Novel Non-Precious Metals for PEMFC: Catalyst Selection Through Molecular Modeling and Durability Studies

2004 DOE Hydrogen, Fuel Cells Infrastructure Technologies Program Review

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Project Objectives

- Synthesize novel non-precious metal electrocatalysts with similar activity and stability as Pt for oxygen reduction reaction.
  - High activity toward oxygen reduction reaction.
  - Mass production method.
  - Corrosion resistance.
  - Low cost.
- Improve understanding of reaction mechanism of oxygen reduction on non-precious catalysts through
  - Theoretical molecular modeling.
  - Electrochemical characterization.
  - Structural studies (XPS, EXAFS, XANES).
  - Correlation between the catalyst composition, heat treatment and catalytic sites for oxygen reduction.
- Demonstrate the potential of the novel non-precious electrocatalysts to substitute Pt catalysts currently used in MEA.

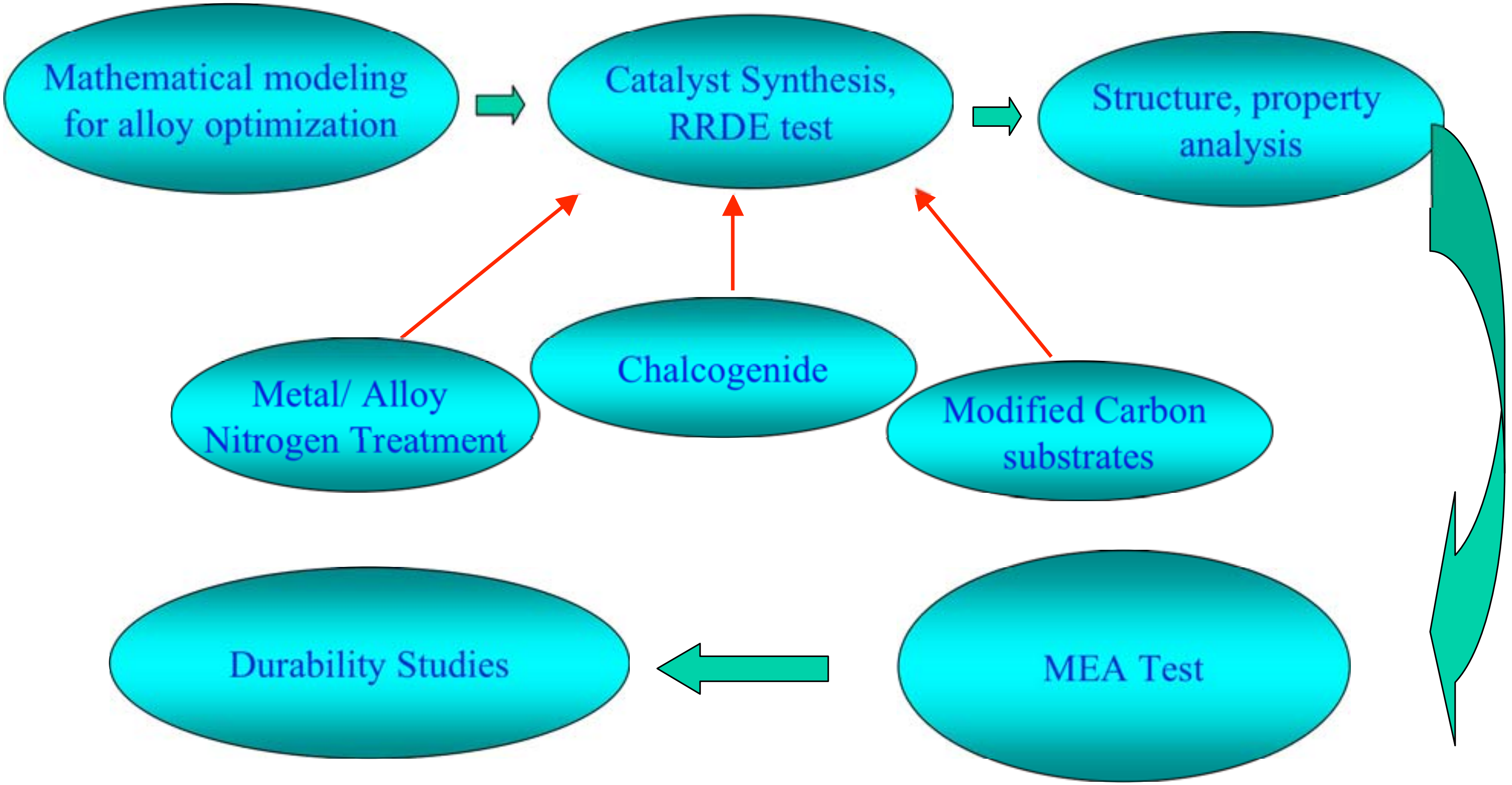
Project Budget

University of South Carolina	Case Western Reserve Univ.	Northeastern University	Cumulative Year 1
Direct $118,697	Direct $65,645	Direct $32,043	Direct $216,385
Indirect $71,298	Indirect $18,892	Indirect $18,425	Indirect $108,615
Total $189,995	Total $84,537	Total $50,468	Total $325,000

