Development of a Handheld Probe for Chemically Reactive Surfaces

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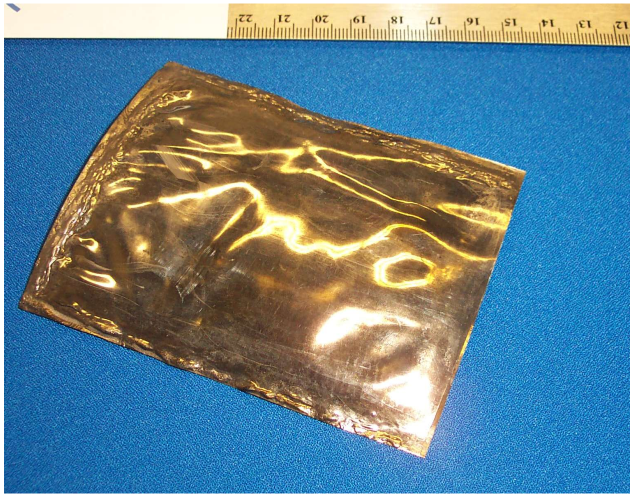
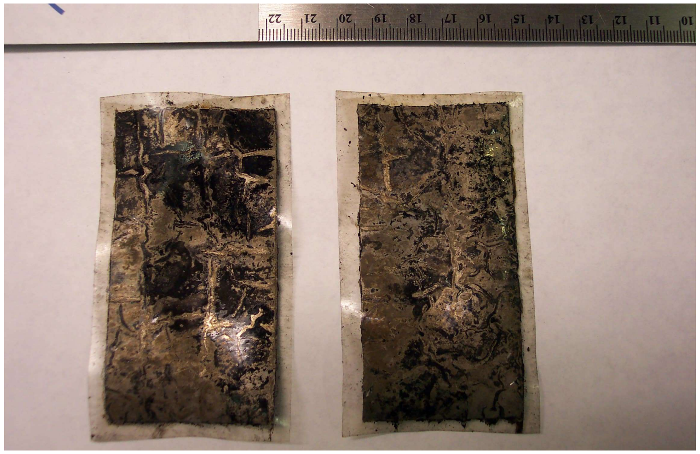
Problem Background

