Molecular-scale, Three-dimensional Non-Platinum Group Metal Electrodes for Catalysis of Fuel Cell Reactions

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Budget: DOE share - $9.58MM over four years;
3M share - in-kind over four years.

Objectives

1) Demonstrate that non-platinum group metal catalysts can be used for oxygen reduction in polymer-coated electrode structures based on polyelectrolyte membranes.
2) Incorporate catalysts into polymer binders of composite electrodes for the construction of MEAs to demonstrate that this is an effective matrix for testing of new catalysts.
3) Demonstrate that the three dimensional structure of polymer-coated electrocatalyst layers can offset slower kinetics of the catalyst centers when compared with two-dimensional platinum or non-platinum catalysts.
4) Demonstrate that significant stability of the matrix is possible.
5) Demonstrate the design, synthesis and scale up of new catalysts capable of performance that is superior to platinum group metals.

Technical Barriers & Targets

- DOE Technical Barriers addressed

C. Electrode Performance –better efficiency.

B. Stack Material and Manufacturing Cost.

E. System Thermal and Water Management.

A. Durability

- DOE Technical Targets

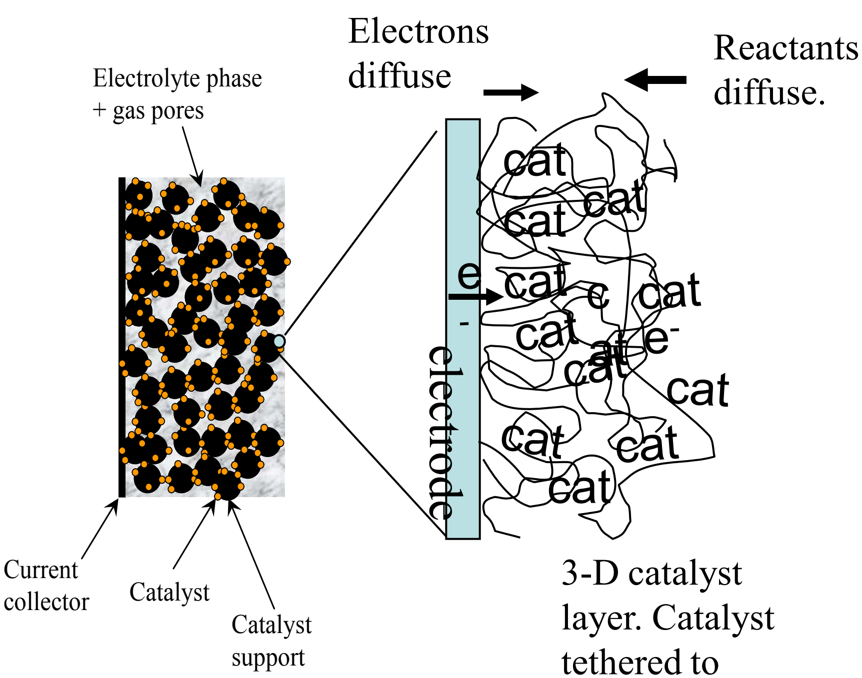
– Non-Pt catalyst activity per volume of supported catalyst – $300 A/cm^3$

– Cost < \$3/kW

– Durability > 5000 hours (> 120^oC)

  - Electrochemical area loss <40%
  - Electrochemical support loss < 30mV after 100hrs @ 1.2V