Technical Barriers and Targets

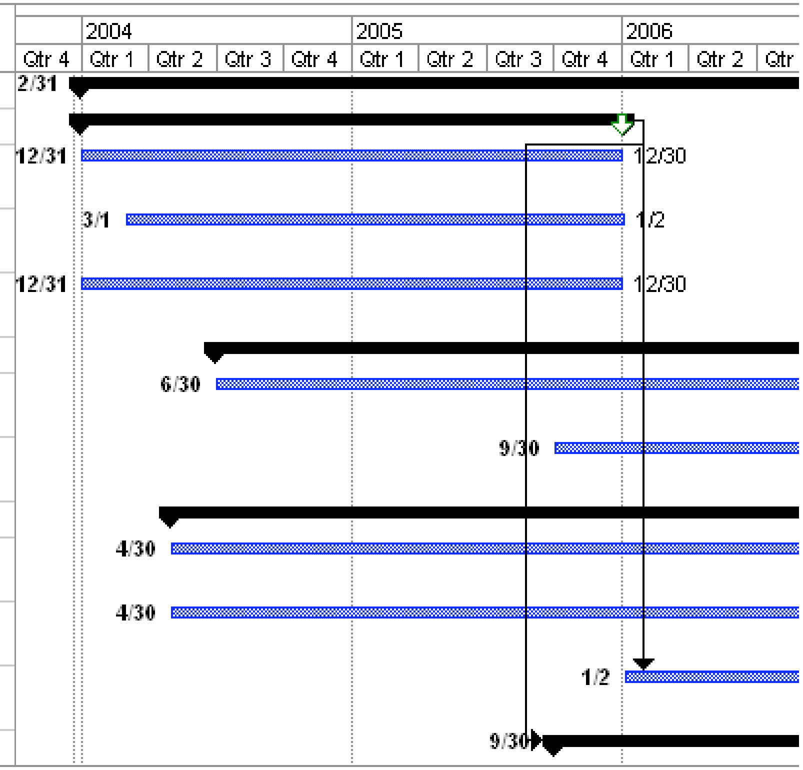
- Electrode performance
  - ✓ Perform at least as good as the conventional Pt catalysts currently in use in MEAs
- Durability
  - ✓ 2000 hours operation with less than 10% power degradation
- Material Cost
  - ✓ cost at least 50% less as compared to a target of 0.2 g (Pt loading)/peak kW

Catalyst Development



Project Timeline

ID	Task Name	Duration	Start	Finish
1	**1 Molecular Modeling of Novel Catalysts**	**32.68 mo**	**Dec 31 '03**	**Sep 30 '06**
2	**2 Synthesis of Novel Catalysts**	**23.77 mo**	**Dec 31 '03**	**Jan 2 '06**
3	2.1 Synthesis of Co or Ni Binary, Ternary and Quarternary metallic nanoclusters	23.77 mo	Dec 31 '03	Dec 30 '05
4	2.2 Synthesis of Binary and Ternary Transition Metal Modified Macrocycles	21.82 mo	Mar 1 '04	Jan 2 '06
5	2.3 Synthesis of non-precious Mn Cu Chalcogen compounds and Co ni Dichalcogenides	23.77 mo	Dec 31 '03	Dec 30 '05
6	**3 Material Characterization of the Catalyst**	**26.77 mo**	**Jun 30 '04**	**Oct 2 '06**
7	3.1 Structure property relationships of Novel Catalysts	26.77 mo	Jun 30 '04	Sep 30 '06
8	3.2 Crystallinity, Grain Structure, Particle size and Surface area of Catalyst	11.91 mo	Sep 30 '05	Oct 2 '06
9	**4 Electrochemical Characterization of the Catalyst**	**28.73 mo**	**Apr 30 '04**	**Oct 2 '06**
10	4.1 Oxygen Reduction Kinetic studies using RDE	28.73 mo	Apr 30 '04	Oct 2 '06
11	4.2 Electrochemical Characterization of Thin Film membrane assemblies	28.73 mo	Apr 30 '04	Oct 2 '06
12	4.3 Optimization Studies	8.9 mo	Jan 2 '06	Sep 30 '06
13	**5 Alloy Optimization through Durability Studies**	**11.91 mo**	**Sep 30 '05**	**Oct 2 '06**



Task Summary and Duration

Subtask Duration

End date for task

Task Milestone

Project links

Project Safety

- All reactors are operated in a vented area
- Hydrogen detector is placed near the hydrogen source
- Reactors using high concentrations of hydrogen have additionally installed a burning flame to eliminate exhausting gas
- All the reactors have being design using leak-proof joints
- Ambient atmosphere pressures are used at all times in the reaction vessels and fuel cell stations
- Only personnel trained in how to operate the reactors and emergency procedures is allowed to use the reactor set-up
  - At least one person trained must present during runs in case of an emergency shutdown

