Hydrogen, Fuel Cells & Infrastructure Technologies Program
2005 Annual Review
Washington, DC, May 23-27, 2005

Non-Precious Metal Catalysts

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Project ID
FC - 11

Project Objective & Focus

Objective:

Develop low-cost non-precious metal oxygen reduction reaction (ORR) catalyst for the polymer electrolyte fuel cell (PEFC) cathode with similar activity and performance durability to the currently used noble-metal based cathode catalysts.

Focus:

- ***Transition metal macrocycles (e.g. pyrolized TPP & TMPP chelates of Co & Co/Fe) – advanced phase; progress to date summarized in this presentation***
- ***Metal chalcogenides (e.g. Ru-based and Ru-free catalysts) – early phase, very promising initial results***
- ***Metal oxides (e.g. NiO, Co_2O_3, $NiCoO_2$, perovskitic LaSrCo oxides, CuMn oxides) – part of future research***

Funding & Milestones

Funding:

FY 2004 *(started January 29, 2004)*	***$118K***
FY 2005	***$350K***

Project reviewed for the first time

2004 & 2005 Milestones:

- ***Develop techniques for electrochemical characterization of non-precious metal catalysts under conditions relevant to fuel cell operation. – June 2004***
- ***Perform initial electrochemical/pH stability experiments on pyrolized macrocycle transition metal (PMTM) catalysts. – March 2005***
- ***Identify active reaction site(s) for oxygen reduction on pyrolized N_4-chelate electrocatalyst in polymer electrolyte fuel cell. – September 2005***

Selected Collaborations & Interactions (c)

- ***Transition Metal Macrocycles***

  University of New Mexico, Professor Plamen Atanassov *– synthesis and supply to LANL of Co, Co/Fe porphyrin catalysts for the presented research; half-cell performance screening; TEM catalyst characterization; more*

- ***Metal Chalcogenide Catalysts***

  Université de Poitiers, Professor Nicolas Alonso-Vante *– synthesis, initial electrochemical & non-electrochemical characterization of chalcogenide catalysts*

  University of Illinois, Professor Andrzej Wieckowski *– alternative method of catalyst synthesis, half-cell performance screening*

- ***Non-Precious Metal Catalysts for Portable Systems***

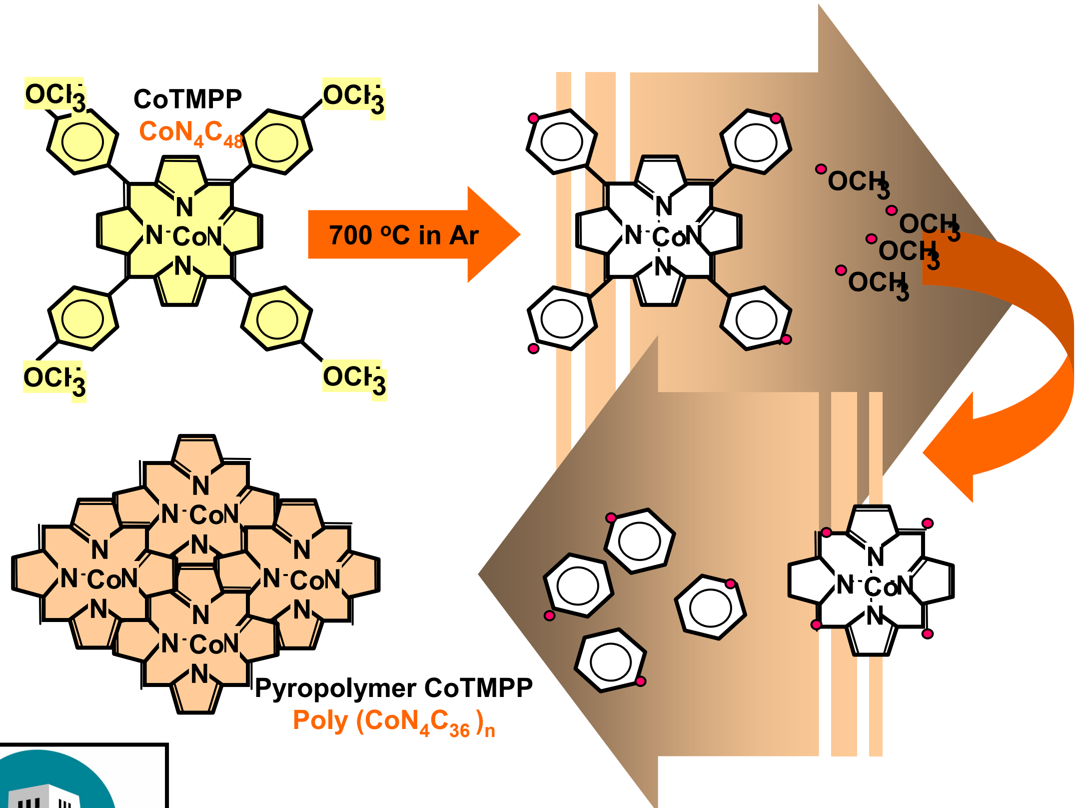
  Mesoscopic Devices, Inc., Valerie Hovland *– catalysts, membranes, MEAs, and feed schemes for mixed-reactant fuel cells*

- ***Activated Polyoxometalates***

  OSRAM SYLVANIA, Joel Christian *– PEFC activity evaluation by LANL*

Pyrolysis of Metal Porphyrins

A Major Chemical Transformation



***(1)* Heat treatment: 18 min - 5 hours: 300°C - 1000°C, inert gas.**

***(2)* Increased ability of the products to decompose peroxide.**

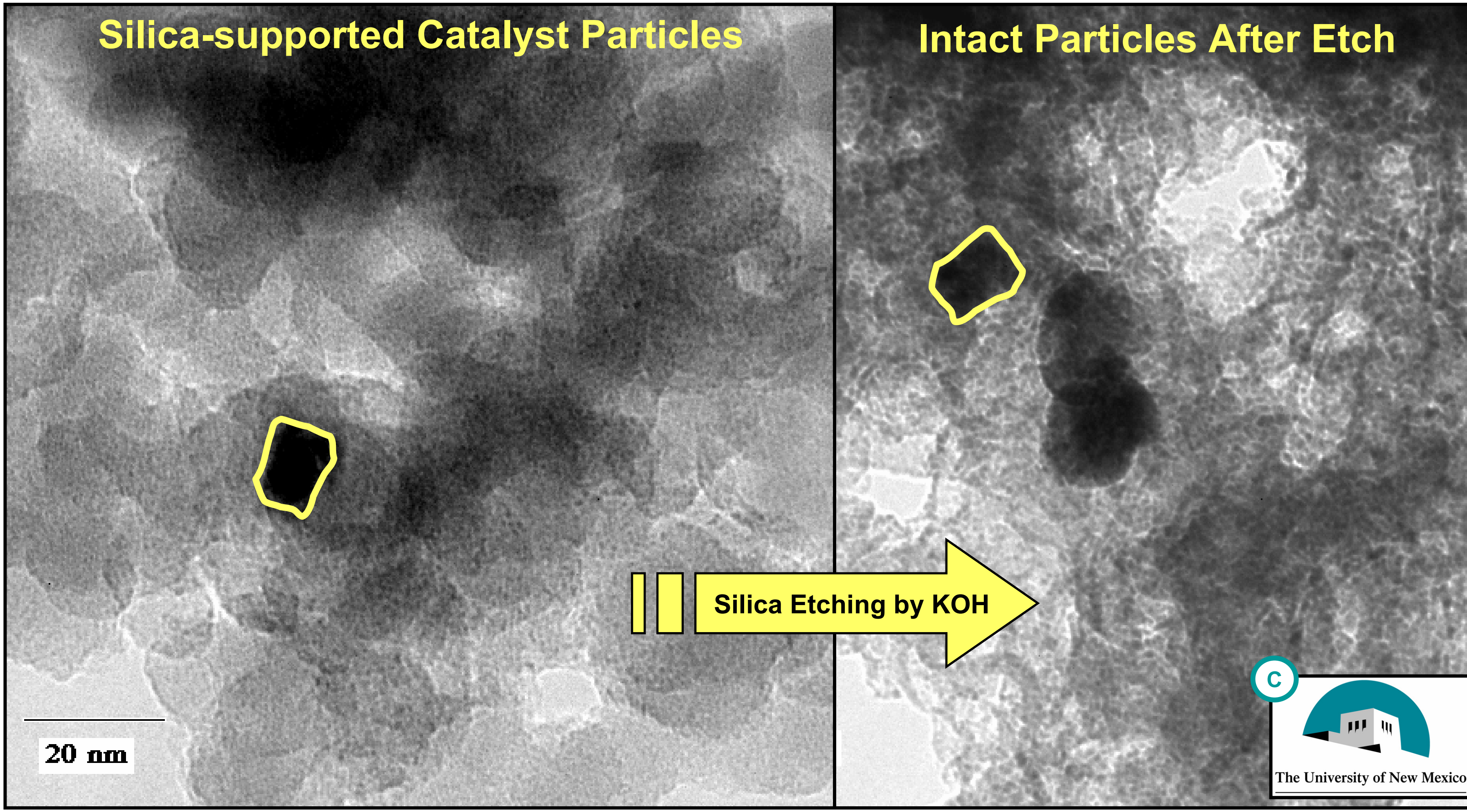
***(3)* Effective peroxide reduction → (i) protection of the catalyst against degradation, (ii) shift in the ORR mechanism towards the $4e^-$ pathway.**