- 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



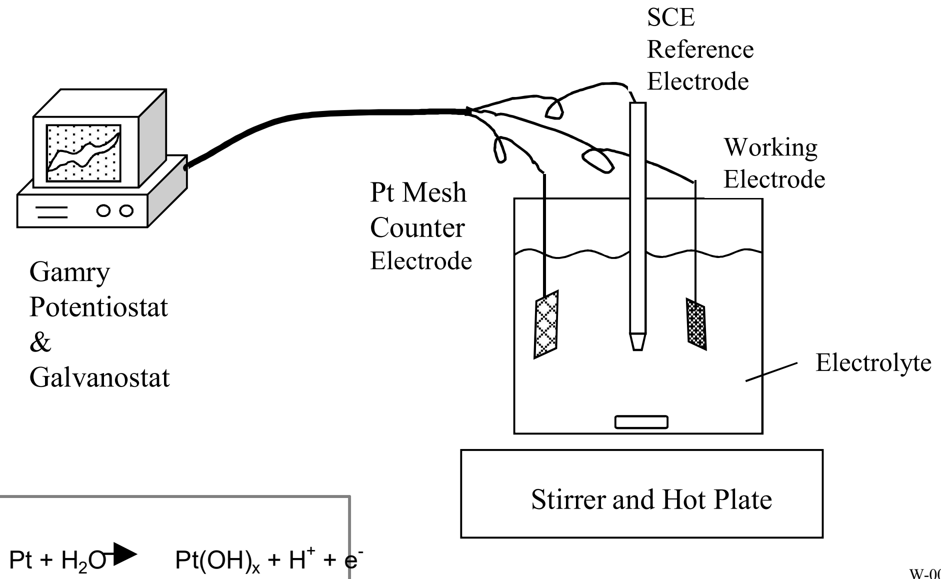


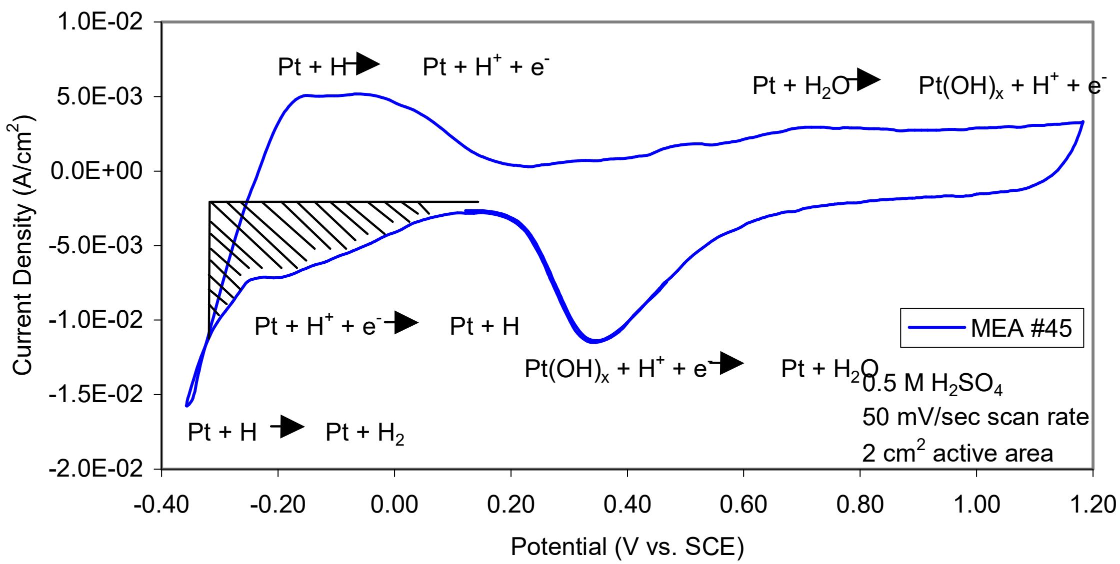
Current Technology

- 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

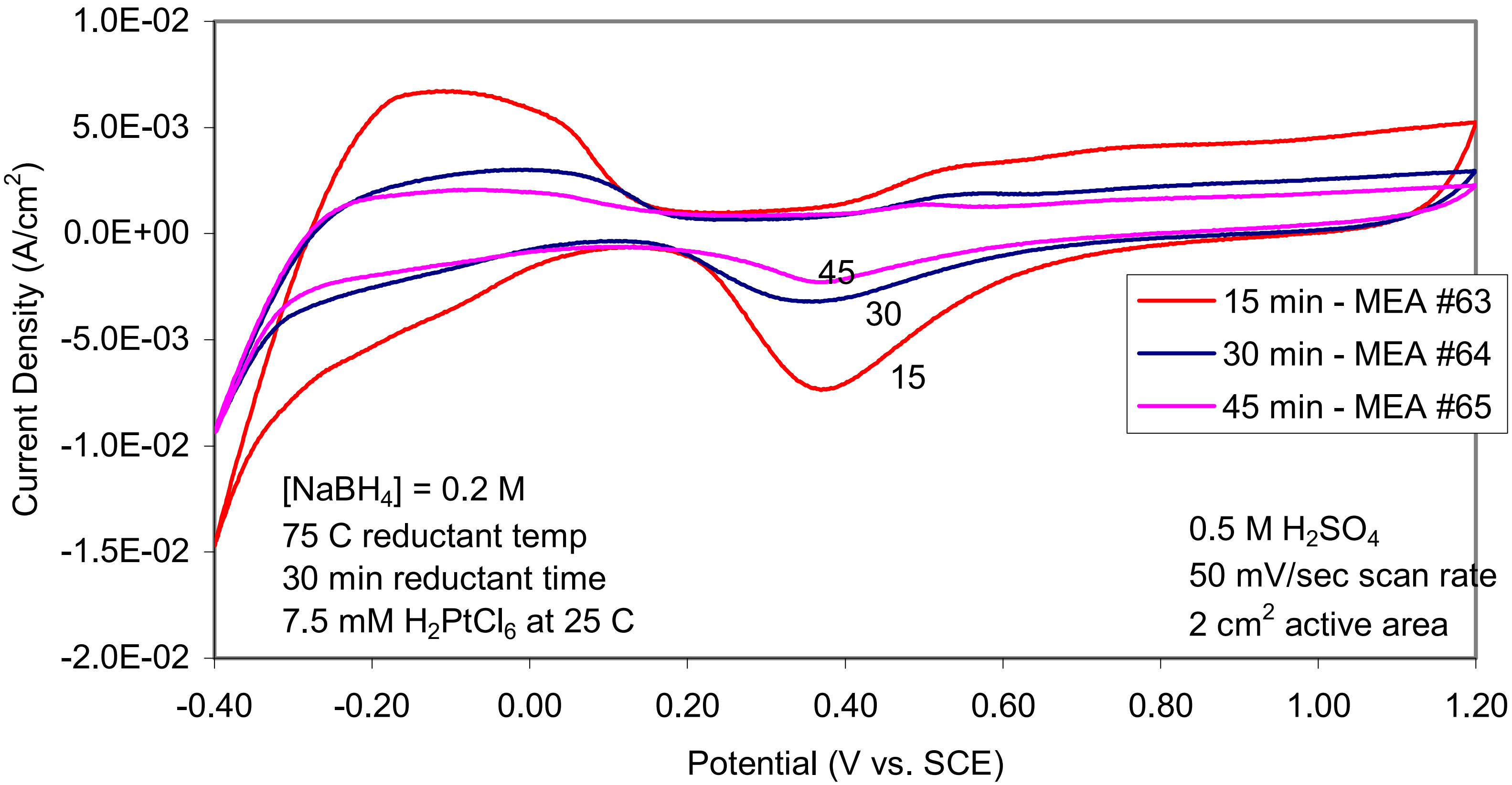
Chemical Reactivity Assessment by Cyclic Voltammetry