Safety Equipment

Furnace for Hydrogen Treatment
at High Temperature
and Safety Equipment

PEM Fuel Cell Dual Station
with a Hydrogen Sensor

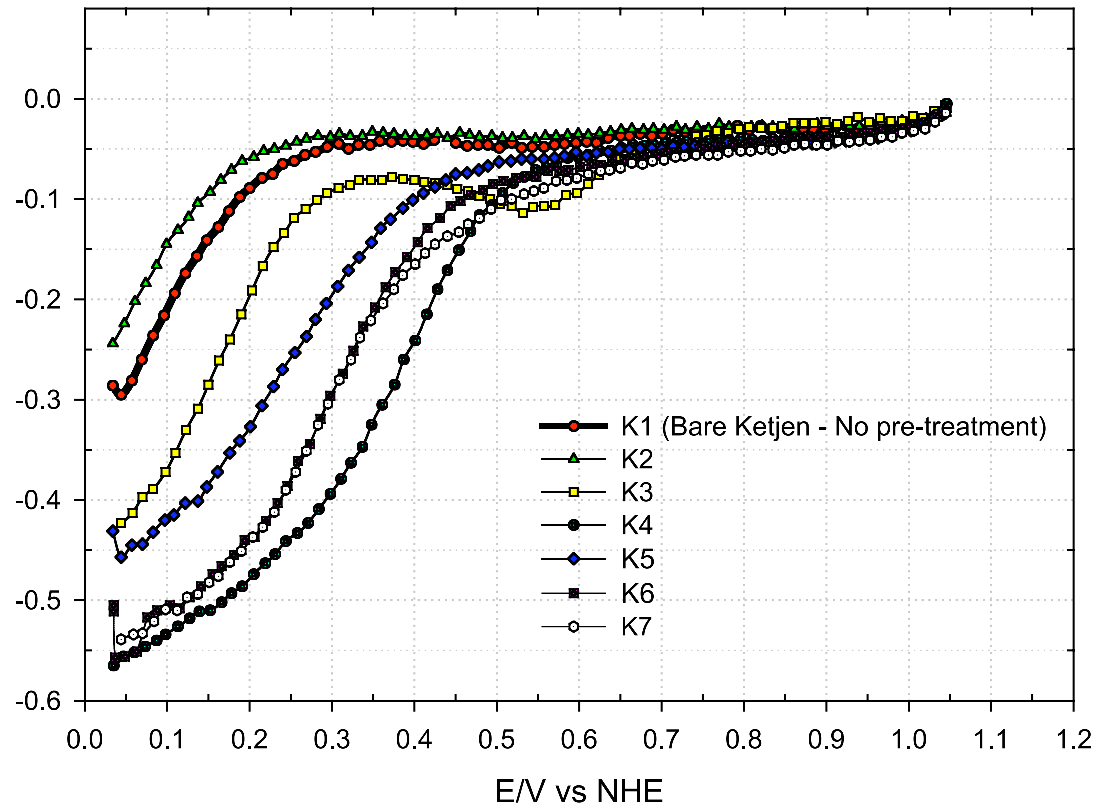
Experimental Set-Up for High Temperature Heat Treatment to Prepare Non-Precious Catalyst

Our Approach

- Develop supported and unsupported catalysts for oxygen reduction
  - Nitrogen contained precursors
  - Transition metal precursors
  - Chalcogenide compounds
- Optimize number of the catalytic sites as a function of
  - Carbon pretreatment.
  - Chemical composition of catalyst.
  - Post treatment of catalyst.
- Accomplish low cost catalyst through
  - Mass production methods.
  - Non precious metals.
  - Low cost precursors.
- Accomplish stable non precious catalysts with
  - High durability (corrosion resistant alloy catalysts).
  - Low peroxide generation.
  - High activity towards oxygen reduction.

Accomplishments

Disk Current of Metal Free Catalyst for Oxygen Reduction Reaction at 900 RPM

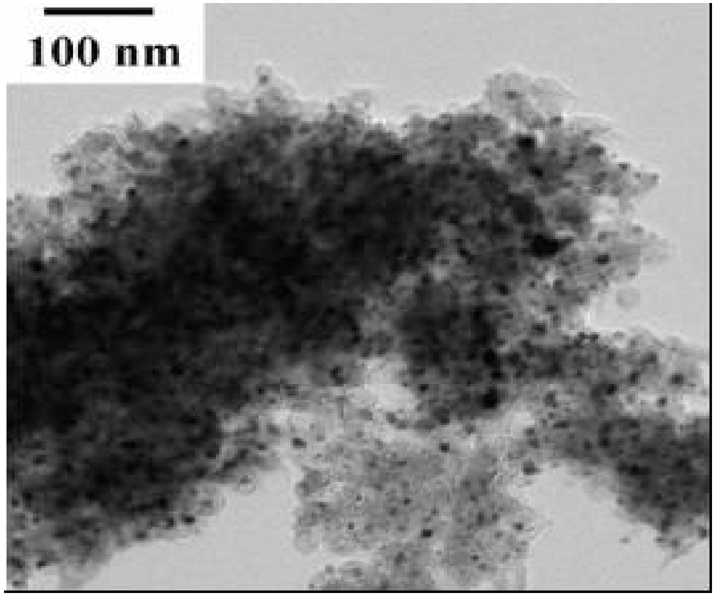


Current Trends in Non Noble Metal Catalyst for Oxygen Reduction and Comparison of Cost