***(4)* Degradation of the original structure and formation of highly condensed phases at high temperatures (T > 400°C).**

***Pyrolysis products:* *(i)* unchanged macrocycle, *(ii)* polymers with different degree of polymerization, *(iii)* smaller compounds of N_4 structure, *(iv)* products consisting of C, N, and metal atoms, *(v)* metal oxides, *(vi)* metal carbides, and *(vii)* metal phases.**

High-Resolution Transmission Electron Microscopy

Key Role of Silica



Well-dispersed, porous and "self-supported" pyropolymer left after KOH etch

Experimental

Cathode, Anode, Fuel Cell Testing

- **Catalyst synthesis** (University of New Mexico)
  - *Silica-supported CoTPP, CoTMPP, Co/Fe(1:1)TPP* [*)]
  - *Pyrolysis at 600 – 700°C in inert gas atmosphere*
  - *Silica support etched in KOH*
- **Membrane-electrode assembly** (5 cm^2)

Cathode:	*2 mg cm^{-2}; pyrolized-porphyrin catalyst mixed with carbon black and recast Nafion®*
Anode:	*6 mg cm^{-2} Pt black*
Membrane:	*Nafion® 117*

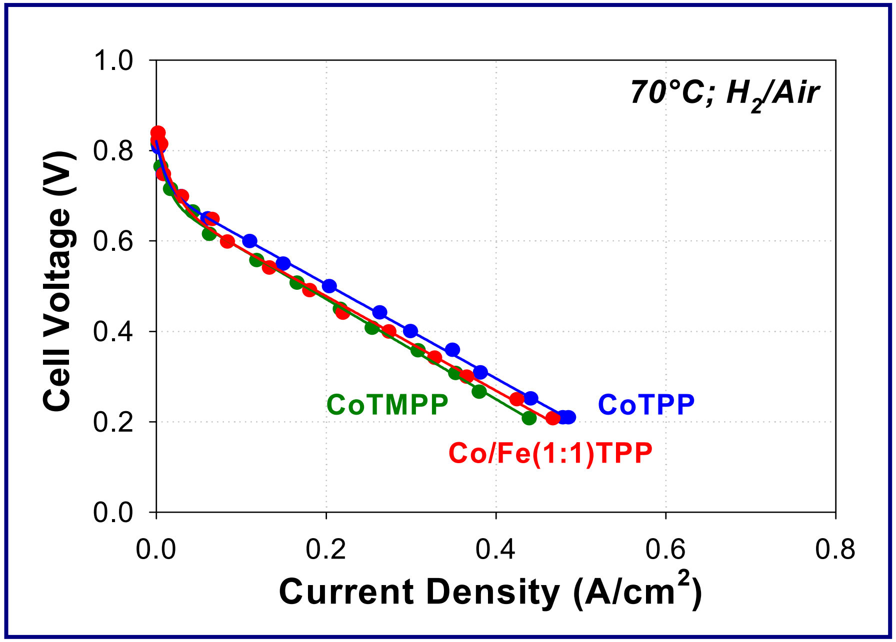
- **Fuel-cell test conditions**

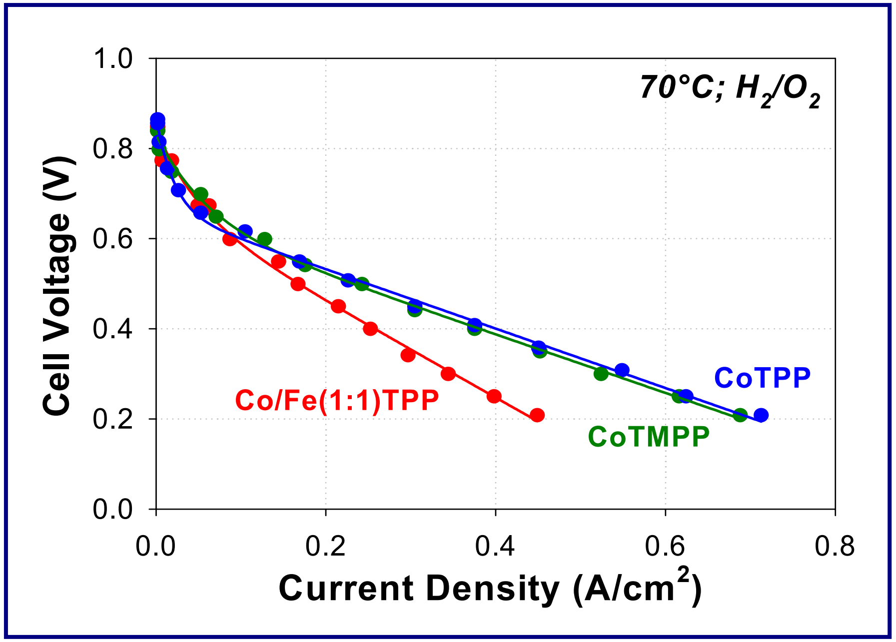
Cathode:	*Air or oxygen, 30-psig or 0-psig backpressure*
Anode:	*H_2, 30-psig or 0-psig backpressure*
Cell temperature:	*30°C, 50°C, 70°C, and 80°C*

[*)] *TPP = tetraphenyl porphyrin; TMPP = tetramethoxyphenyl porphyrin*

Performance at a Glance

Remarkable Oxygen Reduction Activity





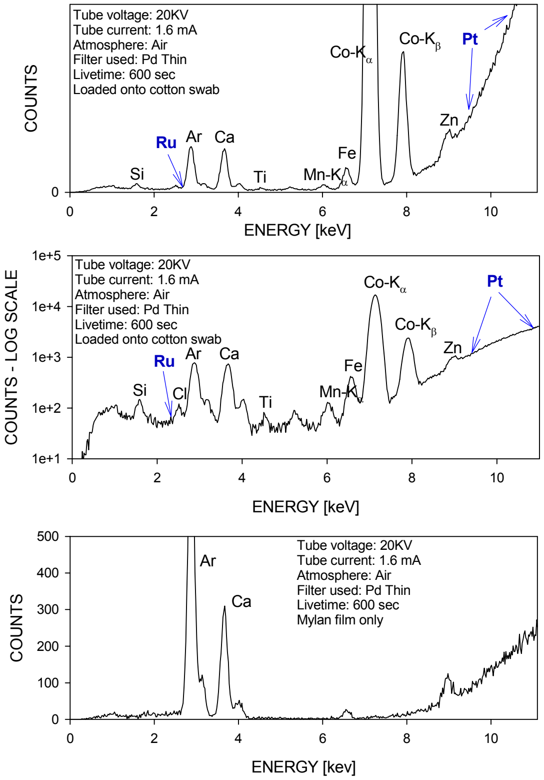
- ***HIGHLIGHT:* Demonstrated high catalytic activity of three metalloporphyrins in H_2-air and H_2-O_2 fuel cells**
- ***Similar performance observed with all catalysts when cathode operated on air***
- ***Diminished performance of Co/Fe(1:1)TPP when exposed to oxygen at high temperature – possible oxidative loss of Fe***

X-Ray Fluorescence (XRF)

No Traces of Noble Metals Detected

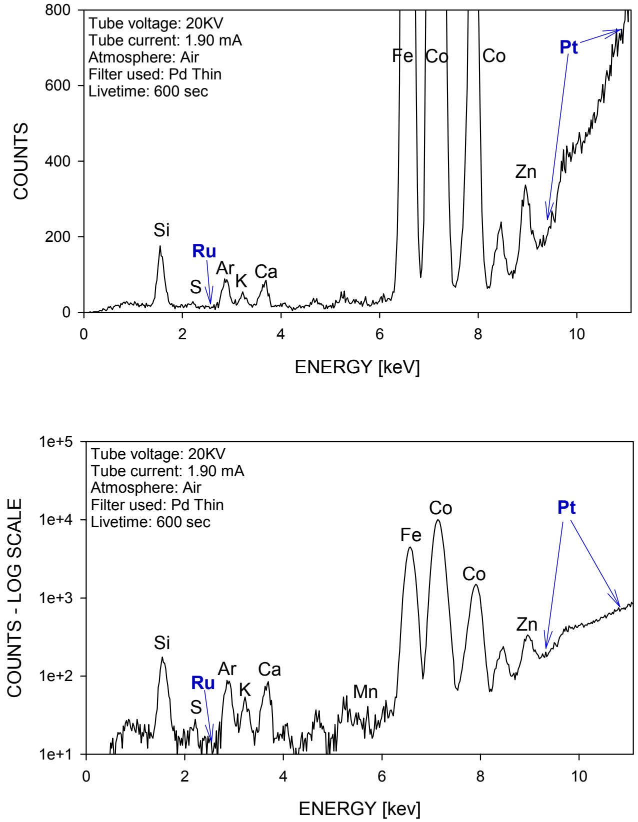
Co Tetra-Phenyl Porphyrin
XRF Spectra

Element	Concentration	Error
Co	85.0%	3.5
Fe	3.4%	1.2
Zn	7.5%	2.9
Mn	0.0%	0.0
Ti	4.0%	1.5