Approach



Gas diffusion electrode structure

3-D catalyst layer. Catalyst tethered to electrode by polymer binders

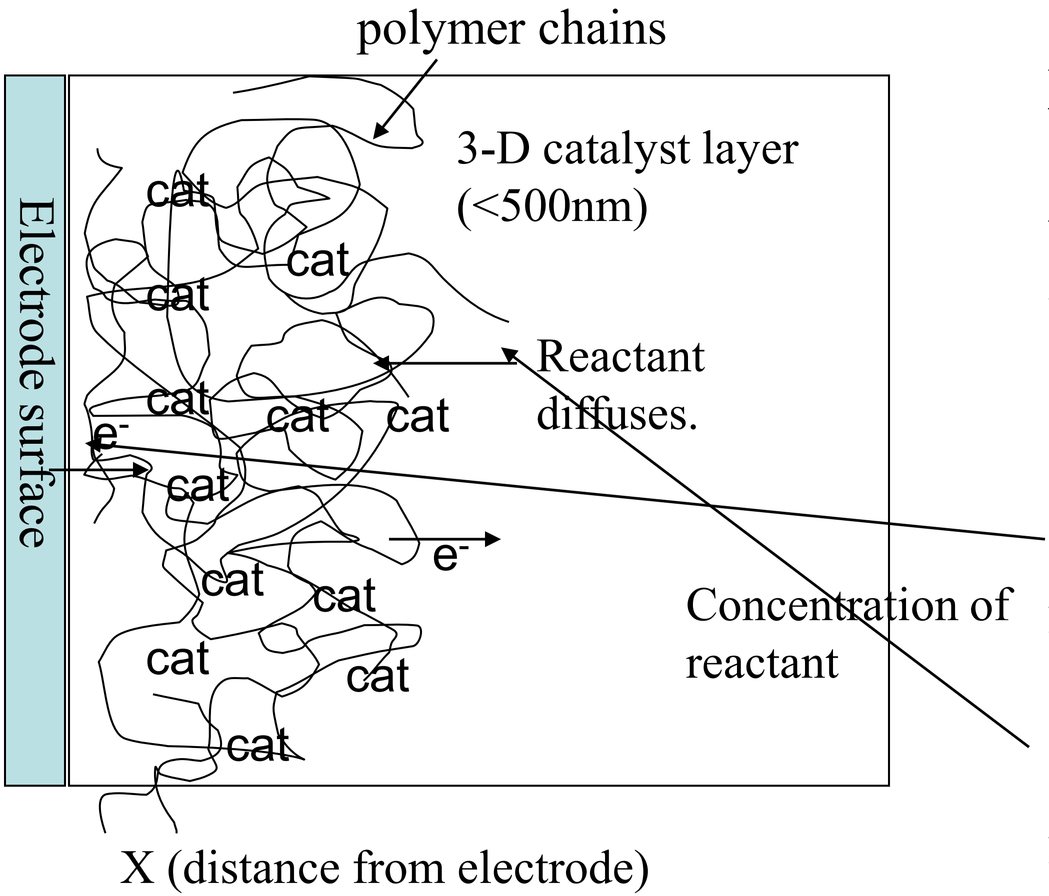
Objectives

- •Develop polymer coated electrodes that can provide viable matrices in MEA’s for use of homogeneous catalysts.
- •Demonstrate how 3D molecular catalyst electrodes can replace Pt.
- •Incorporate catalysts into MEA’s and demonstrate viability
- •Develop non-PGM Catalysts with better overpotential than Pt – e.g. Copper Laccase

cat = e.g. Fe Phenanthroline, Heme structures, cobalt co-ordination complexes, copper complexes, biomimetic homogeneous catalysts.

Two vs. Three Dimensional Catalysts

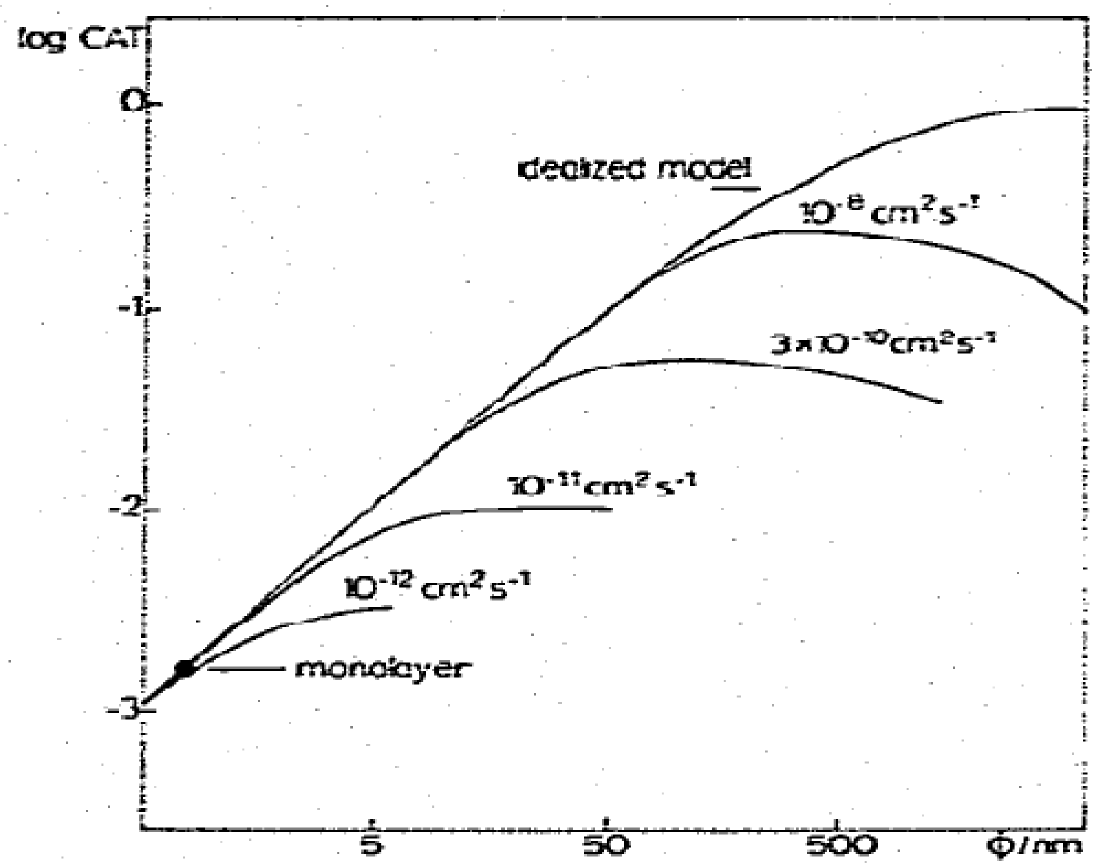
3D catalyst layers allow use of homogeneous catalysts, enzymes, bio- and biomimetic catalysts.