H_2PtCl_6 (Chloro platinic acid)	$43/ 1g	
CoTMPP (cobalt tetramethoxy phenyl porphyrin)	$30.1/ 1g	J. Electro. Anal. 541 (2003) 147
CoPC (Cobalt phthalocyanine)	$12.6/ 1g	J. Power Sources, 46 (1993) 61
CoTPP (Cobalt tetraphenyl porphyrin)	$80/ 1g	Electrochem. Acta 41 (1996) 1689
Precursors used in our study	$0.2 /1g	

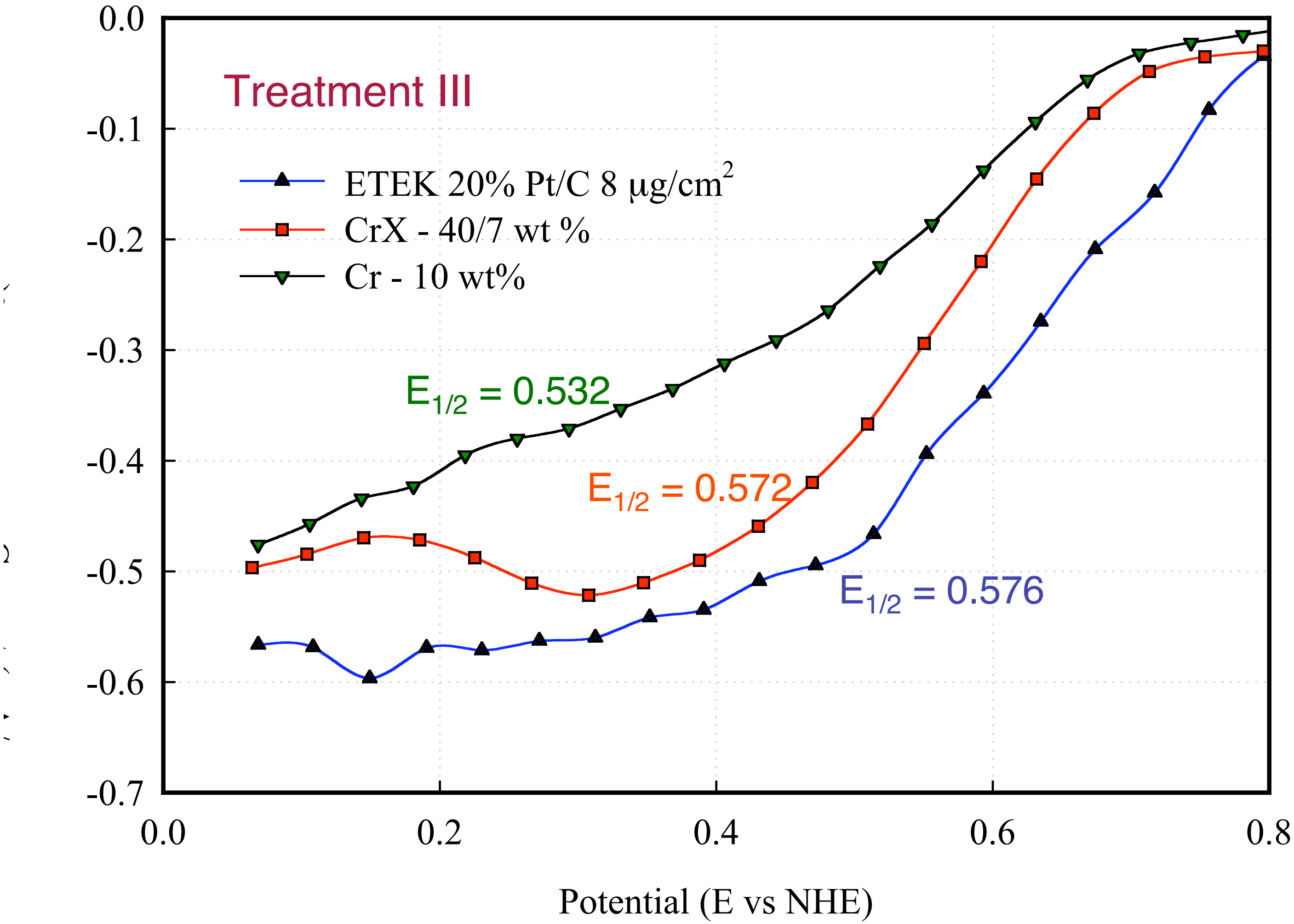
Develop Supported and Unsupported Catalysts for Oxygen Reduction