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





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



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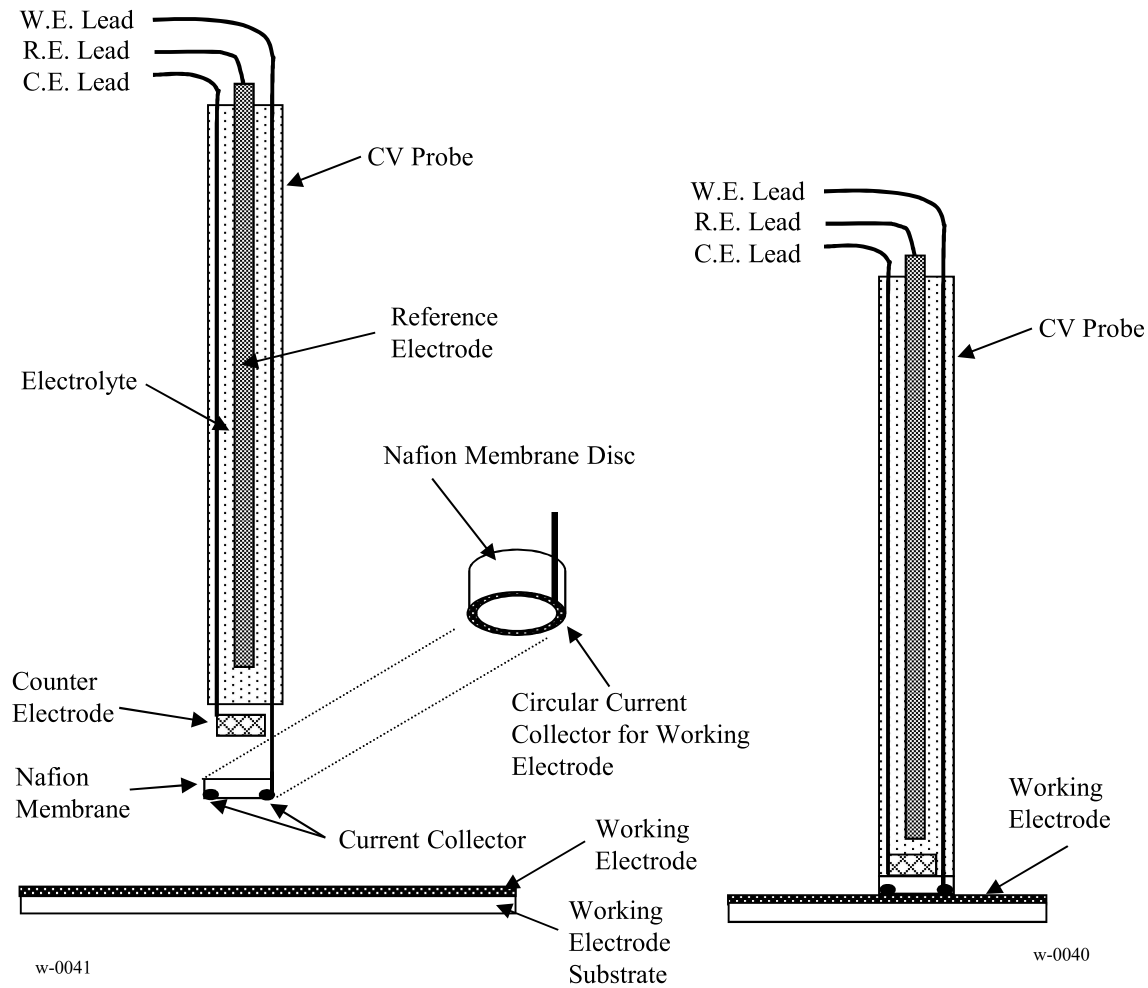
Technical Approach

- 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

Probe Design

- Need to develop a hand-held probe assembly
- Material challenges
  - Working electrode current collector
  - Membrane transducer
  - Electrolyte
  - Housing
- Mechanical challenges
  - Packaging
  - Ergonomics
  - Seals
  - Membrane transducer tightness and flatness



Patent Pending

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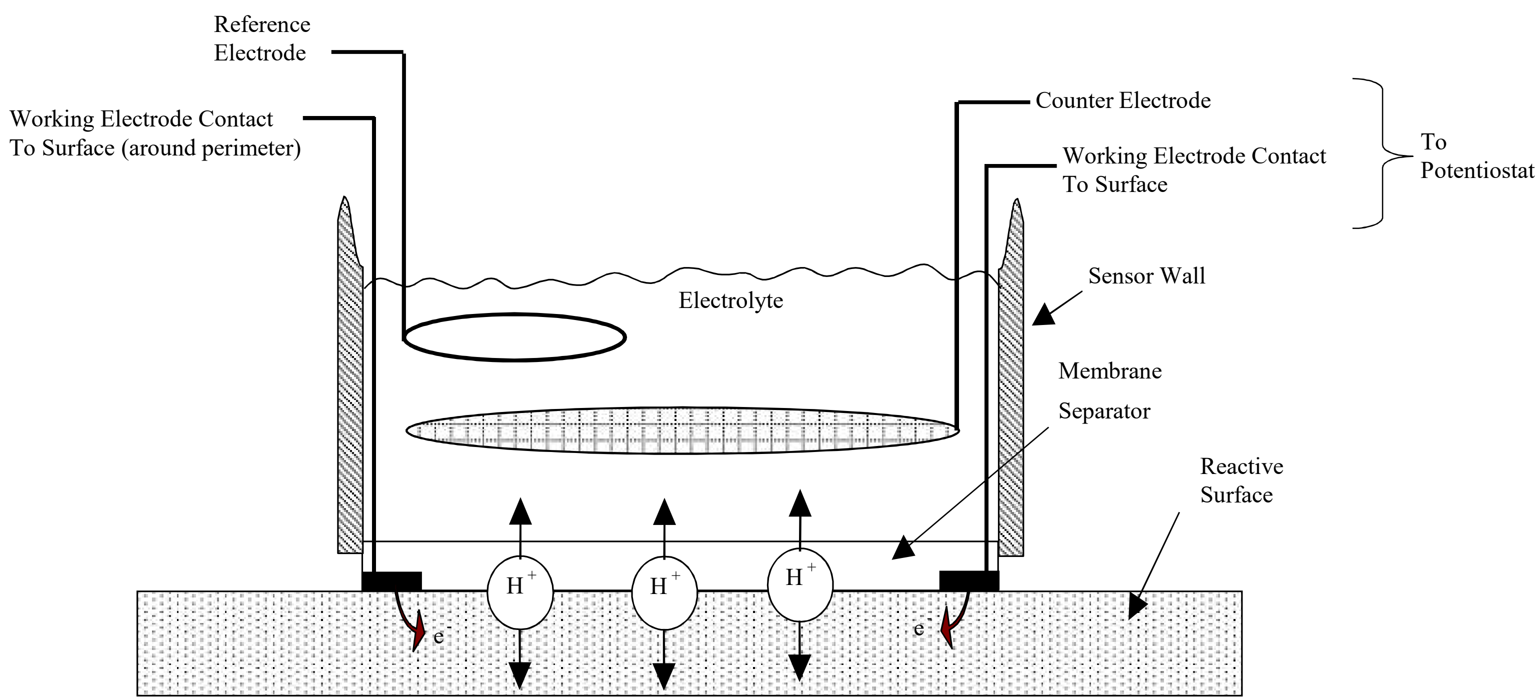
Sensor Operation