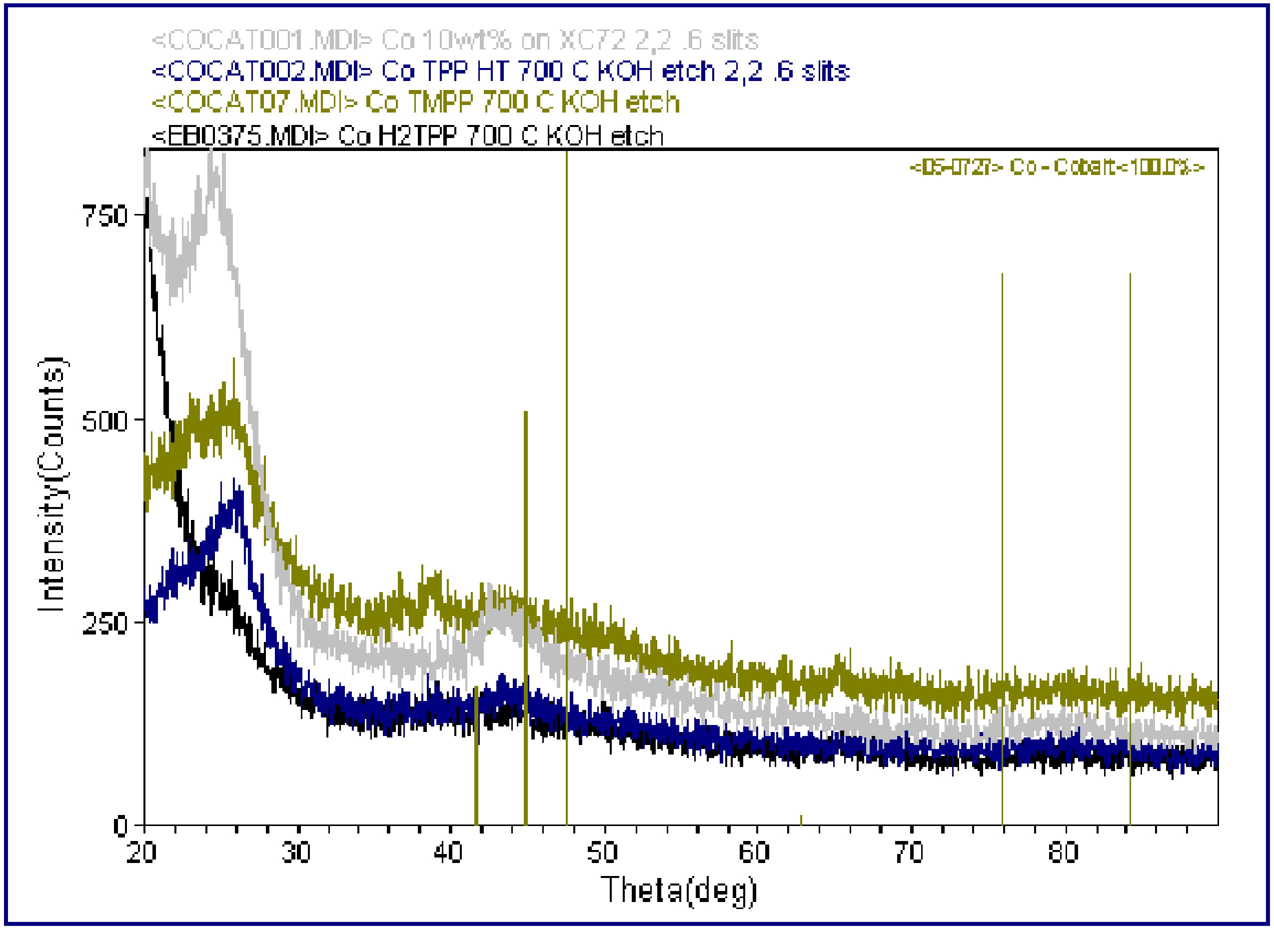
Co/Fe (1:1) tetra-phenyl porphyrin
XRF Spectra

Element	Concentration	Error
Co	50.0%	0.2
Fe	50.0%	0.3



No traces of Pt and Ru in CoTPP and Co/Fe(1:1)TPP catalysts

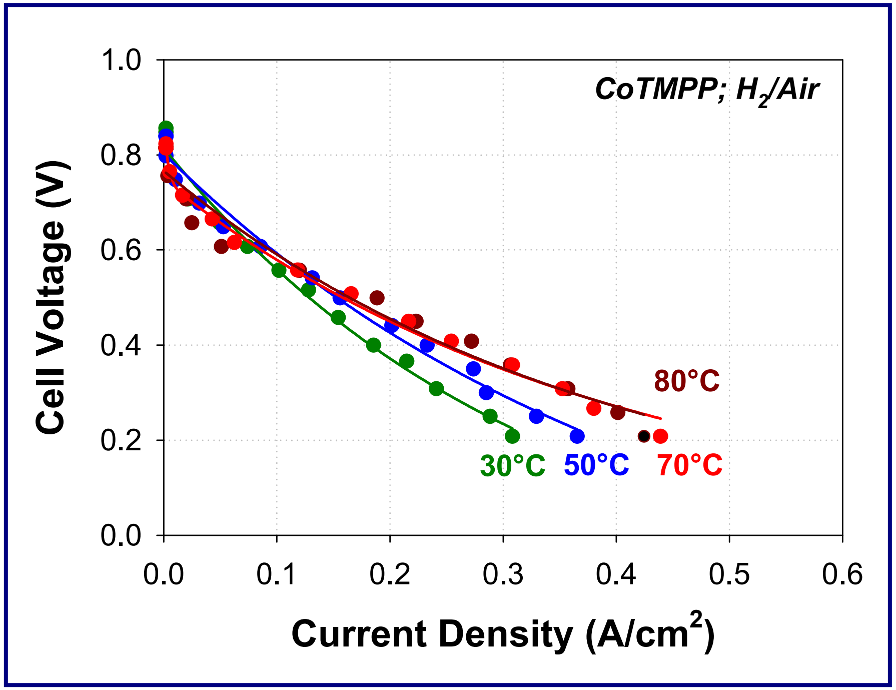
X-Ray Diffraction (XRD)
Is Metallic Co a Factor?

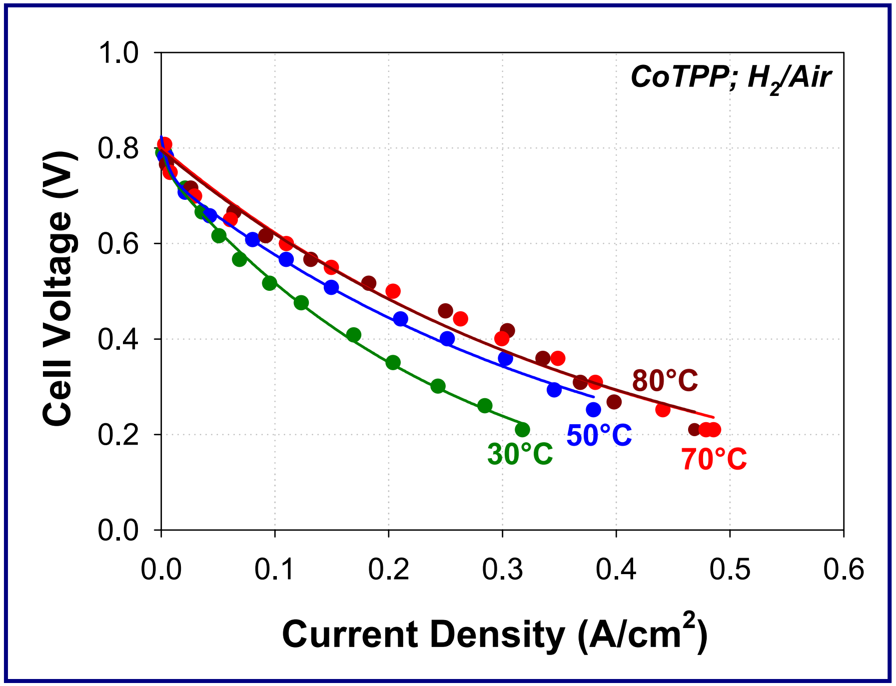


***HIGHLIGHT:* Crystalline metallic Co absent in all cobalt-based catalysts – Co not a factor in ORR catalysis**

Catalyst Activity

Does the Porphyrin Type Matter?

