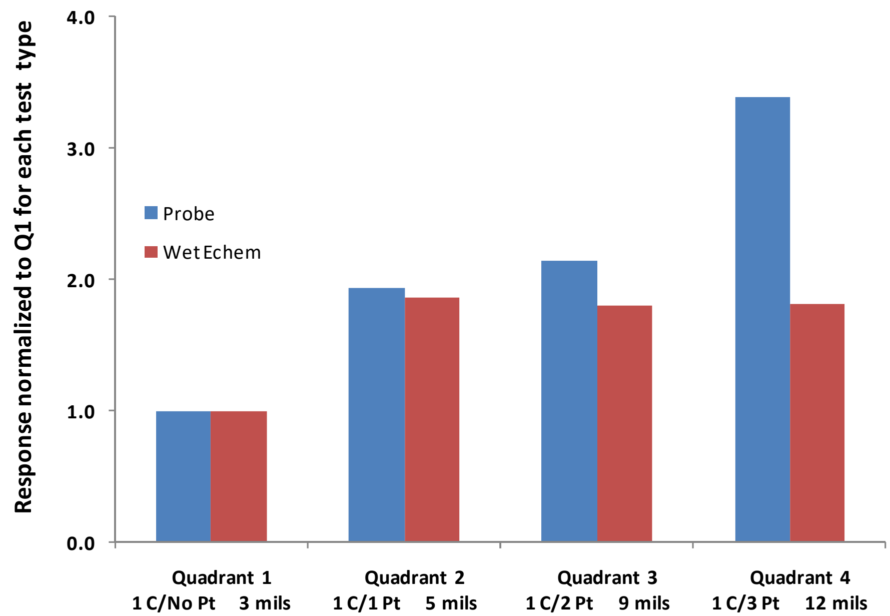
Comparison of Probe vs. Classic Wet-Electrochemical Assessments



Coupon D: concentrations of 0, 0.1, 0.2 and 0.4 mg Pt/cm2 over one carbon layer. Thickness is total for 1C, 0 or 1 Pt layer.



Coupon C: zero to 3 layers Pt over a single C layer
Thickness refers to overall height of C+Pt

Variability of catalytic loading within an electrode detected by the probe

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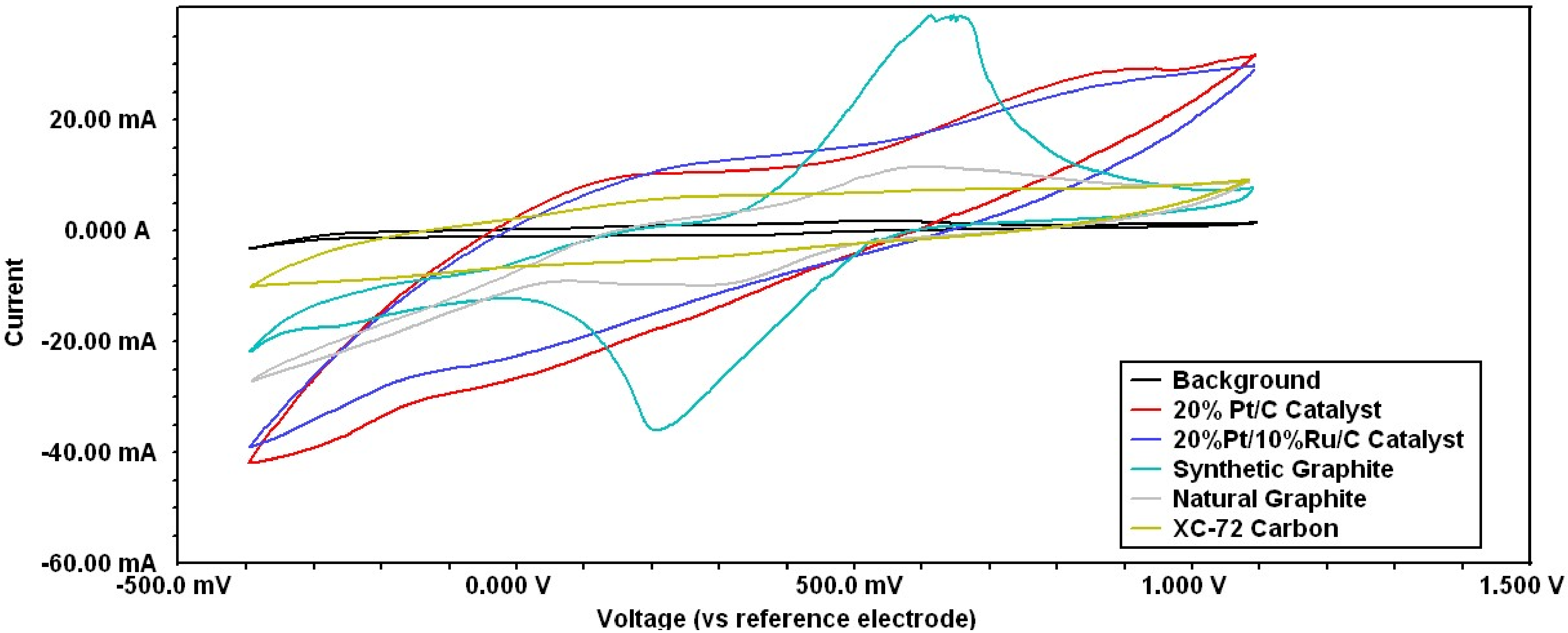
Application to Screening Dry Catalyst Powders by the Hand-Held CV Probe