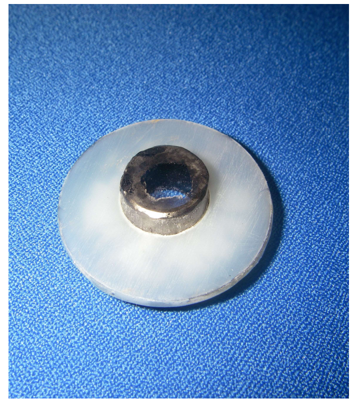


Patent Pending

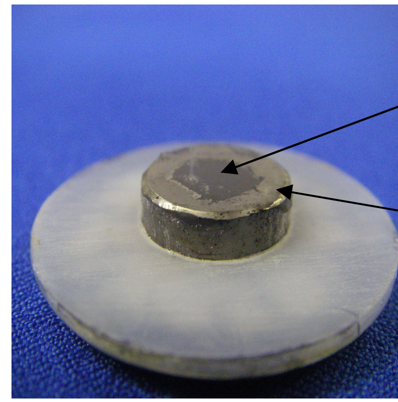
Sensor Manufacturing Process

Platinized Nafion film

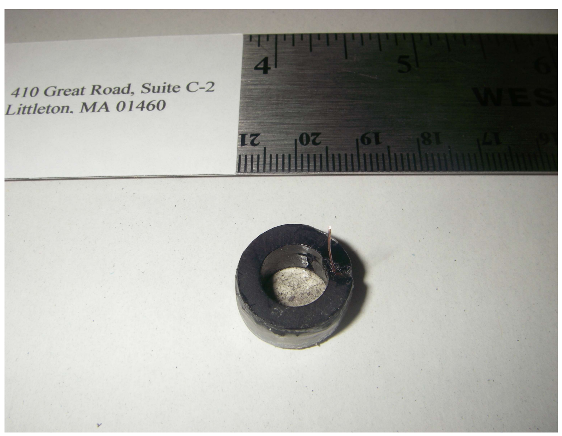
Plastic holder with protruding stem



Conformal membrane about stem



Enlarged view of flat membrane surface



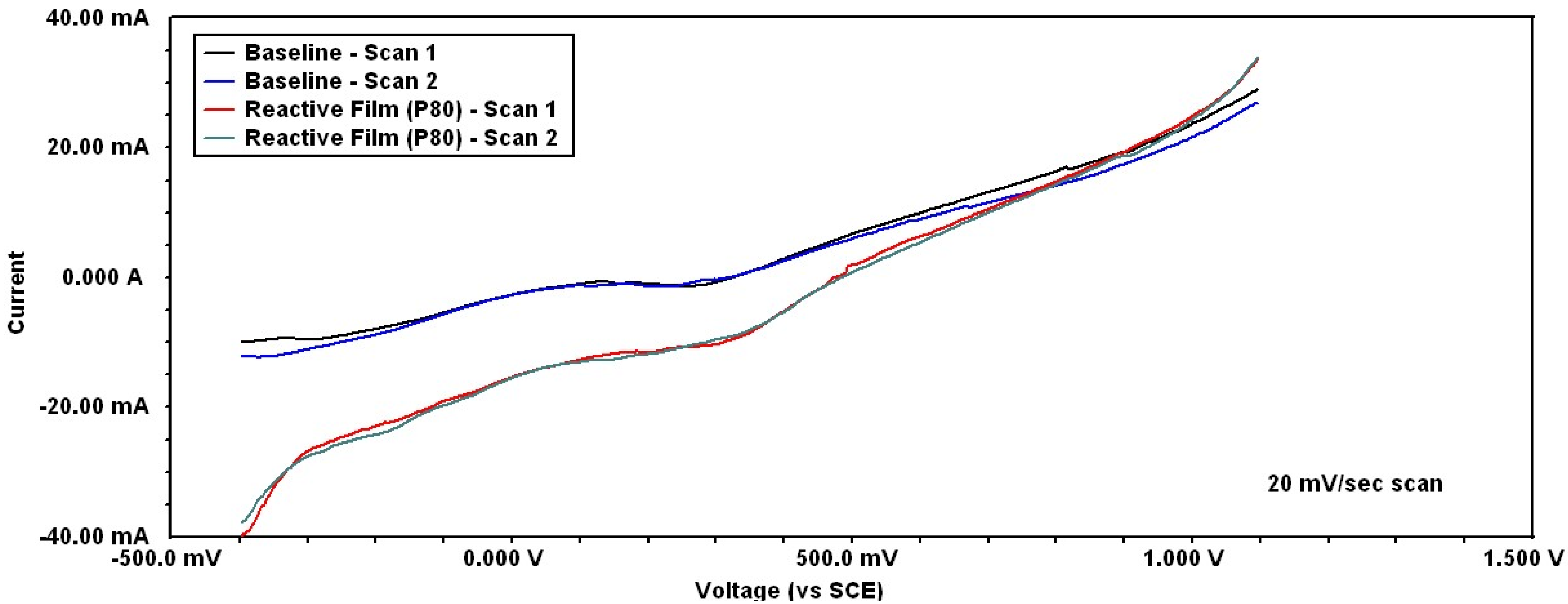
Small membrane transducer assemblies

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
- Solvent Expansion of the Membrane During Manufacture Key to Obtaining a Flat Surface, Even When Subsequently Wetted From Inside the probe

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

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!