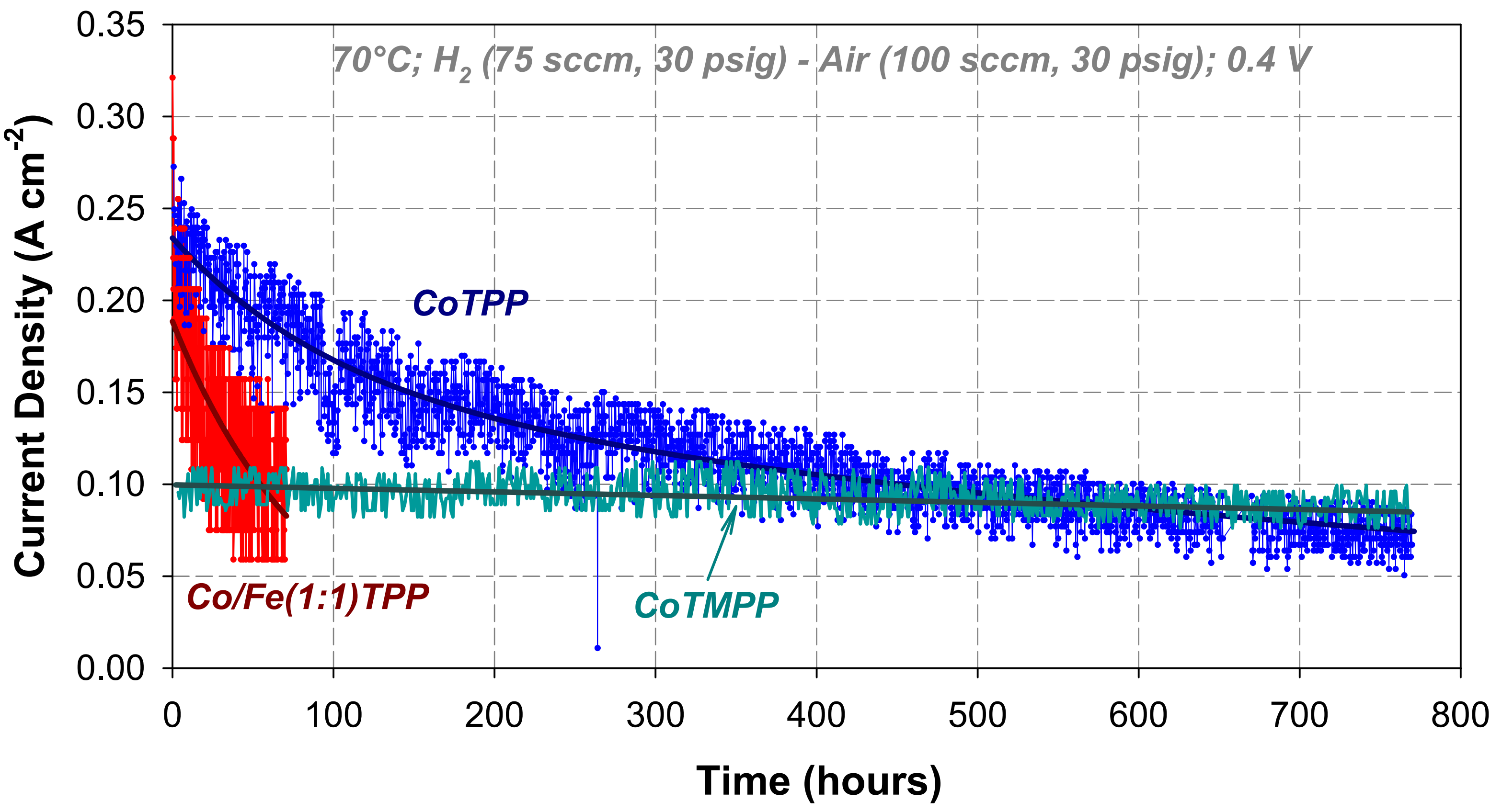




- ***Similar activity of CoTTP and CoTMPP cathodes at lower temperatures***
- ***Slight initial performance advantage of CoTPP catalyst at higher temperatures***
- ***Cathode structure may need further optimization***

Durability

Initial Performance vs. Performance Stability

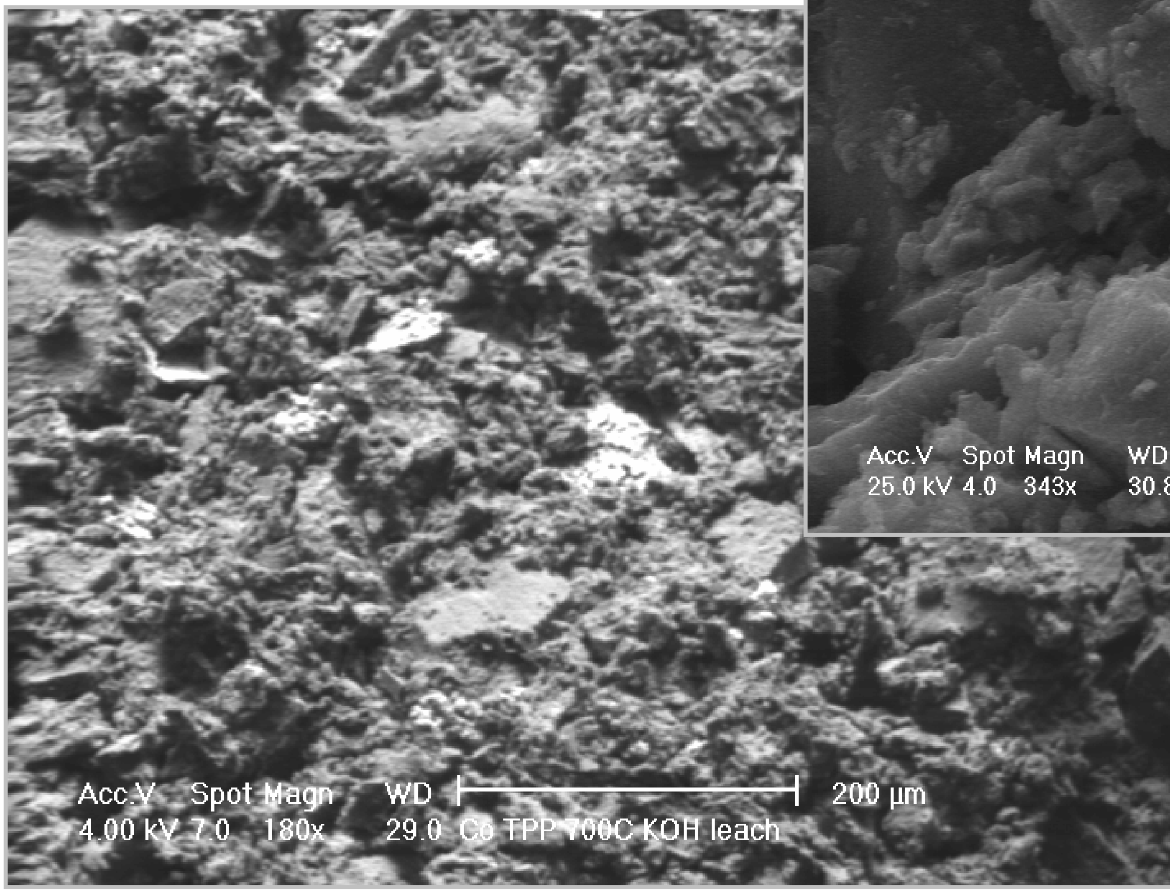


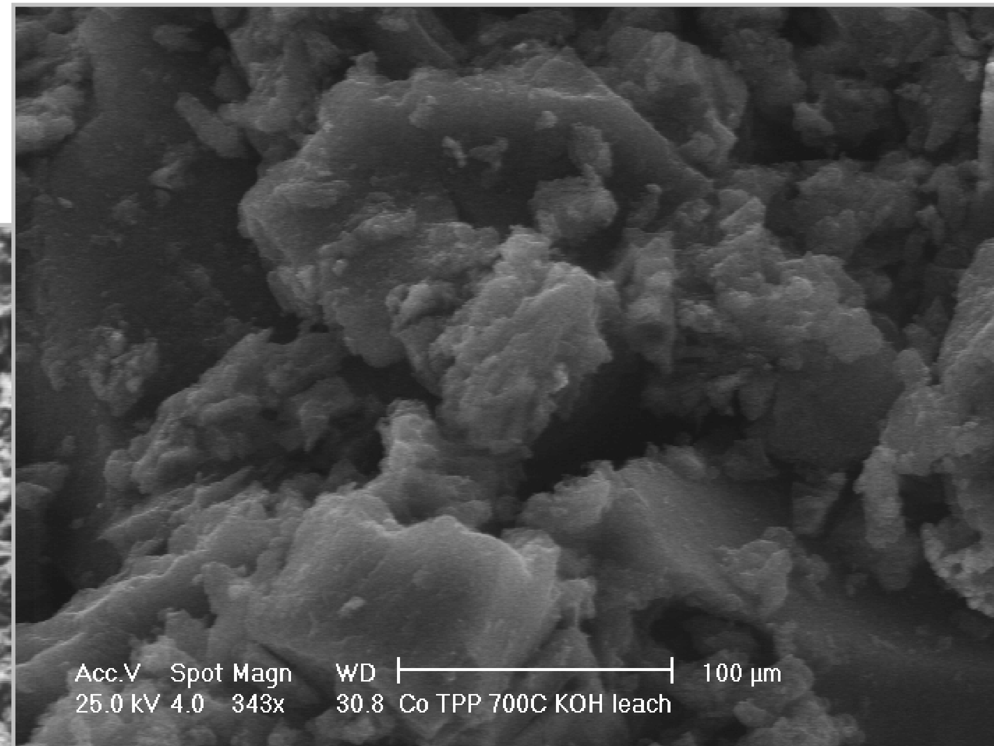
- ***CoTPP – the highest initial performance***
- ***CoTMPP – the best long-term performance stability***

