Combinatorial Synthesis of Oxygen Reduction Electrocatalysts by Spray Pyrolysis

Paul Napolitano, David Dericotte, Rimple Bhatia, Paolina Atanassova, Mark Hampden-Smith, Toivo Kodas
Contents

- SMP powder manufacturing platform
- Combinatorial discovery approach
  - Combinatorial system design
  - Choice, synthesis, characterization and testing of electrocatalysts
  - MEA structure development
- Benchmark synthesis of binary and ternary alloy ORR catalysts
Challenges for Combinatorial Discovery

- The goal of combinatorial discovery is to screen as many materials or properties as possible in a short time = many small size samples
- Discover the materials on the system that will be used for high volume manufacturing to produce the same material highly reproducibly
- Does the microstructure and composition really represent what can be reproduced at a commercial scale?
- Use a powder production system that is sufficiently flexible to reproduce discovered compositions
Technology Platform: SMP’s Spray Based Manufacturing

- Low cost manufacturing
  - Single step processing
  - Highly controllable and reproducible
  - “Green” process with minimal waste streams

- Agile platform
  - Not material specific
  - Inorganics, organics, metals, metal oxides
  - Complex compositions

- Ability to engineer critical properties
  - Particle morphologies and size distributions
  - Bulk and surface chemistries and structures
  - Dispersion, crystallinity and size distribution of catalytically active phase
Technology Platform: Process Flow Diagram

- Independent control over:
  - aggregate morphology and size distribution
  - the dispersion and composition of catalytically active phase
Hierarchical Structure of SMP
Electrocatalyst

Relevant patents: US 6,103,393    US 6,165247    US 6,159,267

PtRu alloy nanocrystals
porous agglomerate of carbon particles
carbon particle
Simultaneous Structure Control

- Scale up reproducibility
- Batch-to-batch reproducibility
- Sub-batch reproducibility

<table>
<thead>
<tr>
<th>Powder batch number</th>
<th>Surface area [m²/g]</th>
<th>Average pore diameter [nm]</th>
<th>Pt crystallite size [Å]</th>
</tr>
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<tbody>
<tr>
<td>163C</td>
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<tr>
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From Combinatorial Discovery to Production

Production
1,000’s Kg range

Pilot
Kgs range

Research
100g range
Title of Project: Development of High-Performance, Low-Pt Cathodes Containing New Catalysts and Layer Structure

Duration: 4 years, September 2001- September 2005

DOE Program Manager: JoAnn Milliken

Subcontractors: DuPont, CFDRC

Stack testing: GM
Technical Goals and Objectives

- Current state of the art:
  - 2002 - 2 gPt/kW at 0.8 V; > 1000 h
  - 0.65 mg Pt/cm² loading
  - recent reports - 1 gPt/kW

- DOE target performance:
  - 2004 - 0.6 gPt/kW at 0.8 V; > 4000 h
  - 0.20 mg Pt/cm² loading
  - 2008 - 0.2 gPt/kW at 0.8 V; > 5000 h
  - 0.05 mg Pt/cm² loading
Technical Concept

Effort 1:
- Discovery of new, low Pt catalyst compositions and particle microstructures

Effort 2:
- Modeling and deposition of engineered cathode layers

Effort 1:
- SMP
- DuPont

Effort 2:
- SMP/
- CFDRC

Short Stack Testing:
- GM
Work Plan Effort 1: Combinatorial Approach

- Combinatorial Catalyst Microstructure Discovery
- Catalyst Screening
- Select best candidate from primary screen
- Produce at larger scale
- MEA Testing

- **Combinatorial Powder Synthesis System (CPSS) - SMP**
  - Synthesis of Binary Alloys and Mixed Metal/Metal Oxides
  - Synthesis of Ternary Alloys

- **Rapid Catalyst Screening for ORR Activity - DuPont**
Combinatorial Approach for Electrocatalyst Discovery

- **SMP combinatorial discovery platform:**
  - Fully automated powder production
  - Compatible with scaled manufacturing

- **Critical elements of the approach:**
  - Some combinatorial platforms rely on high throughput techniques for model systems followed by scale up in supported form
  - **SMP approach will rely on fewer carefully chosen compositions made in supported form**
  - Screening focused on test configurations such as half cell and MEA configurations)
Components of Combinatorial Approach