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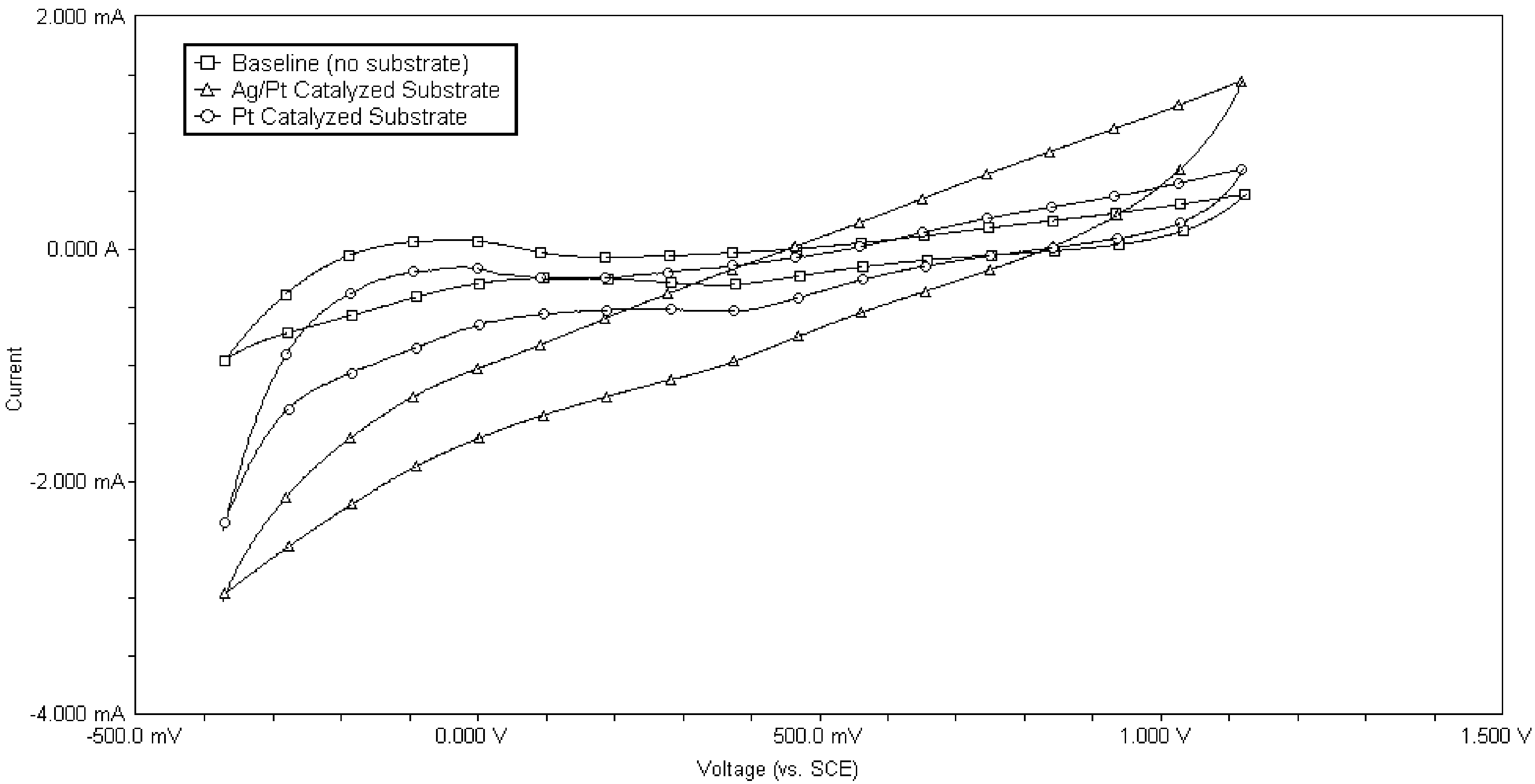
Handheld CV Probe Performance for Characterizing Reactive Films



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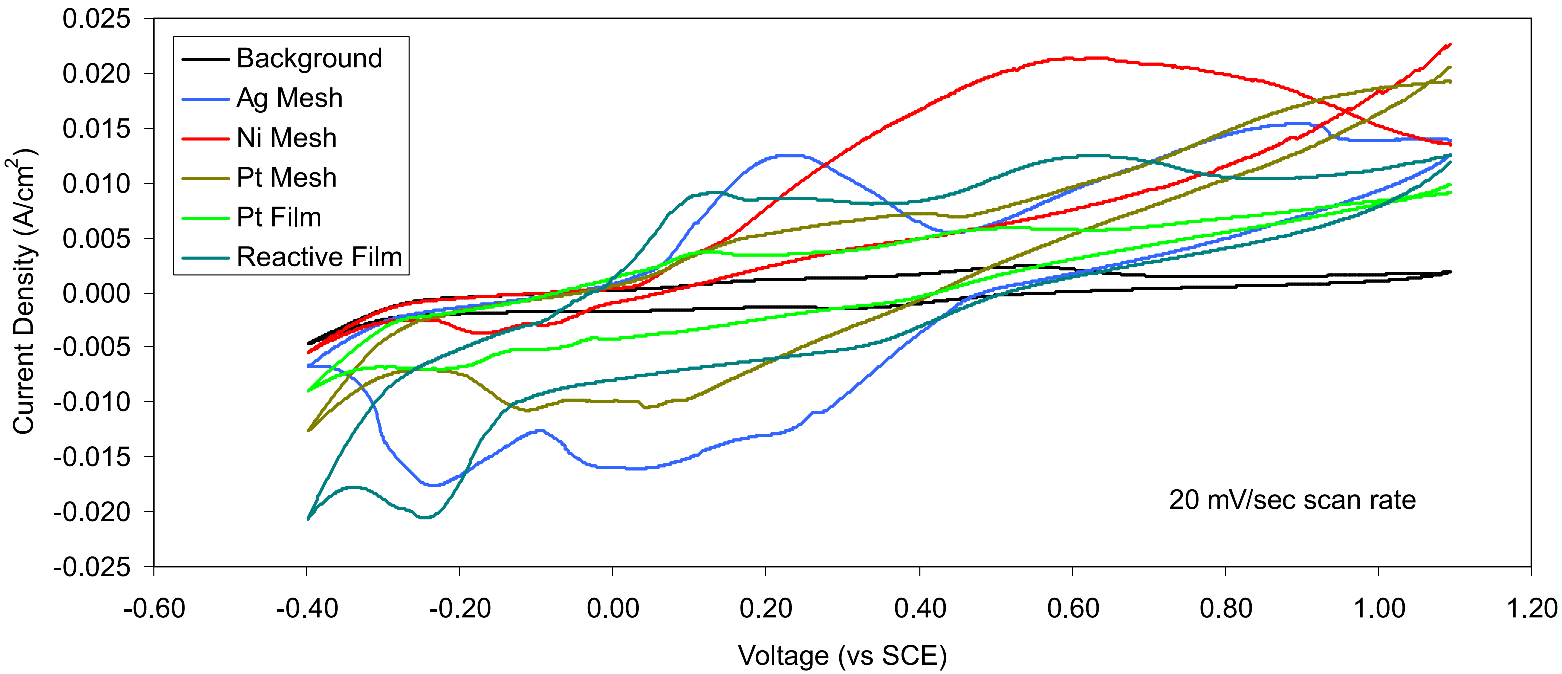
Hand-Held CV Probe Gives Distinctive Responses on Various Catalytic Meshes