- Fe, Co and Cr were loaded on carbon.
- Metals loaded on carbon was followed by several post treatments to obtain oxygen reduction catalysts.
- The catalysts are tested for oxygen reduction activity by RDE measurements

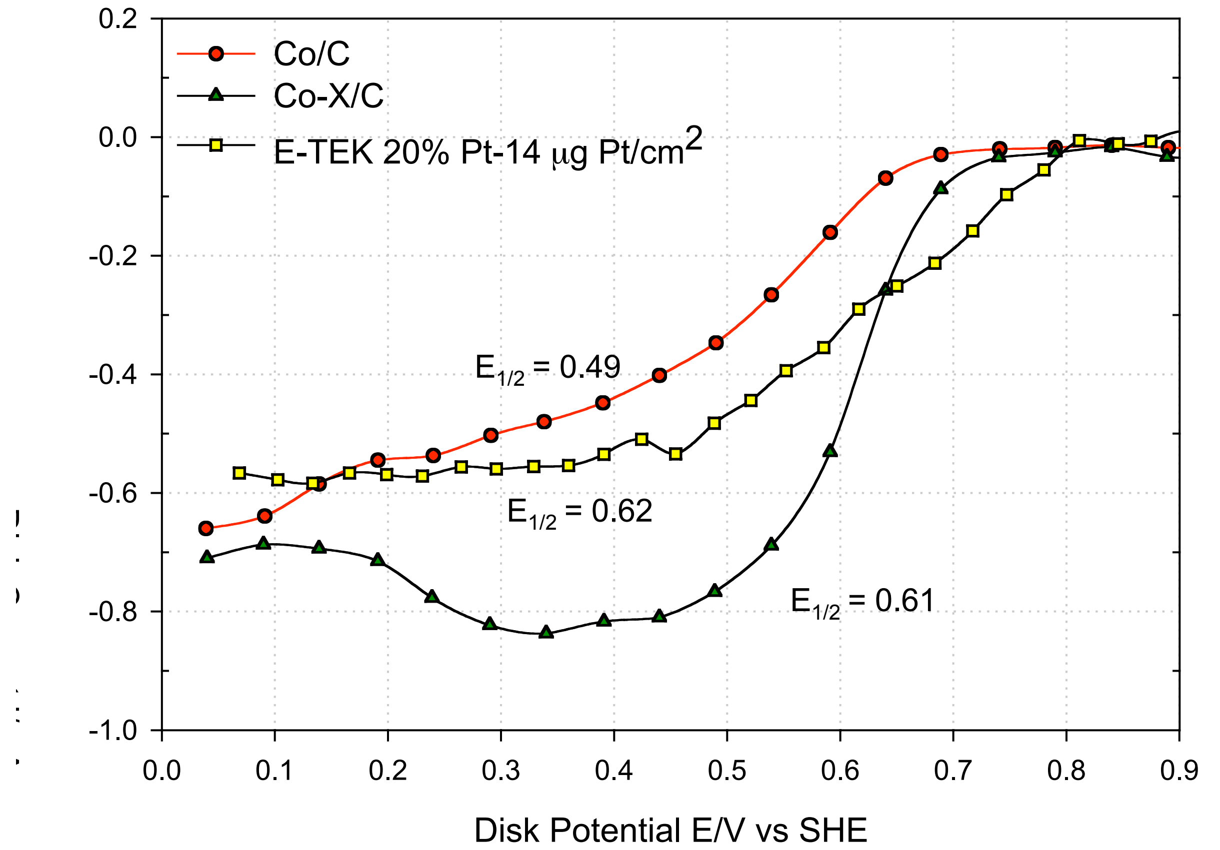


