Concepts of Durable PEFC Cathode Catalysts

IEA Topical Meeting on Electrocatalysis for Fuel Cells
Berlin - Nov 15, 2017
Mission

Advancement of electrochemical energy storage and conversion by
• developing novel electrochemical materials, cells and devices
• providing insight into electrochemical materials, cell and device properties
Electrocatalysis Research at PSI

- Polymer Electrolyte Fuel Cells
- Electrolysis and co-Electrolysis
- Electro catalysis on MEA and Cell Level
- Alternative supports
- Perovskites
- Nanostructured metals
- Strained Surfaces
- Non-PGM Catalysts
- Fundamentals
Catalyst Challenges in PEFCs

\[ \begin{align*}
H_2 & \rightarrow 2H^+ + 2e^- \\
\frac{1}{2} O_2 + 2H^+ + 2e^- & \rightarrow H_2O
\end{align*} \]

Membrane Electrode Assembly (MEA)

Platinum based catalyst:
- Cost means performance
- Catalyst kinetics on cathode side

Platinum based catalyst
Lifetime determining
- Pt dissolution
- Carbon support corrosion

Air

Bipolar Plate

Hydrogen

wet Air

30 nm
Pt-based catalysts account for about 50% of automotive PEFC cost

Fuel cell cost breakdown (500k vehicles/a)

- Catalyst: 48%
- Bipolar plates: 23%
- Membrane: 11%
- GDLs: 6%
- Frames & gaskets: 5%
- Stack balance: 7%

High Pt loadings are needed due to limited activity and stability of current catalysts for the oxygen reduction reaction (ORR) at the cathode of polymer electrolyte fuel cells (PEFCs)

Concepts to improve Pt Activity (BOL/EOL)

Reduction of high Pt use in PEFCs

Increasing catalyst activity
(mass activity of $0.44 \text{ A/mg}_{\text{Pt}} @ 0.9 \text{ V}_{\text{RHE}})^2$

Increasing catalyst/support stability
(end-of-life mass activity $> 0.25 \text{ A/mg}_{\text{Pt}})^2$

High Pt dispersion

Pt-NNM (non noble metal) alloys

Low surface area graphitized supports

Conductive metal (oxide) supports

Unsupported/nanostructured catalysts

Research on unsupported Pt-NNM alloy catalysts
Research on Pt supported on metal oxides

1. Alternative Supports (Carbon-free)

- Pt
- Carbon
- Non-carbon support, e.g. metal oxide

Binninger et al., Chem. Mater. (2017)

Sketch not to scale
Concepts to Overcome Pt/C Stability Limits

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Binninger et al., Chem. Mater. (2017)

2. No Supports

- Pt
- Carbon

3M NSTF

M. Debe et al., ECS Trans. 2006, 3(1), 835-853
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W. Liu et al., Angew. Chem. 52 (2013) 9849
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Pt degradation mechanisms

1. Pt dissolution into the electrolyte: $Pt \rightarrow Pt^{2+} + 2e^-$
   - Loss of Pt mass
   - Loss of Pt surface area
   - Shrinkage/disappearance of Pt nanoparticles

2. Pt dissolution and redeposition on larger Pt particles
   (Electrochemical Ostwald ripening)
   - Loss of Pt surface area
   - Shrinkage/disappearance of small Pt nanoparticles
   - Growth of large Pt nanoparticles
   - Shift Pt particle size distribution to larger diameters

3. Support corrosion
   - Collapse of electrode structure
   - Agglomeration of Pt nanoparticles
   - Loss of electrochemically active Pt surface area
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In situ Anomalous SAXS study of support-dependent Pt degradation

Catalysts:
- 20 wt.% Pt/C (Vulcan)
- 20 wt.% Pt/C (graphite onions)
- 10 wt.% Pt/Sb\textsubscript{0.1}Sn\textsubscript{0.9}O\textsubscript{2}