Active Reaction Site

Scanning Electron Microscopy (SEM)

SEM images of CoTPP catalyst at 180× and 343 × magnifications

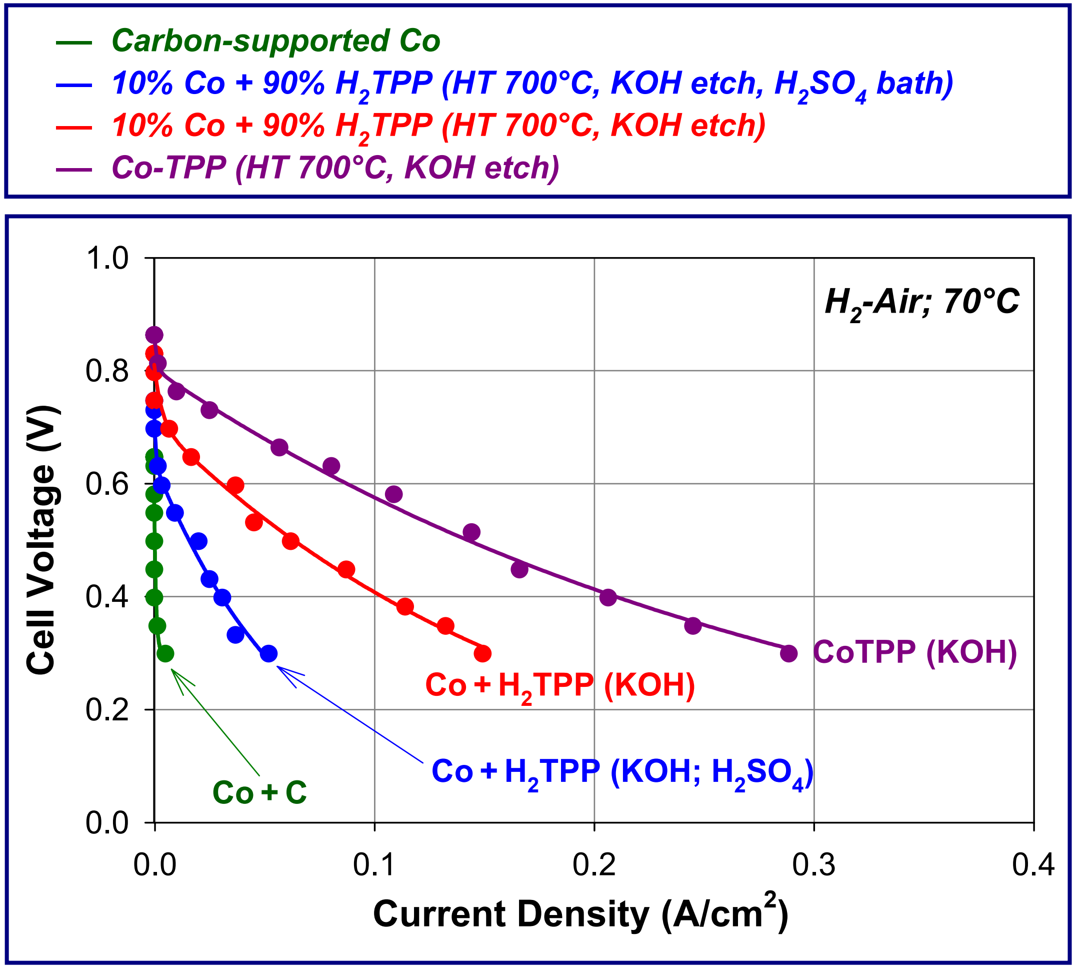




Highly non-homogeneous catalyst morphology

Active Reation Site

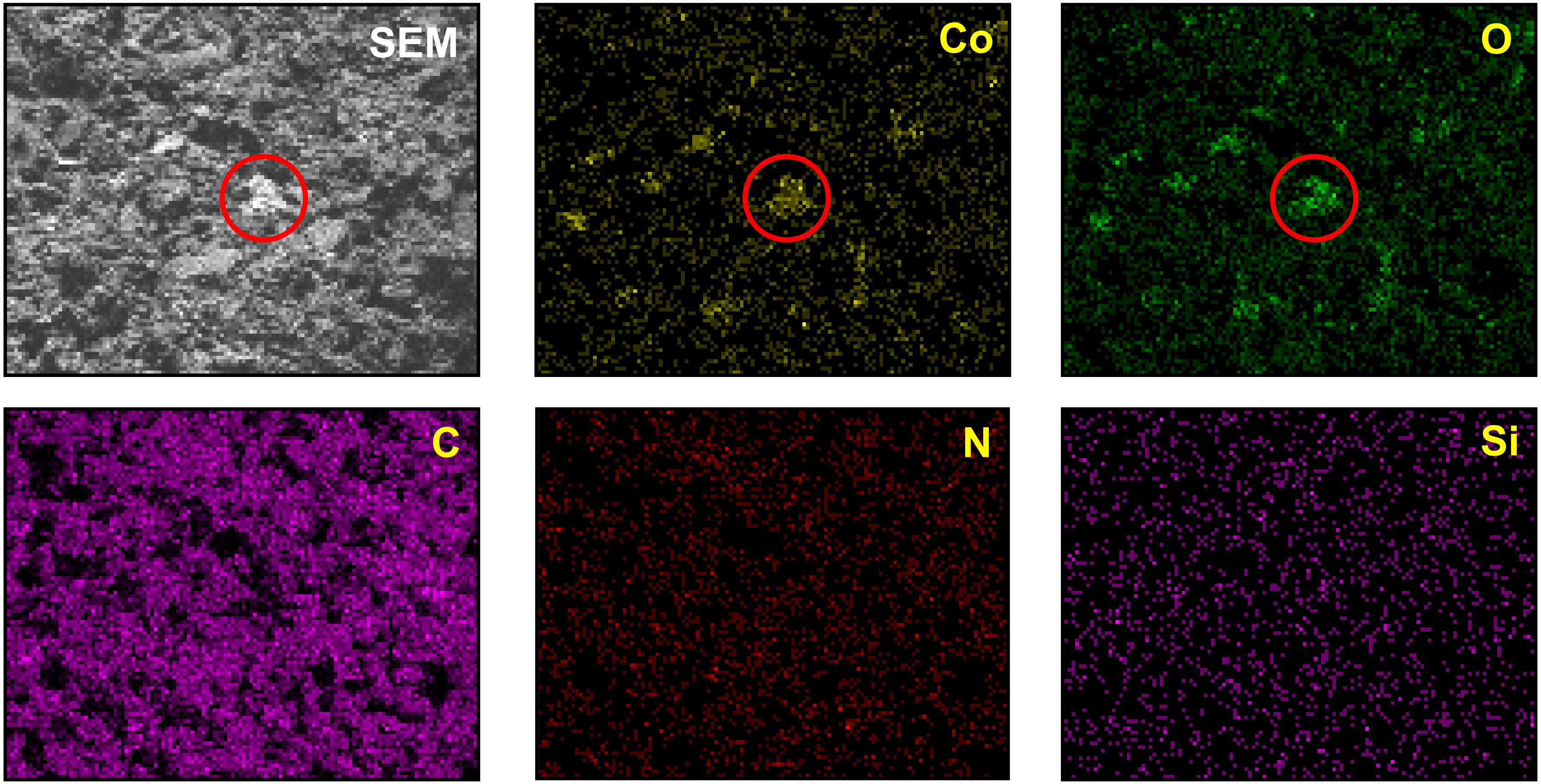
Source of Catalytic Activity



***HIGHLIGHT:* Cobalt species, not N_4-sites, appear to play major role in oxygen reduction at the CoTPP electrocatalysts**