Catalyst Loading → Post Treatments → RDE measurements

Effect of Addition of X to Cr/C toward Oxygen Reduction Reaction at 900 RPM

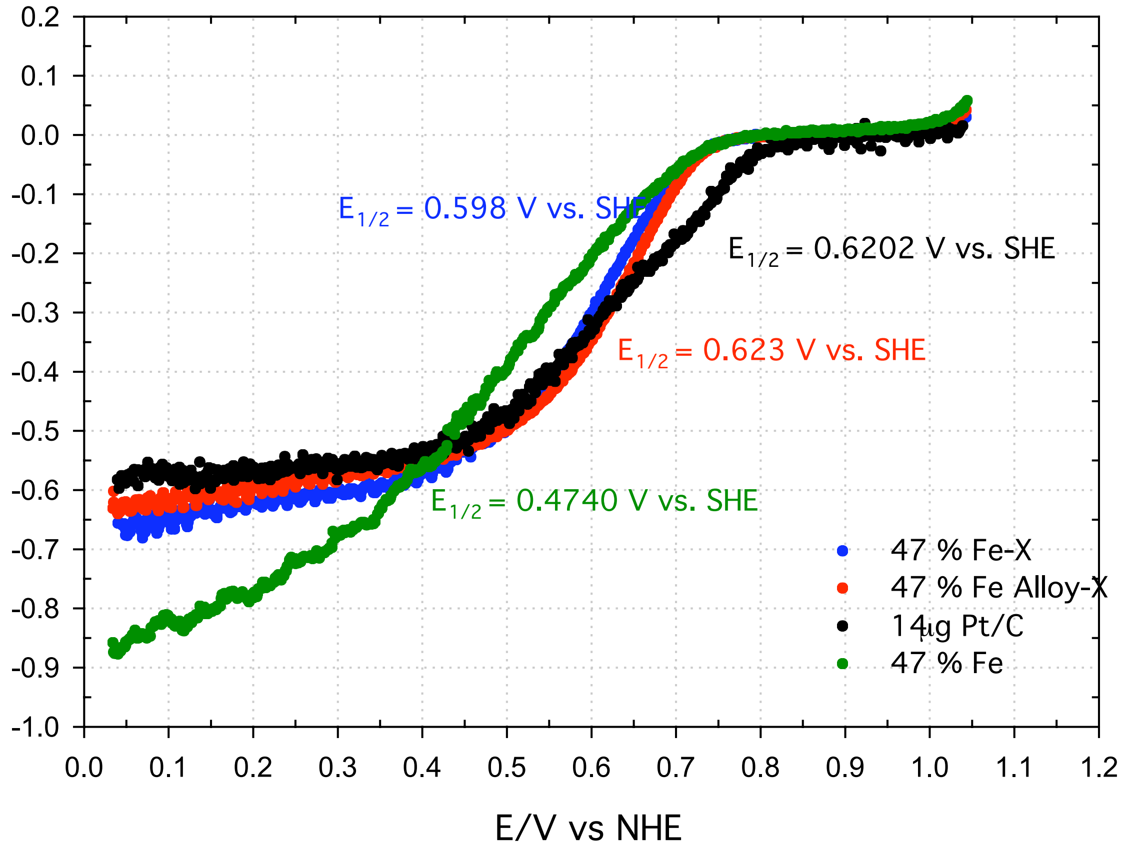


Effect of Addition of X to Co/C toward Oxygen Reduction Reaction at 900 RPM

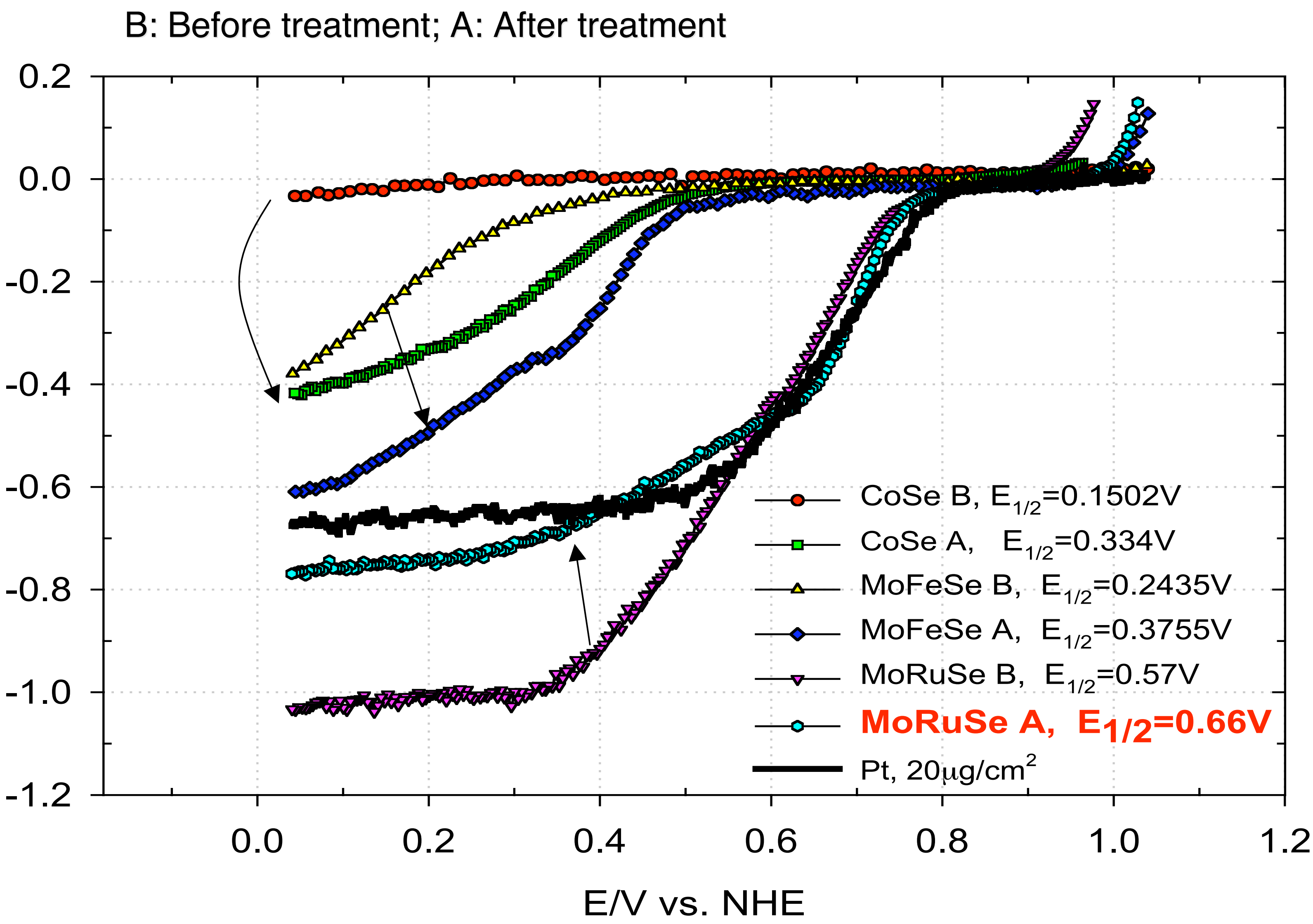