Polymer-coated electrode provides dynamic 3-D catalyst layer that makes up for slow kinetics of the catalyst by 3-D supply of substrate to catalytic centers- geometric effect. Reaction rate limited by rate of charge transport from electrode to catalyst and/or rate of diffusion of reactants into polymer layer

Effect of Film Thickness

Saveant, J. Electroanal Chem.,114 (1980),159

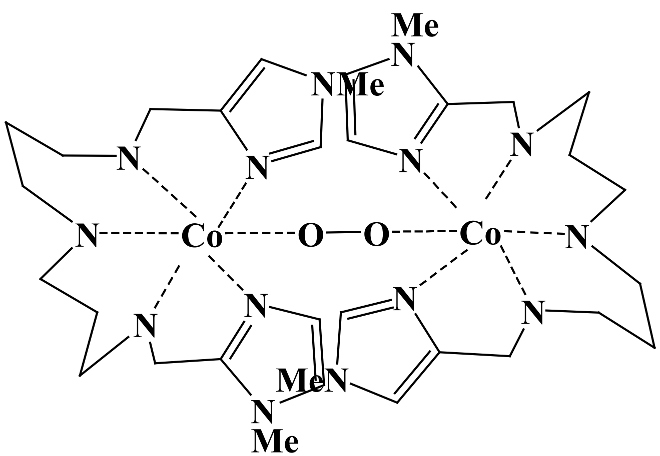


Catalytic efficiency, CAT, at a redox polymer electrode as a function of the film thickness, φ, for various values of the diffusion coefficient of the substrate through the film (indicated on each curve). Assumes substrate diffusion is rate-limiting.

Optimum thickness is 100-500nm, which is similar to binder thicknesses. 500nm is equivalent to ~ 100 catalyst monolayers. Thus approach provides 100x density without increasing electrode thickness.

Co-operativity Effects for better Oxygen Reduction Efficiency? Modeling and Experiment.