Active Reaction Site

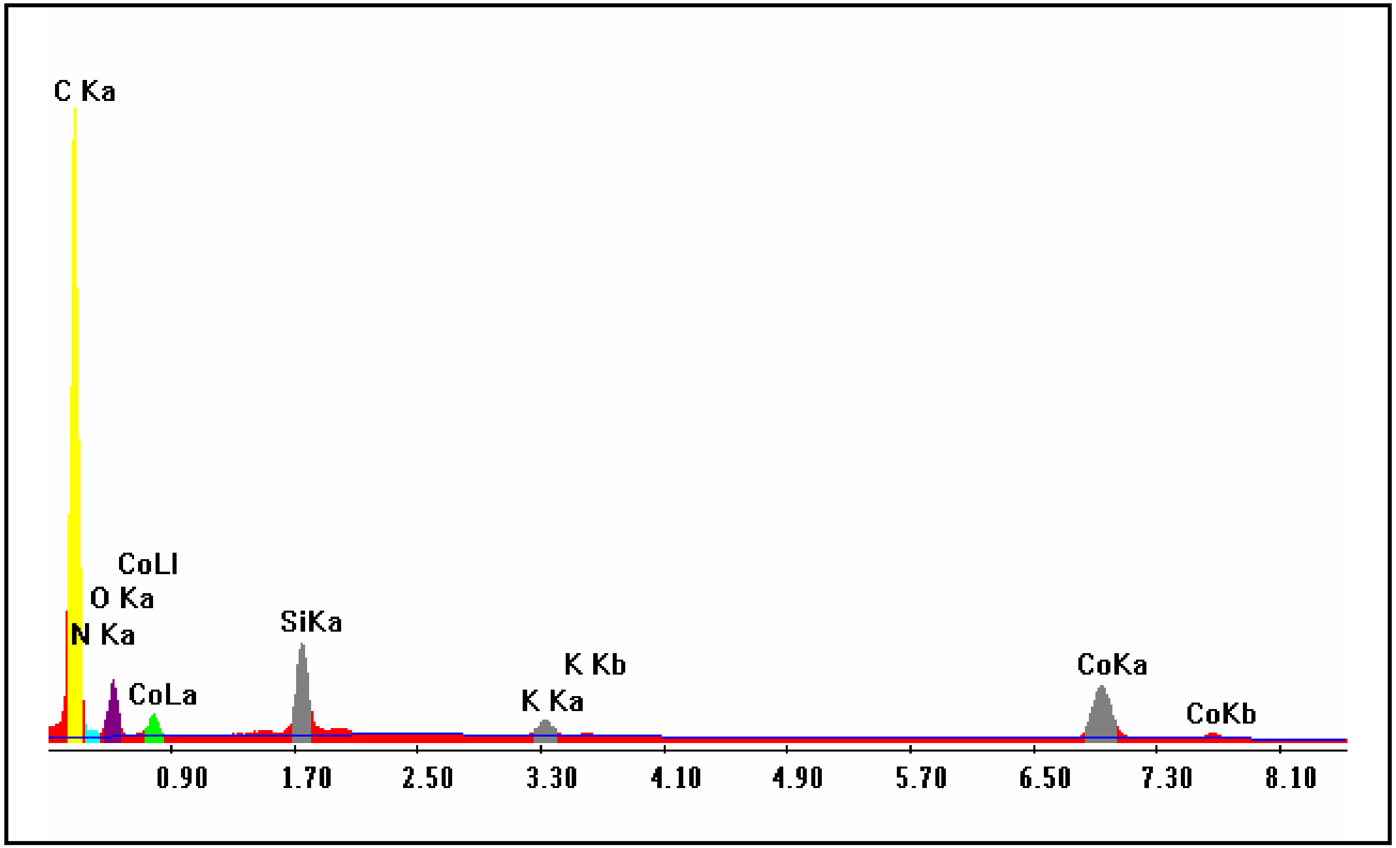
EDX Mapping of CoTPP Catalyst



- ***HIGHLIGHT:* Excellent correlation in the distribution of cobalt and oxygen**
- ***Nitrogen distributed uniformly, not correlated with cobalt or oxygen***
- ***Silicon (from remaining silica) and potassium (from KOH) uniformly distributed***

Active Reaction Site

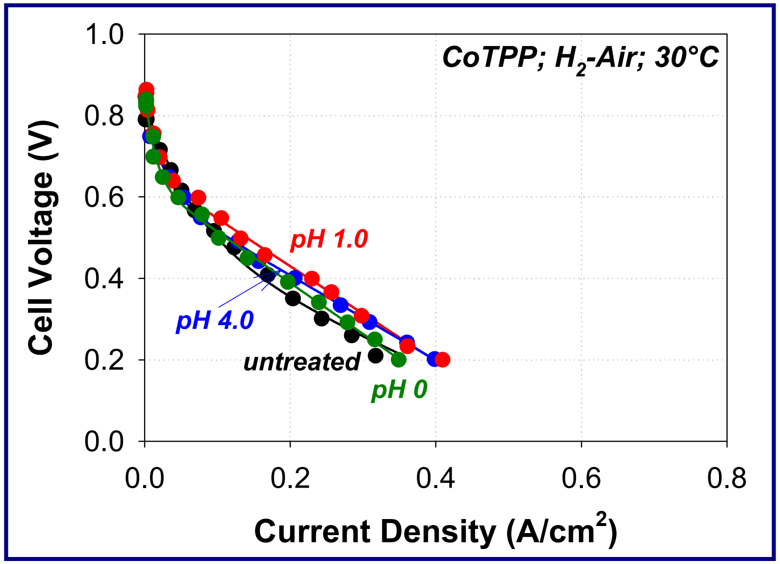
EDX Spectrum of CoTPP Catalyst

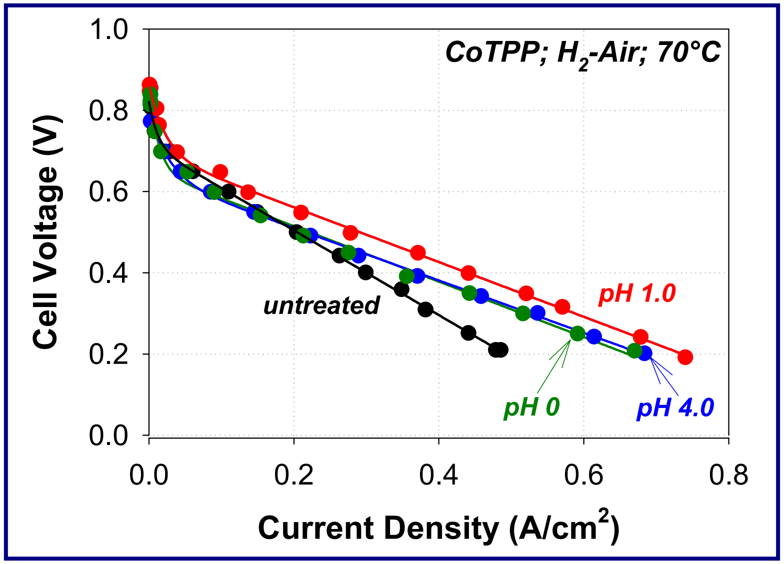


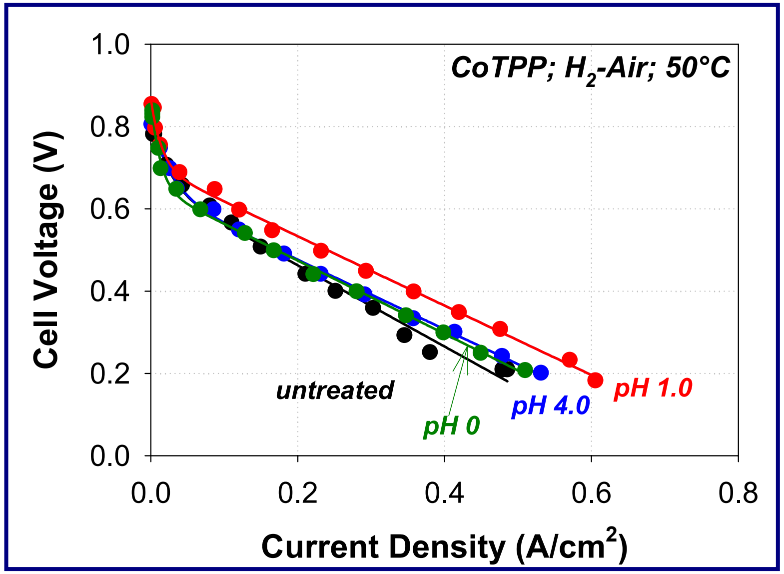
- ***HIGHLIGHT:* Very little nitrogen relative to cobalt**
- ***Noticeable presence of silicon and potassium***
- ***Potential for further catalyst performance improvement via removal of Si and K***