Effect of alloying for the Different Transition Metal Based Catalysts

Disk current at scan rate of 5mV/s rotated at 900 rpm

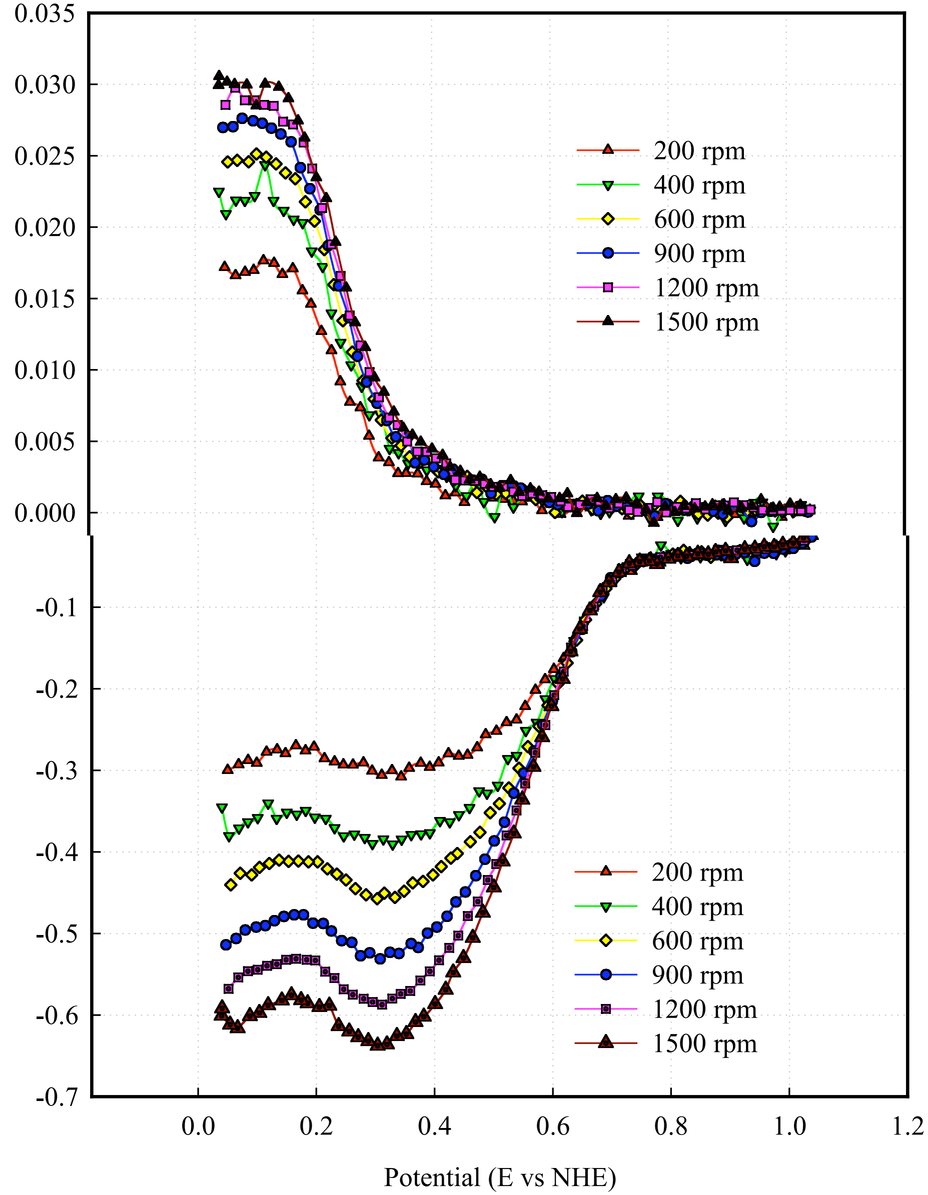


Effect of Treatment on Oxygen reduction for Unsupported Chalcogenide Catalysts at 900 RPM