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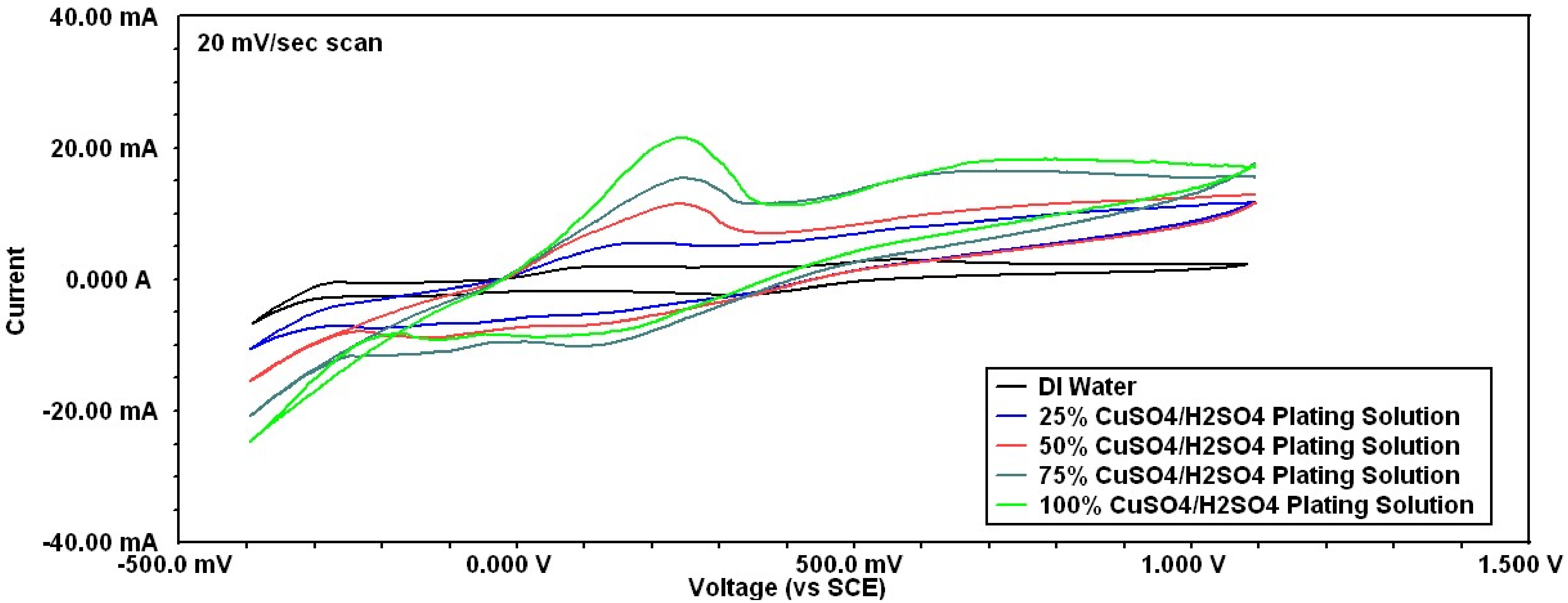
Hand-Held CV Probe Can also be Used to Measure Changes in Solution Concentrations