Effect of pH

Dilute Acid Post-Treatment of Catalyst Powders

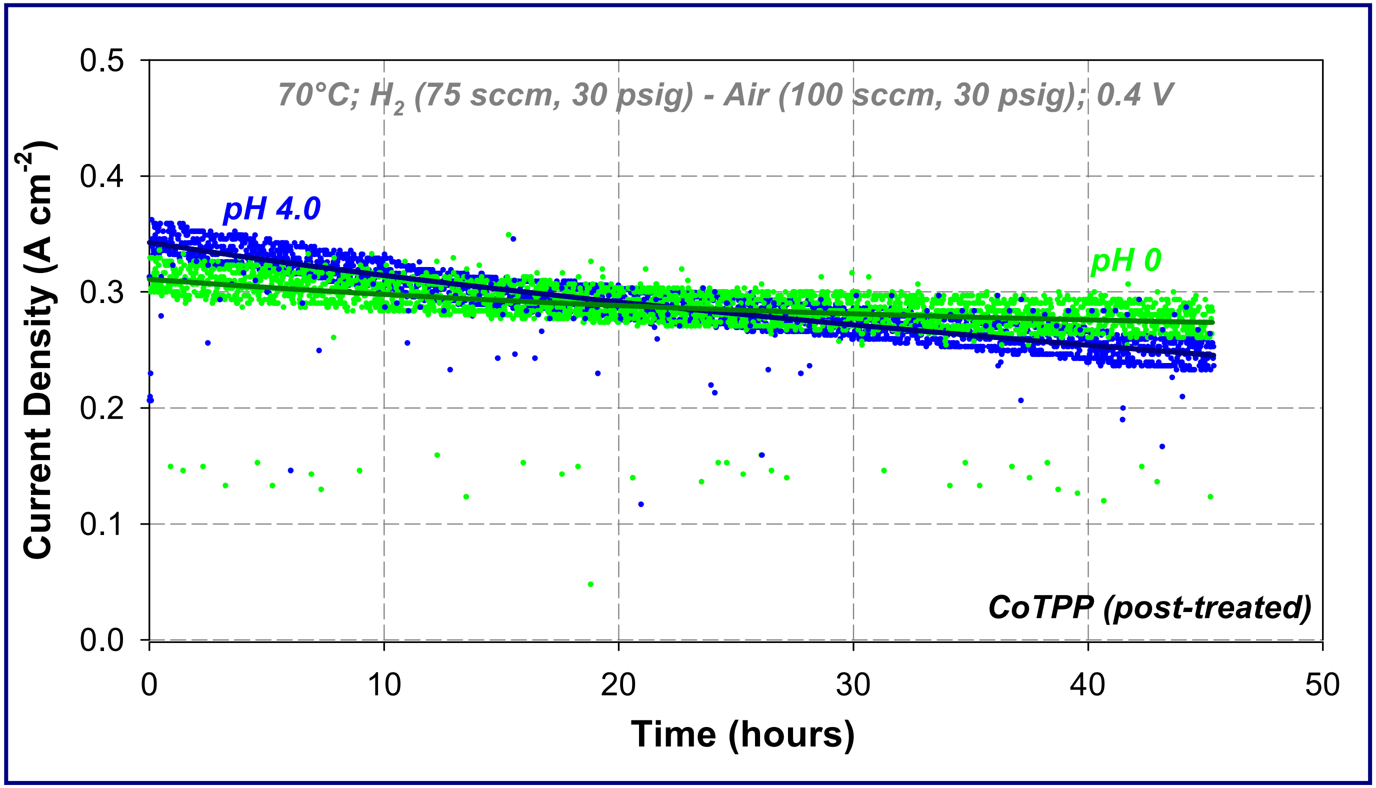






- ***HIGHLIGHT:* *Post-treatment with dilute acid – a promising method of enhancing catalyst activity***
- ***pH 1.0 treatment leading to the highest increase in catalytic activity, up to 100 mV at 50-70°C***
- ***Improved air access due to the removal of inactive species – a likely reason for improved catalyst performance***

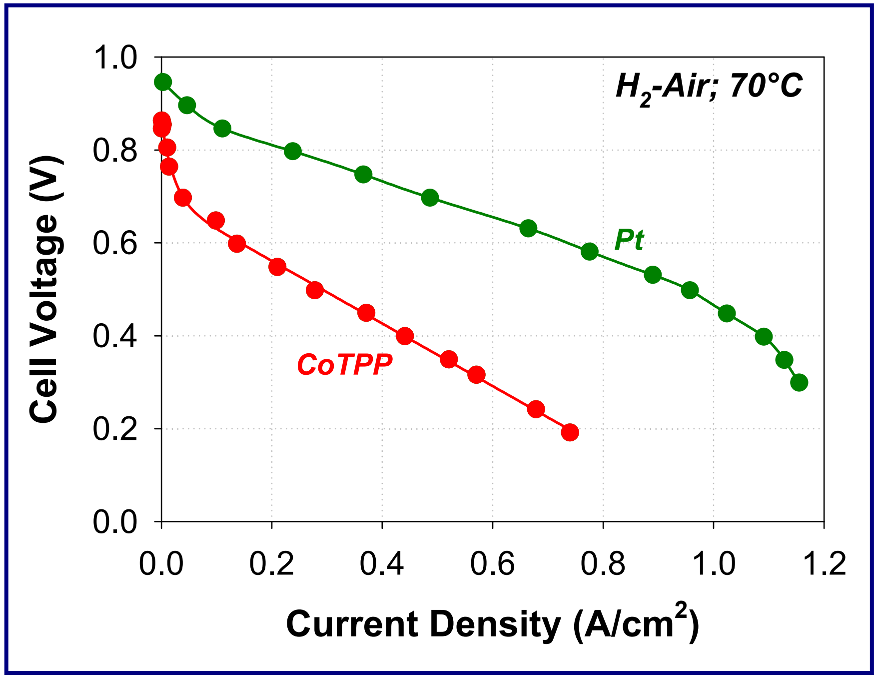
Effect of pH
Performance Stability

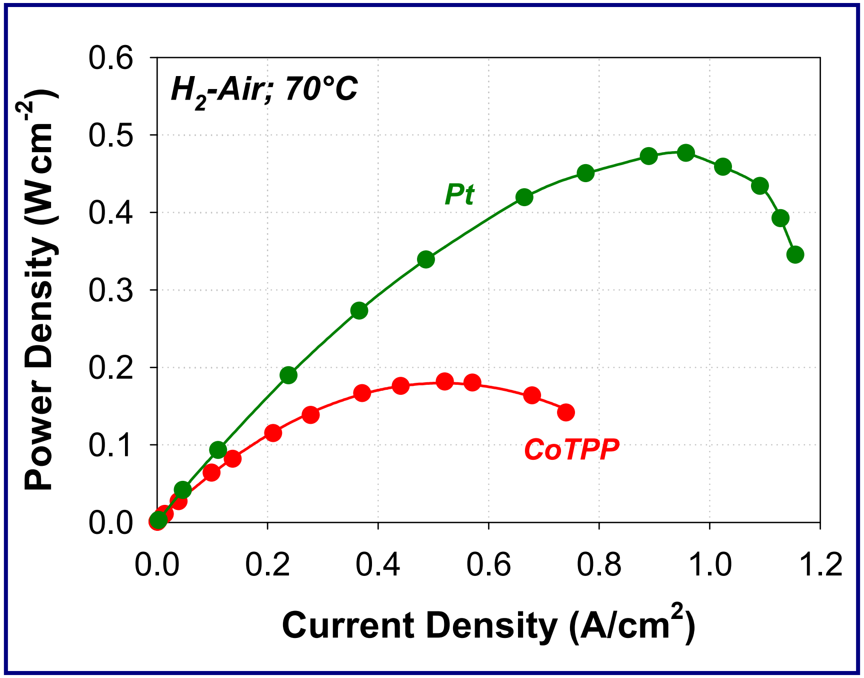


- ***HIGHLIGHT:*** ***pH treatment leading to significant gains in both short- and long-term performance of CoTPP catalyst***
- ***CoTPP treated at pH 4.0 – good initial performer***
  CoTPP treated at pH 0 – the most stable catalyst

Co-TPP vs. Pt at the Fuel Cell Cathode

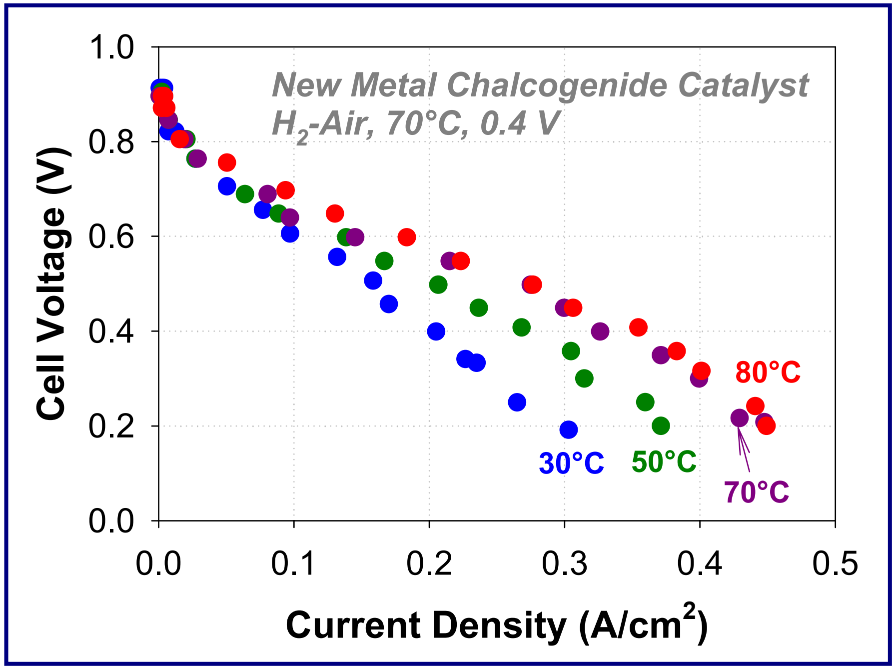
Performance Comparison

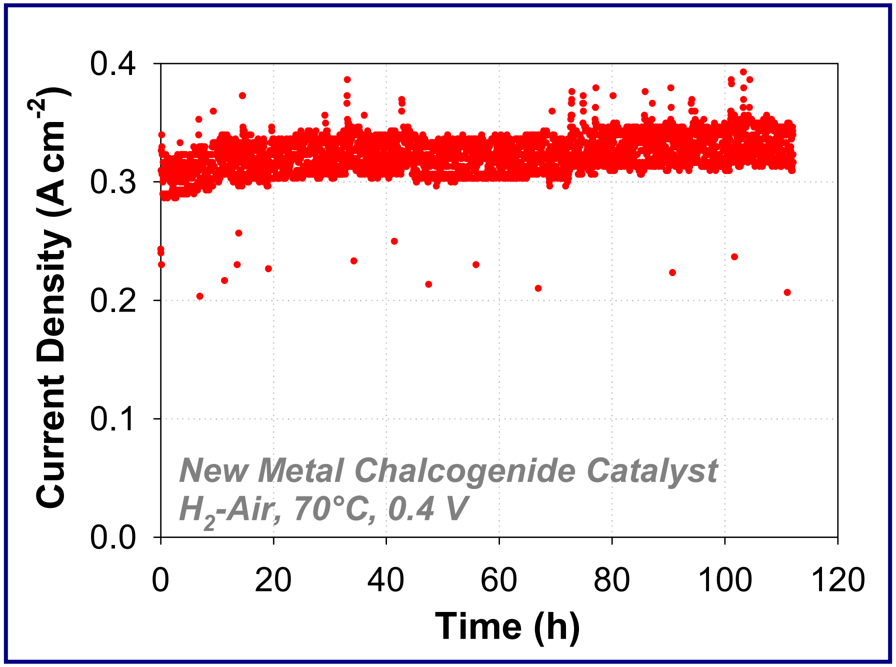




- ***HIGHLIGHT:** H_2-air cell operated with a post-treated CoTPP cathode capable of delivering up to **0.180 W cm^{-2}**, ca. 1/3 of the cell with a Pt cathode at the same loading (2 mg cm^{-2})*
- ***In addition to further improvements in the activity and stability of metalloporphyrin catalysts, an increase in operating potential, by as much as 100 mV, is needed for better efficiency***