Disc and Ring currents obtained for CrX/C alloy catalyst

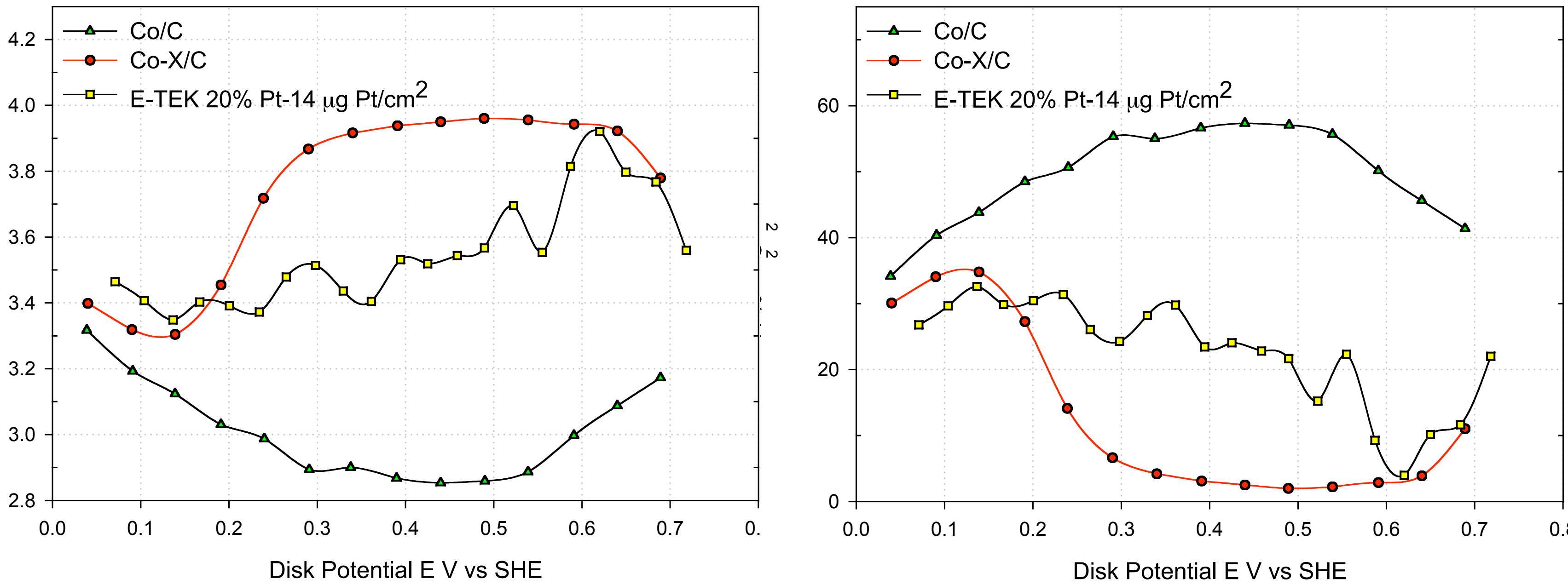
Treatment III



900rpm

$E_{1/2}$ =0.572 V

Average Number of Electrons Transferred and % Peroxide Produced in Co/C and Co-X/C



Comparison Between Non Precious Catalyst and Commercial Pt/C Catalyst

Catalyst	E_{half} (V vs. NHE)	Average No. of Electrons	% H_2O_2
Cr/C	0.506	3.6	20.29
Co/C	0.49	2.85	57.5
Fe/C	0.47	3.3	31
CrX/C	0.572	3.9	7.84
CoX/C	0.61	3.95	2.5
Fe alloy-X/C	0.62	3.6	19
MoRuSe/C	0.66	3.9	2.7
24 μg Pt/cm^2 (20wt% Pt/C)	0.67	3.8	10

Conclusions

- Novel non-precious metal catalysts were developed for oxygen reduction which have performance comparable to Pt under RRDE test conditions.
- Novel treatments were developed for synthesis of Cr-X Co-X, Fe-X and Mo-Ru-S. These alloys have improved activity for oxygen reduction , with number of exchange electrons close to four and showed a decreased activity for H_2O_2 generation.
- The pretreatment, the allying element and the post treatment are critical in order to obtain high catalyst performance.

Interactions & Collaborations

Dr. Branko Popov
PI and Team Leader,
University of South Carolina
(Development of Novel Catalyst)

Dr. Al Anderson
Case Western Reserve University
(Molecular Modeling of Catalyst)

Dr. Sanjeev Mukherjee
North Eastern University
(XANES Studies on Catalysts)

Dr. Ralph White
Dr. John Vanzee
Dr. John Weidner
University of South Carolina
(Modeling of Catalyst Kinetics and Catalyst Stability)

Future Work

- To decrease the alloy activation overvoltage by optimizing the wt % of the catalyst and the alloying element.
- To increase the active sites for oxygen reduction by optimizing the post treatments.
- To study nitrogen containing precursors for oxygen reduction.
- To define the structural properties of the of active site.
- To optimize the catalyst performance through molecular modeling.
- To perform stability studies.
- To perform MEA testing.