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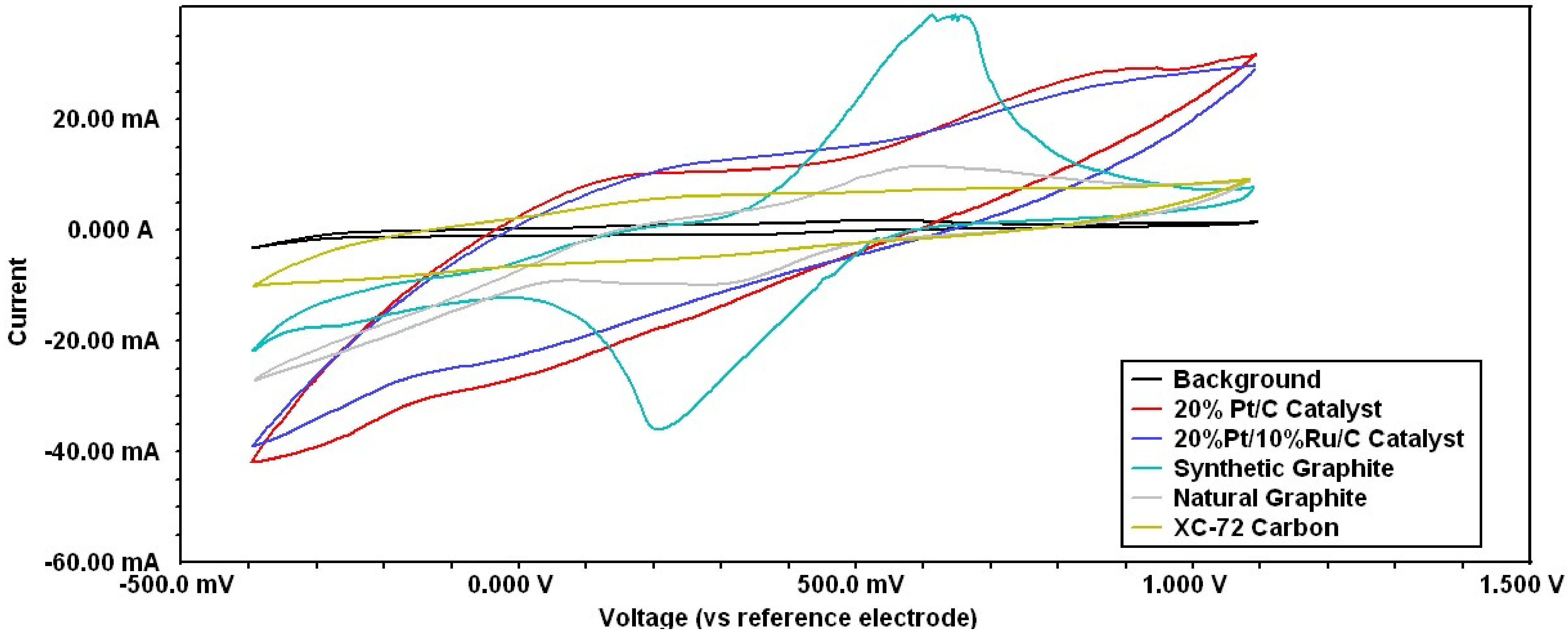
Dry Catalyst Powders Can be Screened by the Hand-Held CV Probe



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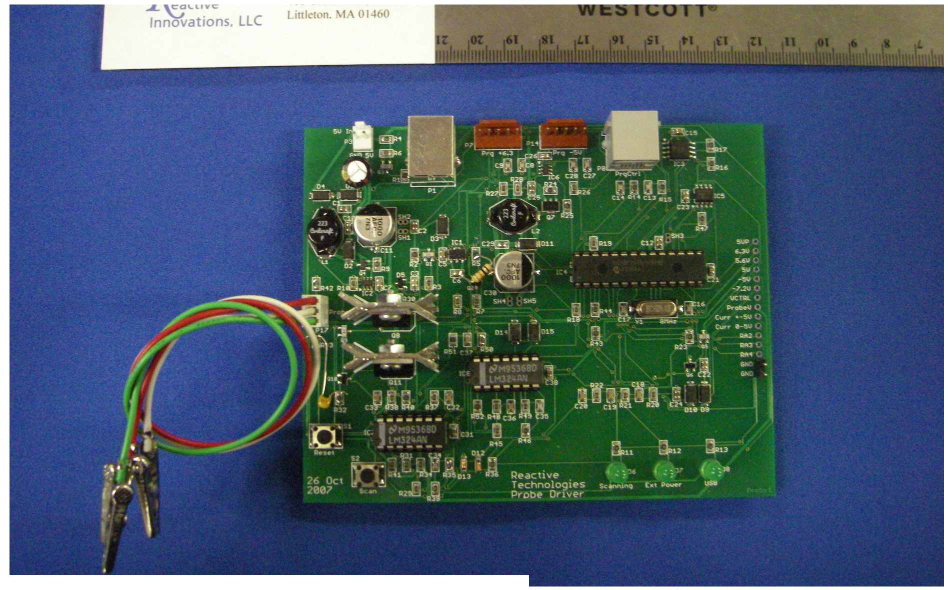
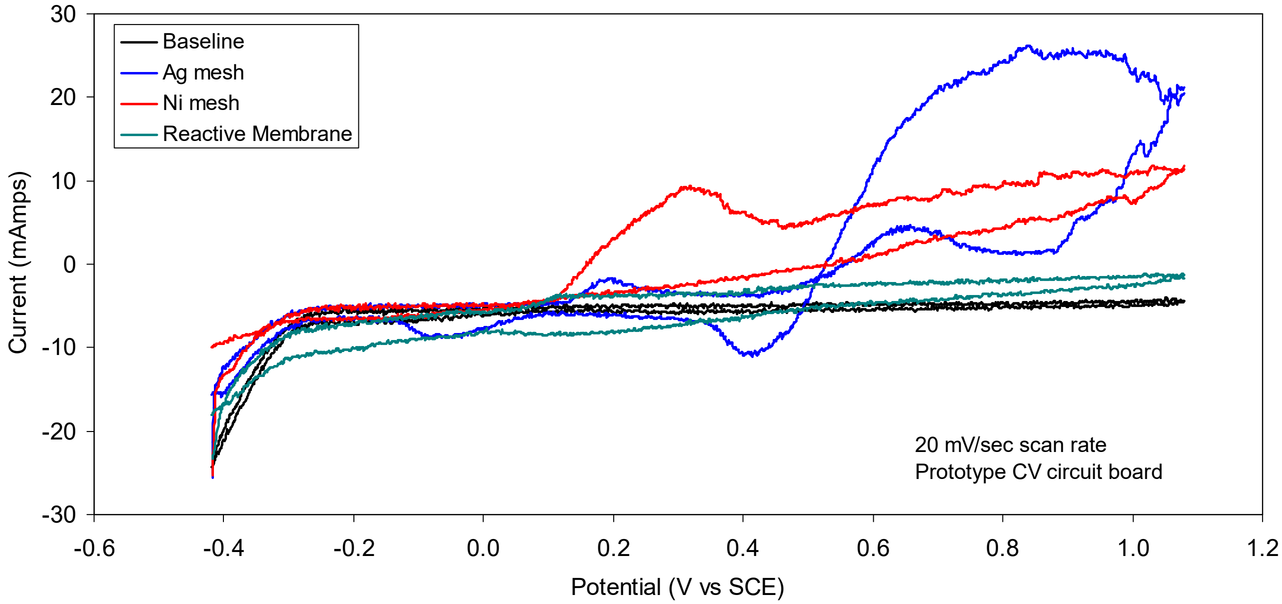
Compact Electrical Circuit for Driving the Cyclic Voltammetry Process Allows it to be Packaged into a Hand-Held Probe