- **Selection of composition/structure targets** and benchmarking against literature/existing catalysts
- Ensure **high speed generation of samples** with variations in the composition and microstructure: an order of magnitude higher number of samples
- Ensure **rapid primary screens** to evaluate structure/performance of electrocatalyst powders:
  - XRD for structure evaluation (crystallinity, dispersion, alloying)
  - rapid EC performance evaluation in half cell configuration
Combinatorial Powder Synthesis System (CPSS)

Precursor 1 → Reactor
Precursor 2 → Reactor
Precursor 3 → Reactor
Droplet generator

Precursor containers
Flow controllers

Composition

Microstructure

• Surface area
• Dispersion
• Composition
• Crystallinity
• Phase
• Surface composition
• Morphology
• Porosity
• Pore structure
• Particle size & distribution

Concentration
Precursor 1
Precursor 2
Precursor 3

Time
Profile 1
Profile 2
Profile 3

Time
SMP Powder Production Process

Atomization Zone
- Reservoir
- Carrier Gas

OR
- Carrier Gas

Reaction Zone

Collection Zone
- Filter Media
- Exhaust Gas

Multi-zone Furnace

Profile 1
Profile 2
Profile 3

Time
Process Automation

Multi-zone Furnace

Profile 1
Profile 2
Profile 3

Time
## Automation and Upgrades

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<tr>
<th>Process Step</th>
<th>Current Limitation</th>
<th>Modification</th>
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<tr>
<td>Precursor delivery</td>
<td>➢ Static precursor composition</td>
<td>➢ Automate delivery</td>
</tr>
<tr>
<td></td>
<td></td>
<td>➢ Add “on-the-fly” preparation</td>
</tr>
<tr>
<td>Automation</td>
<td>➢ Operator required to:</td>
<td>➢ Automate system to:</td>
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<tr>
<td></td>
<td>• adjust furnace temp</td>
<td>• adjust furnace temp</td>
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<tr>
<td></td>
<td>• adjust gas flow rate</td>
<td>• adjust gas flow rate</td>
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<tr>
<td></td>
<td>• replace collection media</td>
<td>• isolate powder sample</td>
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<tr>
<td>Data Collection</td>
<td>➢ Limited data collection performed by operator</td>
<td>➢ Use SCADA to acquire more data, control process variables, perform statistical analysis</td>
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<tr>
<td>Safety</td>
<td>➢ Safety systems installed to protect operator, system and powder</td>
<td>➢ Improve further safety controls</td>
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Selection of Composition/Structure Targets

Selection criteria for electrocatalyst compositions:

- Cost of components - raw materials, precursor cost
- Cost of manufacturing (precursors, processing steps) - fab cost
- Demonstrated performance advantage
- Possible performance advantage based on established general trends
- Long term stability
  - stable in acidic media/resistant to corrosion
  - sustainable performance at high potentials
  - sustainable dispersion of the active phase

Demonstrate synthesis of complex known compositions and benchmark performance

Develop methodology to down select in the compositional space
Selection of Composition Targets

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**SUPERIOR MicroPowders**
Selection of Composition Targets for Binary Metal-Metal Oxide EC

- Highly oxophillic, soluble oxides, poison to PEM
- Oxides susceptible to corrosion

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<tr>
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<th>Be</th>
<th>Na</th>
<th>Mg</th>
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<tr>
<td>Yb</td>
<td>Lu</td>
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</table>
Further Down Selection: Cost of Raw Materials

Cost [$/100 g]

Elements

- Rh
- Os
- Ir
- Pt
- Au
- V
- Cu
- Zn
- Nb
- Mo
- Ag
- Sn
- Sb
- Hf
- Ta
- W
- Re
- Bi

Cost Range: $0 - $14000

0 5 10 15 20 25

Cost [$/100 g]
Further Selection Refinement: Activity in ORR

- Role of electronic and geometric parameters
  - d-band vacancy; % d character, latent heat of sublimation, heat of adsorption, strength of adsorption bond (M-O)
  - crystal structure; interatomic distance, crystallite size, defects

- Two main trends in dependence of electrochemical performance as function of physicochemical property:
  - "volcano" type - current density v.s M-O bond strength, latent heat of sublimation, d-band vacancies of electrode metal, % d-character
  - linear type - specific activity vs. nearest-neighbor distance

- Particle-size effects
  - change in concentration of various crystallographic sites with change in particle size

Examples of Particle Size Effects

Mass-averaged distribution for MAD (111), MAD (e-c)

Surface-averaged distribution for SAD (111), SAD (e-c)