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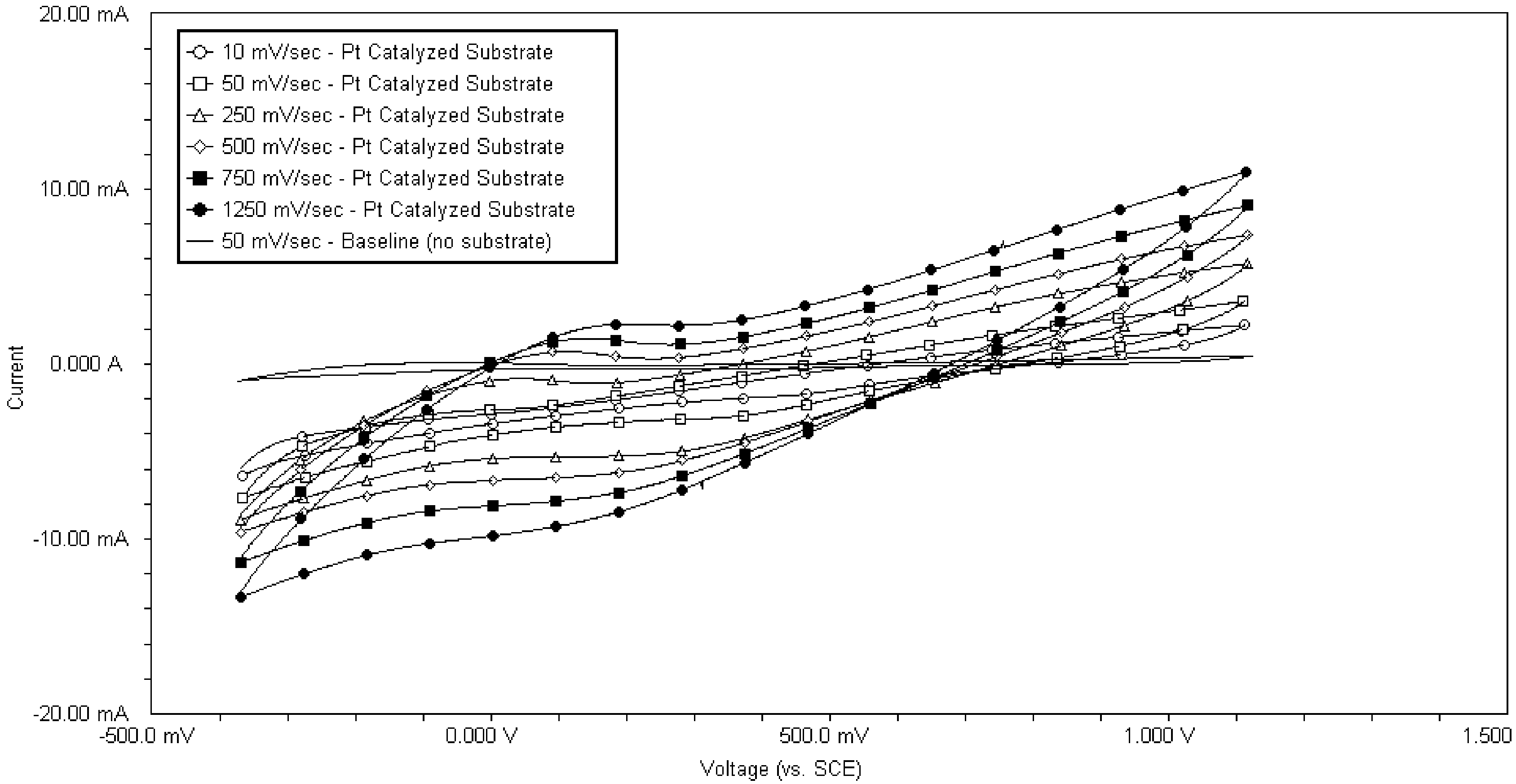
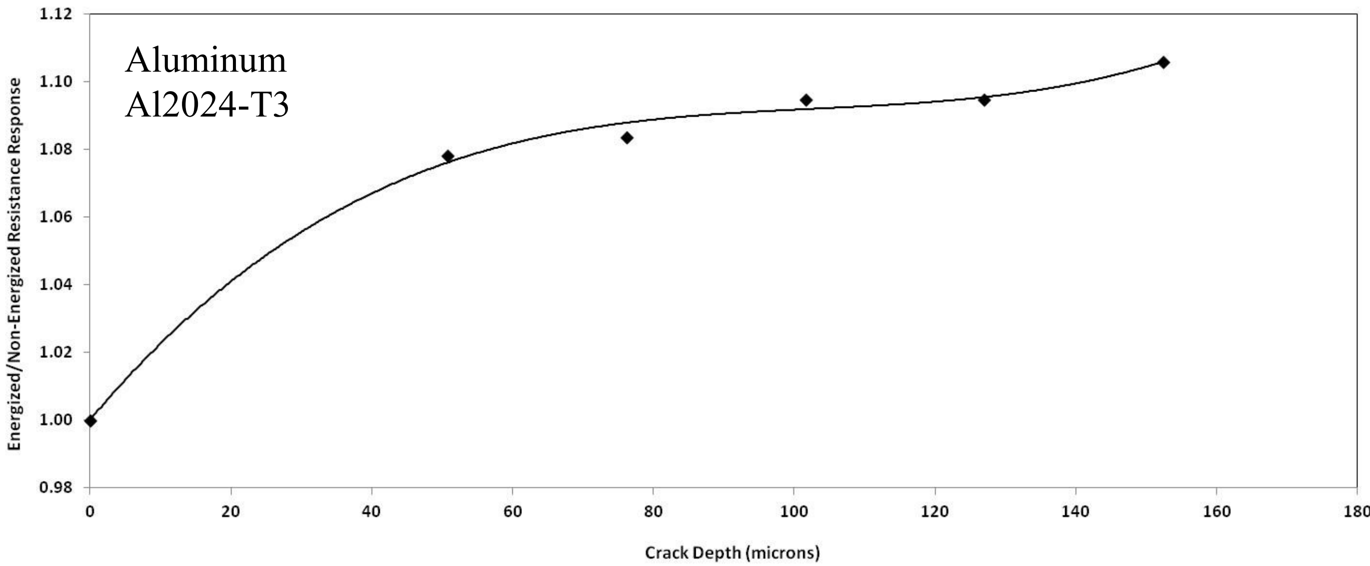
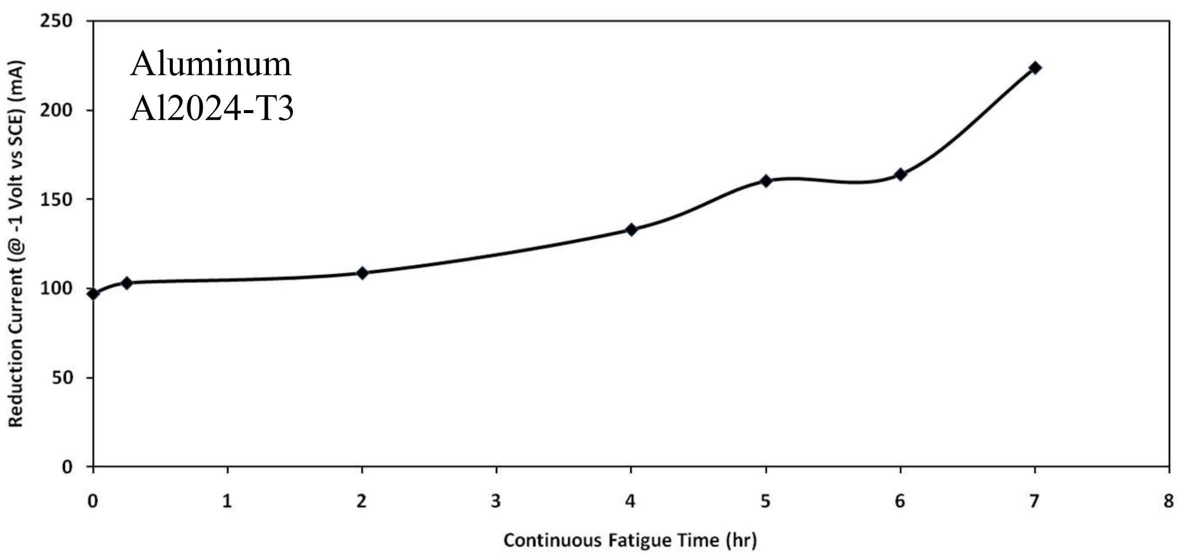
High Scan Rate Capability – Implications for Continuous Manufacturing Quality Control of MEAs



Extensions: Handheld Characterization Probe for Assessing Cracks and Fatigue on Metallic Substrates



Increasing electrochemical signal up to 150 micron deep cracks (statically-induced)



Increased electrochemical signal up to 50,000 cycles

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Summary of a Hand-Held Reactive Surface Probe

- Developed and demonstrated a reactive surface probe
  - Applicable for Manufacturers to Researchers
- Enabling technology is a membrane transducer
- Similar cyclic voltammetry responses for the sensor and wet electrochemical techniques
- Compact electrical circuit can drive the electrochemical interrogation process
- Broad applications of the sensor probe
  - varying types of catalytic surfaces
  - catalytic powders
  - extensions to mechanical damage on metallic surfaces

Acknowledgment

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