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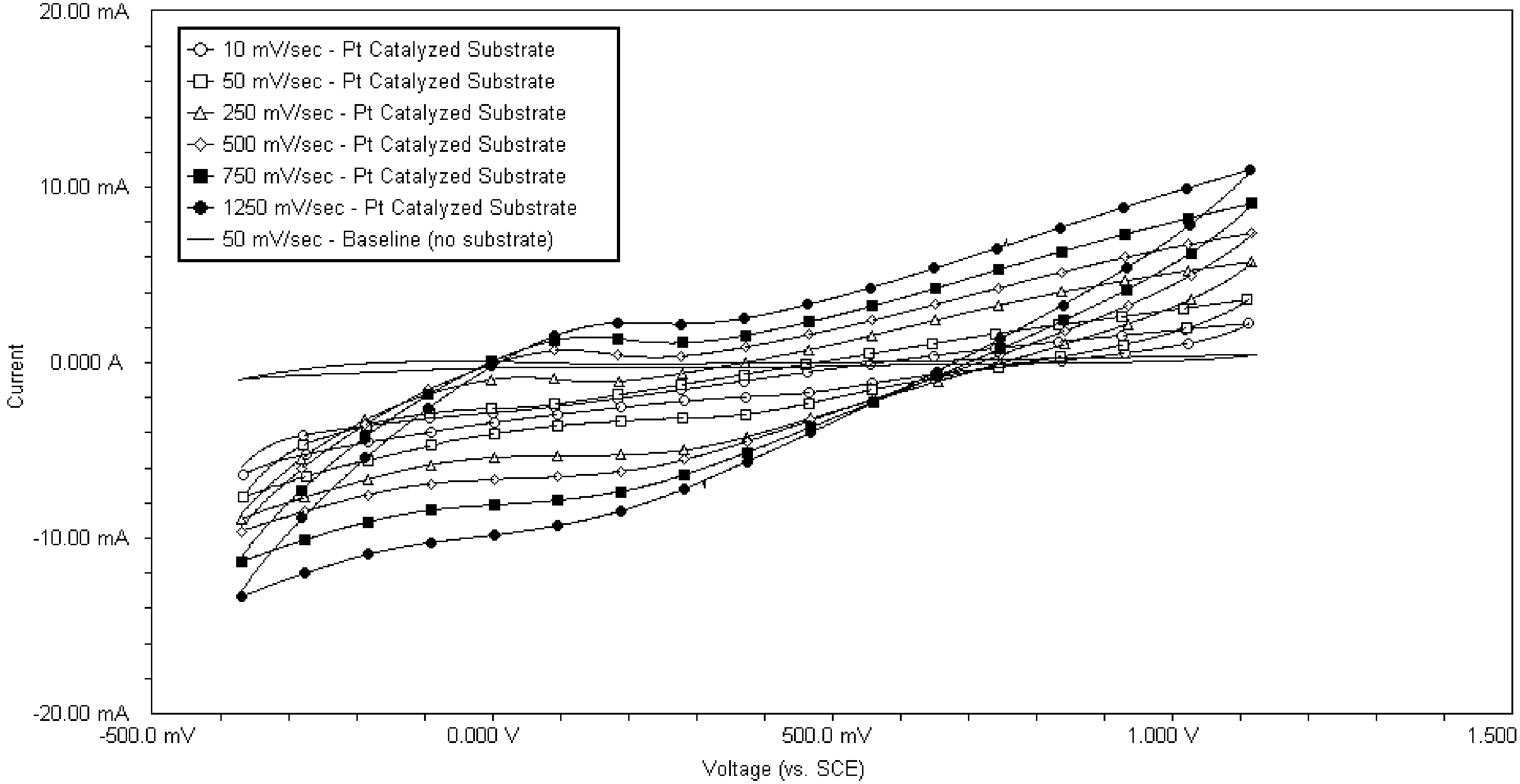
High Scan Rate Capability – Implications for Continuous Manufacturing Assessments



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Summary of a Hand-Held Reactive Surface Probe

- Developed and demonstrated a reactive surface probe that can be touched up against a reactive surface and used to quickly assess the propensity of the surface to chemically react without destroying the sample
  - Applicable for Manufacturers to Researchers
- Enabling technology is a membrane transducer that separates the classic 3-electrode arrangement away from the reactive surface allowing it to be interrogated via an electrochemical charge transfer process
- We found similar cyclic voltammetry response measures for our sensor to that obtained using wet electrochemical techniques as well as showed reproducible scans with the sensor probe
- We showed that we can drive the electrochemical interrogation process with a compact electrical circuit that can be packaged into a single hand-held wand assembly
- Broad applications of the sensor probe were also shown giving distinct response measures for varying types of catalytic surfaces, plating bath compositional variations, and catalytic powders

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