Particle size (nm)
**Synthesis of Pt and Pt-alloys Electro catalysts**

- **Pt precursor development** to ensure compatibility with various other precursors used for alloys
- **Optimization of active phase loadings and type of carbon support**
  - 5, 10, 20, 30 wt.% Pt/SB
  - 60 wt.% Pt/C (high surface area support)
- **Synthesis of selected binary and ternary alloys**
  - binary - Pt\(_x\)Co\(_y\); Pt\(_x\)Pd\(_y\); Pt\(_x\)Cr\(_y\); Pt\(_x\)Ru\(_y\);
  - ternary - Pt\(_x\)Ni\(_y\)Co\(_z\); Pt\(_x\)Cr\(_y\)Co\(_z\);
- **XRD used as a primary screen for degree of alloying and dispersion of active phase**
Synthesis of Ternary Pt-alloys Electro catalysts
Performance of Ternary Pt-alloys Electrocatlysts

20 wt.% Pt\textsubscript{x}Ni\textsubscript{y}Co\textsubscript{z} or Pt/Vulcan XC-72

80 C, 1.5/2.5 stoich at 1A/cm\textsuperscript{2}, 100% RH, Air 30 psig, 15 min/point

0.25 mgM/cm\textsuperscript{2} total loading
Nafion 112
20 wt.% Pt/C
4.2 gPt/kW
20 wt.% Pt\textsubscript{x}Ni\textsubscript{y}Co\textsubscript{z}/C
2.6 gPt/kW
40 % improvement vs. Pt/C
Performance of Ternary Pt-alloys Electro catalysts

After structure optimization

0.25 mgM/cm² total loading
Nafion 112
20 wt.%
PtₓNiᵧCo₂/C
1.5 gPt/kW

20 wt.% PtₓNiᵧCo₂
80 C, 1.5/2.5 stoich at 1 A/cm², 100% RH, 30 psig,
15 min/point
**MEA Structure Optimization**

- **Optimization of catalyst and ionomer loadings**
  - 0.1 - 0.6 mg M/cm²
  - In combination with various wt.% M/carbon catalysts

- **Testing with variations in the:**
  - Membrane Nafion 112, Nafion 117, Nafion 1035
  - Catalyst (carbon): Ionomer ratio in the electrode inks
  - GDL type
  - Humidification level for gases

- **Electrode deposition technique**
  - Method A
  - Method B
Various Catalysts and Pt loadings

80 °C, 30 psig, 100% RH gases, flow at 1.2/2.5 stoic @ 1A/sqcm

Potential [mV] vs. Current density [mA/cm²] for different Pt loadings:
- 0.65 mgPt/sqcm
- 0.45 mgPt/sq cm
- 0.25 mgPt/sqcm
Various Catalysts and Pt loadings

<table>
<thead>
<tr>
<th>Pt loading [mgPt/cm²]</th>
<th>gPt/kW</th>
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<tbody>
<tr>
<td>2.1</td>
<td>0.25</td>
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<tr>
<td>1.9</td>
<td>0.45</td>
</tr>
<tr>
<td>2.2</td>
<td>0.65</td>
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</table>
Deposition Method A vs. B

- Method A:
  - 6.3 gPt/kW
  - 20wt.%Pt/C
  - Nafion 112

- Method B:
  - 0.25 mgPt/cm² total loading
  - Current: 1.9 gPt/kW
Performance Targets

<table>
<thead>
<tr>
<th>Project year</th>
<th>P [W/cm²]</th>
<th>Pt loading [mgPt/cm²]</th>
<th>gPt/kW</th>
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<tr>
<td>1</td>
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<td>0.25</td>
<td>0.25</td>
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<tr>
<td>2</td>
<td>0.16</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>3</td>
<td>0.24</td>
<td>0.25</td>
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<tr>
<td>4</td>
<td>0.32</td>
<td>0.25</td>
<td>0.6</td>
</tr>
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</table>
Accomplishments

- Combinatorial system designed and assembly on schedule
- Rapid screening method in place and benchmarked
- Binary and ternary Pt-Alloy catalysts synthesized and improved performance demonstrated
- Strategy for combinatorial approach in place
- All critical components for combinatorial discovery based on spray pyrolysis approach in place
- Spray-based powder manufacturing offers the best opportunity to reproduce the discovery and scale the commercially useful volumes
Acknowledgements

- DOE OTT, Award DE-FC0402AL67620, Topic 1A1
- DOE Program Manager: JoAnn Milliken
- SMP for cost share funding
- The whole SMP team and especially:
  Jim Brewster, Jenny Plakio, Heat Quiggle