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 – 300A/cm³
  – Cost < $3/kW
  – Durability > 5000 hours (> 120°C)
    • Electrochemical area loss < 40%
    • Electrochemical support loss < 30mV after 100hrs @ 1.2V
Approach

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

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\text{cat} = \text{e.g. Fe Phenanthroline, Heme structures, cobalt co-ordination complexes, copper complexes, biomimetic homogeneous catalysts.}
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Two vs. Three Dimensional Catalysts

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

Polymers-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, \( \varphi \), 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 \( \sim 100 \) 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

Enzyme ORR catalysts.
Copper catalyst centers are held in place by IMIDAZOLE

E. De Castro, B. D. Zenner, J. P. Ciccone, L. A. Deardurff, and J. B. Kerr,

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.
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.