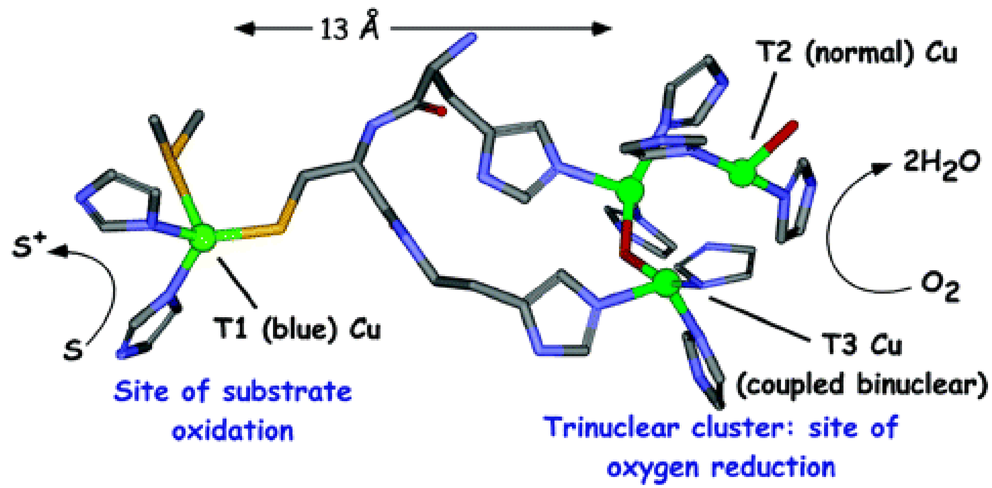
Oxygen separation systems



E. De Castro, B. D. Zenner, J. P. Ciccone, L. A. Deardurff, and J. B. Kerr, USP 4,959,135 (1990).

Enzyme ORR catalysts.

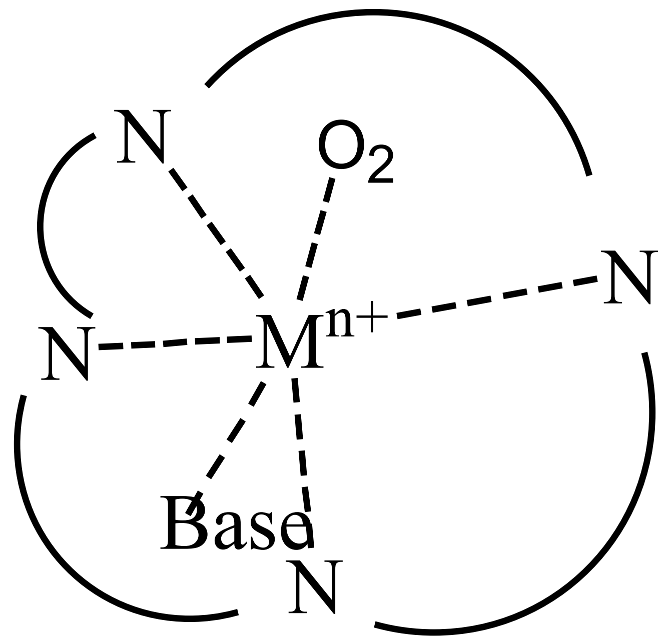
Copper catalyst centers are held in place by IMIDAZOLE



Nature chooses imidazole
as a base in the presence of oxygen.
Copper catalysts better than platinum?

Novel Catalyst design

- Metal center provides low overpotential for charge injection from electrode.
- Ligands tune binding strength and lability that controls turnover frequency (TOF)
- Adjust ligand flexibility and basicity to increase TOF. Novel ligand design.
- More than one metal center to provide cooperativity (e.g. hemoglobin, copper laccase enzyme for O_2 reduction).
- Learn from enzyme catalyst centers. New catalyst design in Cross-cutting Area.

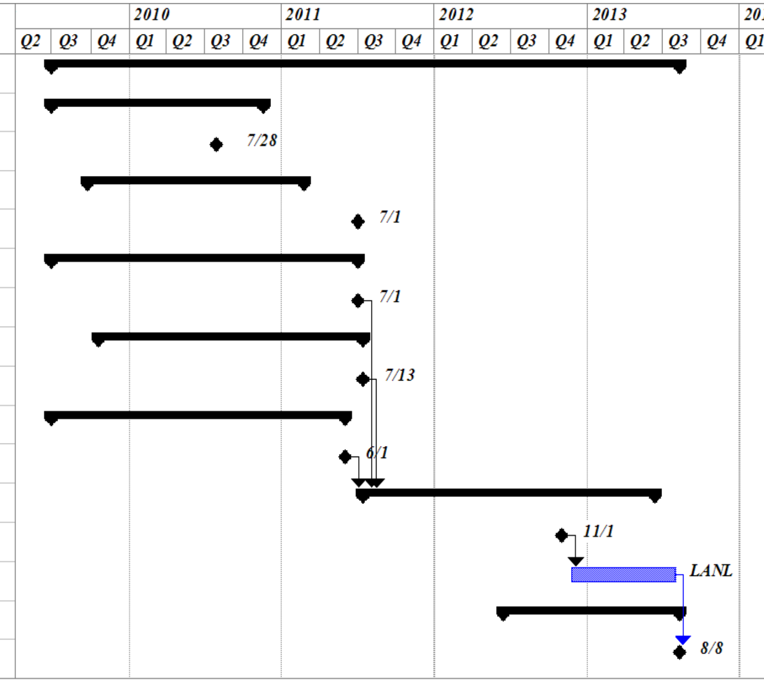


Project provides polymer matrices to mount new electrocatalysts in practical systems which facilitate both electron and proton transport.