The Latest
Metal Chalcogenides

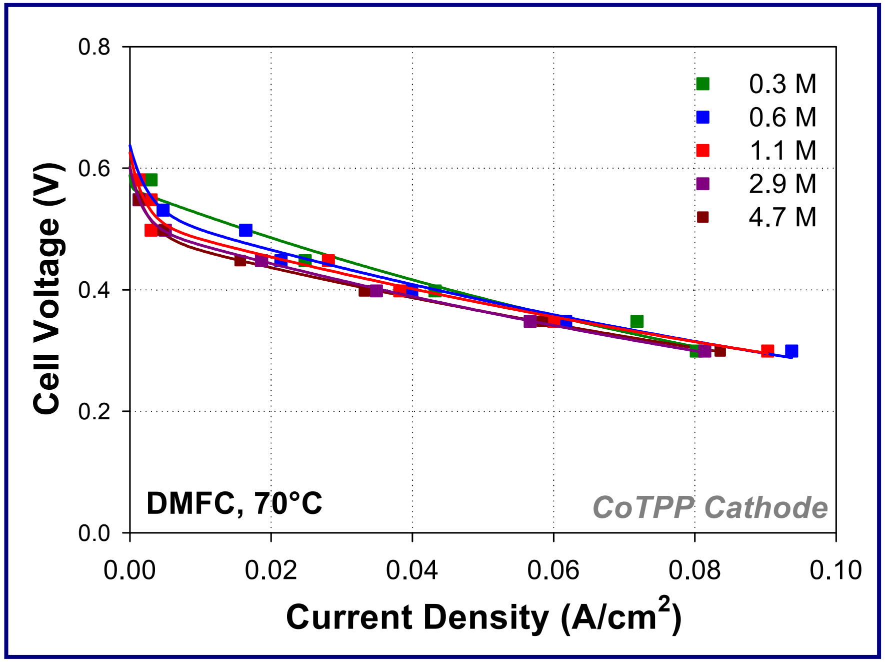


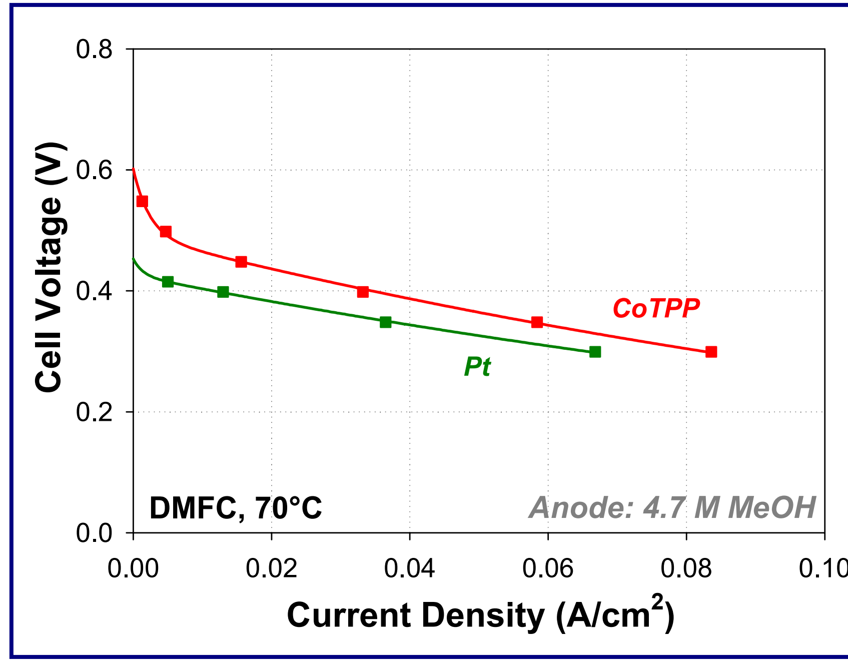


***HIGHLIGHT:* New chalcogenide catalyst exceeding the performance of best post-treated metalloporphyrins <u>without any performance drop</u> over the first 110 hours!**

(c) Collaboration with Université de Poitiers and University of Illinois

Additional Benefit
Crossover Methanol Tolerance





- ***HIGHLIGHT:* Very good methanol tolerance of CoTPP cathode catalyst in cells with up to ~ 5 M methanol concentration in the anode feed stream**
- ***Non-precious metal catalyst outperforming Pt black catalyst (2 mg cm^2 loading) in cells with high MeOH anode concentration***
- ***HIGHLIGHT:* New metal chalcogenide catalyst found tolerant up to 17 M methanol**

Progress Towards Milestones

- *Develop techniques for electrochemical characterization of non-precious metal catalysts under conditions relevant to fuel cell operation (June 2004).*

  Milestone fully achieved – Implemented electrochemical techniques: (i) fuel cell testing: hydrogen-air, DMFC; (ii) rotating disk electrode (RDE) & rotating ring-disk electrode (RRDE); (iii) ultramicroelectrodes.

- *Perform initial electrochemical/pH stability experiments on pyrolized macrocycle transition metal (PMTM) catalysts (March 2005).*

  Milestone achieved & exceeded – Performance stability determined with three different metalloporphyrin catalysts; effect of acidity on initial and long-term performance of catalysts studied at three pH values used in "post-treatment".

- *Identify active reaction site(s) for oxygen reduction on pyrolized N_4-chelate electrocatalyst in polymer electrolyte fuel cell (September 2005).*

  Milestone on schedule – Results obtained to date make N_4-site questionable as the active reduction center; good correlation between cobalt and oxygen distribution points to major role of cobalt oxides (hydroxides).

Research Plans

Remainder of FY 2005

- *Identify and characterize the active site (or sites) for oxygen reduction reaction (ORR) at the metalloporphyrin surface.*

FY 2006 Objectives

- *Determine distribution of active ORR sites on the surface of metalloporphyrins as a function of (i) catalyst type, (ii) fabrication technique and conditions, (iii) catalyst "post-treatment" (including in-depth determination of the effect of solution pH).*
- *Investigate structures potentially leading to the protection of active ORR site(s) in acidic media and thus improved activity and durability of metalloporphyrin catalysts.*
- *Lower high-frequency resistance of membrane-electrode assemblies with non-precious metal cathode catalysts.*
- *Perform performance study of metal chalcogenides as very promising alternatives to metalloporphyrins.*

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Conference Presentations

1. 205th Meeting of the Electrochemical Society, San Antonio, Texas, May 9 – 13, 2004. Title: "Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells: Fuel Cell Evaluation of Oxygen Reduction Catalyst" S. Levendosky, P. Atanassov, J. Davey and P. Zelenay.

2. 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, October 3 – 8, 2004. Title: "Non-Platinum Electrocatalysts for Polymer Electrolyte Fuel Cells: Methanol-Tolerant Cathode Catalyst," S. Levendosky, P. Atanassov, B. Piela and P. Zelenay.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Leak in the hydrogen supply resulting in accumulation of the gas in the room, which could then lead to explosion upon ignition.

Hydrogen Safety

Our approach to dealing with this hazard is as follows:

- ***Hydrogen sensors, interlocked with the hydrogen gas supply, have been installed in the laboratories with hydrogen supply from gas cylinders or from a hydrogen generator.***
- ***Hydrogen sensors have been installed at just below the ceiling where gas accumulation is most severe; also, two sensors are installed in every room for redundancy; the alarm is set off at 10% of Lower Flammability Limit (LFL).***
- ***In laboratories that use bottled hydrogen, only a single cylinder is used at any given time; the cylinder size is limited to ensure that the LFL is not exceeded even upon complete release of a full cylinder.***
- ***All work has been reviewed and approved through Los Alamos National Laboratory's safety programs:***
  - ***Hazard Control Plan (HCP) - hazard based safety review***
  - ***Integrated Work Document (IWD) - task based safety review***
  - ***Integrated Safety Management (ISM)***