Development of Alternative and Durable High Performance Cathode Supports for PEM Fuel Cells

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Overview

Timeline

• Project start date Jan 2007
• Project end date Dec 2010
• Percent complete 8%

Budget

• Total project funding
  – DOE share $4,234K
  – Contractor share $255K
• Funding received in FY07
  – $1,241 (federal, requested)
  – $820K (federal, approved)
  – $72K (cost share)
• Funding reduced in FY07 due to late start. Hence project duration extended by 4 months to Dec 2010

Barriers

• Barriers addressed
  – A. Durability of cathode catalyst supports
  – C. Performance of cathode supported catalyst

Partners

• Ballard Power Systems – guidance on fuel cell testing
• Oak Ridge National Laboratory – mesoporous carbon supports
• University of Delaware – Tungsten carbide support
• Pacific Northwest National Laboratory
  – cathode synthesis and cathode/fuel cell testing
  – project management
## Objectives

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<td>Overall</td>
<td>• Develop and evaluate new classes of alternative and durable high-performance cathode supports</td>
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| 2007 | • Fundamental understanding of model systems  
      • Synthesis of high surface area cathode supports  
      • Downselect carbon support with potential for better stability than commercial carbon black support |
| 2008 | • Identify lead cathode compositions with potential for better durability than carbon black supported Pt cathode |
| 2009 | • Identify compositions with mass activity of > 0.44 A/mg Pt and 5X better stability than carbon black supported catalyst for cell demonstration. |
| 2010 | • Demonstrate durability under accelerated test protocols that meet lifetime criteria under development at DOE |
Approach

• Develop and evaluate new classes of alternative and durable cathode supports using graphitized carbons as scaffolds and protect the carbon surface with
  – Tungsten carbide (WC)
  – Oxycarbides
  – Conductive metal oxides (ITO)
• Enhance Pt dispersion and stability on these new classes of cathode supports.
• Conduct electrochemical tests on above supported catalysts
Technical Accomplishments

• Synthesized Pt/WC
  – Surface preparation of polycrystalline W
  – Decomposition of ethylene over hot filament and annealing by resistive heating at 1200K to form WC
  – Analysis of surface composition using XPS

• Synthesized WC on different carbon substrates using PVD, CVD and TPR

• Established protocol for synthesis of highly stable mesoporous carbons retaining porosities under graphitization conditions

• Conducted preliminary TGA corrosion tests of graphitized ordered mesoporous carbon loaded with Pt

• Loaded Pt on various supports by incipient wetness

• Controlled Pt particle size by varying the incipient wetness process parameters such as solvent, Pt loading, carbon surface properties and post-incipient wetness process conditions.

• Conducted preliminary electrochemical experiments to determine ECSA, performance and stability of supported catalyst
Synthesis of Pt/WC

- Decomposition of ethylene over hot filament
- Annealing by resistive heating to \( \sim 1200 \) K to form WC
- Analysis of surface composition using XPS
Synthesis of WC on Different Carbon Substrates: PVD, CVD and TPR

• PVD reactive deposition with post annealing produced pure WC on various carbon substrates for fuel cell testing

• Similar WC films produced from CVD synthesis

• Supported WC particles produced by temperature programmed reaction (TPR)
Synthesis of Highly Stable Mesoporous Carbons

Goal: Develop and evaluate new classes of alternative and durable high-performance cathode supports
• synthesis of ordered mesoporous carbon catalyst supports
• synthesis of carbon-supported WC.

Accomplishments:
*Synthesis* – Established the protocol for synthesis of highly stable mesoporous carbons retaining porosities under graphitization conditions.
*Processing* – Mesoporous carbons were used to disperse conducting oxide materials.
Preliminary TGA Corrosion Tests of Graphitized Ordered Mesoporous Carbon (OMC) Loaded with Pt

TGA in air

Weight Percentage (%)

OMC 14% Pt

VXC 72 10% Pt

OMC 10% Pt

Temperature (°C)

Weight Percentage (%)
Pt Loading by Incipient Wetness

10%Pt/Carbon(Vulcan X72C) 20%Pt/MWCNT

2θ / degrees

Intensity/ arbitrary units

*: Pt

20%Pt/MWCNT
20%Pt/C
10%Pt/C(~2 nm)
C(Vulcan)
Durability Testing of Cathode Catalyst

Oxygen reduction by Linear Scan Voltammetry (LSV) using rotating disc electrode

- Fresh electrode
- 75 min hold at 1.6V vs SHE
- 100 mV/sec

ECSA by H2 desorption

- 75 min hold at 1.6V vs. SHE
- 100 mV/sec

- All potentials shown are vs. Ag/AgCl
- Gold RDE, Pt wire counter, 0.5M H2SO4
- Determine ECSA and oxygen reduction current of fresh electrode
- Scan from 0.6-1.1V vs SHE for 300 cycles at 100 mV/sec
- No ECSA loss and no decrease in oxygen reduction current (data not shown)
- Hold at 1.6V vs SHE for 75 minutes
- Significant ECSA loss and decrease in oxygen reduction current
Future Work

FY07

• Continue development of MWCNTs and mesoporous carbon support coated with WC, oxycarbides and conductive metal oxides

• Continue development of Pt supported on above materials
  – Develop fundamental understanding of interfacial interaction between Pt/C and Pt/WC by STM
  – In-Situ XPS and electrochemical measurements to determine stability

• Continue electrochemical evaluation of support and supported catalyst
  – Chronoamperometric measurement of oxidation current during hold at various oxidation potentials
  – Periodic determination of ECSA loss and decrease in oxygen reduction current

FY08

• Identify lead cathode compositions which have high potential for achieving better durability than carbon black supported Pt cathode
Summary

• Synthesized Pt/WC and ordered mesoporous carbon supports

• Developing fundamental understanding of interfacial interaction between Pt/C and Pt/WC by STM ongoing

• Conducted *in situ* XPS and electrochemical measurements to determine stability

• Loaded Pt on mesoporous carbon and commercial supports by incipient wetness

• Started electrochemical testing of supported catalysts to determine performance and stability