Project Schedule

Milestones & Go/No-Go Decisions.

ID	Task Name
1	**Non-PGM Electrodes for Catalysis of Fuel Cell Reactions**
2	**Development of synthesis, and electrochemical screening methods**
8	***Oxygen reduction catalysis demonstrated with polymer coated electrodes***
9	**MEA fabrication and testing methods development**
13	***Go/No-Go Decision(do tethered complexes work in MEAs?)***
14	**Develop optimization Methods for electrode structures**
17	***Methods of optimization of tethered catalysts demonstrated in MEAs***
18	**Develop durability testing**
22	***Durability and degradation testing developed***
23	**New Catalyst development**
27	***New Catalyst development methods demonstrated***
28	**MEA fabrication and testing with new ORR catalysts**
34	***Satisfactory performance from single cell MEA***
35	Short stack Build and test
36	**Hydrogen Oxidation Catalysts**
39	***Project completion -Final Report and Proposal for Further Work.***



Milestone 1. Oxygen reduction catalysis demonstrated with polymer coated electrodes(12mo).

Milestone 2. Go/No-Go Decision. Oxygen reduction catalysis demonstrated with polymer-bound catalyst layers in MEAs (24mo).

Milestone 3. Methods of optimization of catalysts demonstrated in MEAs (24mo).

Milestone 4. Durability and degradation testing developed (24mo).

Milestone 5. New catalyst development methods demonstrated (24mo).

Milestone 6. Satisfactory performance from single cell MEAs (39mo). Go/No-Go decision to build stack and test.

Budget & Tasks.

- Years 1-4. LBNL $1515k; LANL $1065k; 3M in kind
- Polymer Synthesis – LBNL and LANL
- Perfluorinated Polymer Synthesis – 3M
- Catalyst preparation and testing – LBNL/LANL
- Catalyst Modeling – LBNL/LANL
- Catalyst attachment to polymers – All
  - Electrochemical testing - LBNL/LANL/3M
  - Morphological testing – LBNL/LANL
  - Chemical Degradation testing- 3M/LBNL
- Macroscopic modeling of transport properties - LBNL
- LANL and 3M make and test MEA’s.
- Stack construction and testing – LANL (Giner subcontract)

Full Project Schedule.

ID	Task Name
1	**Non-PGM Electrodes for Catalysis of Fuel Cell Reactions**
2	**Development of synthesis, and electrochemical screening methods**
3	Synthesis of basic polyelectrolyte polymers with functionalizable side chains
4	Polyarylenesulfone & Polystyrene backbones
5	Perfluorinated polymers
6	Develop catalyst characterization in solutions - water and protic ionic liquids
7	Characterize activity on polymer coated electrodes -simple tethered catalysts
8	***Oxygen reduction catalysis demonstrated with polymer coated electrodes***
9	**MEA fabrication and testing methods development**
10	Characterize mechanical and morphological properties of polymers
11	Characterize polymer with bound catalysts and with electrode support materials
12	Prepare and test MEAs with base polymers with bound non-platinum catalysts.
13	***Go/No-Go Decision(do tethered complexes work in MEAs?)***
14	**Develop optimization Methods for electrode structures**
15	Develop macroscopic property model for MEA operation
16	Use model to optimize catalyst loading, polymer morphology, charge transport
17	***Methods of optimization of tethered catalysts demonstrated in MEAs***
18	**Develop durability testing**
19	Catalyst degradation mechanisms
20	Polymer matrix degradation - chemical and physical modes
21	Degradation and durability testing of MEAs
22	***Durability and degradation testing developed***
23	**New Catalyst development**
24	Fundamental modeling of catalyst chemistry for ORR
25	Synthesis and screening of new catalyst structures for ORR
26	test new catalysts in polymer matrices
27	***New Catalyst development methods demonstrated***
28	**MEA fabrication and testing with new ORR catalysts**
29	New polymer synthesis for better performance
30	New catalyst design, synthesis and screening
31	Transport measurement and modeling
32	Optimization of MEA structures
33	Durability Testing/Lifetime extension
34	***Satisfactory performance from single cell MEA***
35	Short stack Build and test
36	**Hydrogen Oxidation Catalysts**
37	Design, synthesize and screen
38	Fabricate and test MEAs witn non-PGM anode catalysts
39	***Project completion -Final Report and Proposal for Further Work.***