Binninger et al., JES 163 (2016) H906
Binninger et al., Chem. Mater. 29 (2017) 2831
The Technique II: Small-Angle X-ray Scattering

Small-Angle X-ray Scattering (SAXS):

• XRD scattering angles $2\theta \leq 5$-$10^\circ$
• SAXS pattern is determined by the central forward scattering peak
• Information about catalyst particle size and shape at the **nanometer scale**
• Pt nanoparticle size distribution
• Statistical properties of **entire** catalyst sample (TEM: individual particles)
• Quantitative information: Total Pt mass in nanoparticle phase
Start/Stop degradation protocol:
1000 CV cycles at 50 mV/s between
0.5 $V_{RHE}$ — 1.5 $V_{RHE}$ in 0.1 M HClO$_4$
Analysis of ASAXS Results

• Under chosen experimental conditions, mainly Ostwald ripening is occurring
• ATO supported Pt: Ostwald ripening is suppressed
Explanation: Electrochemical Transistor Effect

Sb$_{0.1}$Sn$_{0.9}$O$_2$ n-type semiconductor / electrolyte interface

Open Circuit (equilibrium)

Potential control (closed circuit)

U < $U_{fb}$  

U = $U_{fb}$ (flat-band potential)  

U > $U_{fb}$

Explanation: Electrochemical Transistor Effect

\[ U < U_{fb} \]

Switch: ON

Protection of Pt nanoparticles from dissolution at high potentials

\[ U > U_{fb} \]

Switch: OFF

\[ U_{fb} \approx 0.85 \text{ V} \]

Binninger et al., Chem. Mater. 29 (2017) 2831
• Transition metal oxides are significantly enhancing stability of PEFC cathodes

• Specifically semi-conducting oxides (n-type) with high flat band potential are very promising
  – Electrochemical transistor effect protects Pt NP from dissolution
  – Reducing support conductivity at potentials above the flat band potential basically disconnects Pt NP electrically, therefore particle stability is enhanced
1. Alternative Supports (Carbon-free)

Pt

Carbon

non-carbon support
e.g. metal oxide

Binninger et al.,

Pt

sketch not to scale

2. No Supports

Pt

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Metal aerogels

W. Liu et al., Angew. Chem. 52 (2013) 9849
Activities of Pt/alloys

Volcano plot assembled based on
Stephens et al., EES 5 (2012) 6744
Liu et al., Angew. Chem. 52 (2013) 9849
Henning et al., JES 163 (2016) F1;

Aerogel data:

Activity vs Pt @ 0.9V

$\Delta G_{OH^*}$, $\Delta G_{Pt}$ [eV]

Overpotential determined by

$\Delta G_1$ $\Delta G_2$

PtCu aerogel
PtPd aerogel
Pt$_3$Y
PtCu$_{dealloyed}$
Pt$_3$La
Pt$_3$Fe
Pt$_3$Ni
Pt$_3$Sc
Pt$_3$Ti
Pt/In(111)
Pt/Pd(111)
Pt/C
Pt/Pd(Pt,Fe,Fe)(111)
Pt/Au(111)
Pt/Au(111)
Pt/Ir(111)

Aerogel data:
Liu et al., Angew. Chem. 52 (2013) 9849
Henning et al., JES 163 (2016) F1;

Reaction coordinate

$\Delta G_1$ $\Delta G_2$

$O_2 + 4H^+ + 4e^-$
$OOH^* + 3H^* + 3e^*$
$O^* + H_2O + 2H^* + 2e^*$
$OH^* + H_2O + H^* + e^*$
$2H_2O$

### Activities of Pt/alloy 'nano-systems'

<table>
<thead>
<tr>
<th>Alloy Type</th>
<th>Reference(s)</th>
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<tbody>
<tr>
<td>PtNi/C [78,79]</td>
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<tr>
<td>Pt/C TKK (TEC1050E) [74,75]</td>
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<tr>
<td>MSTF PtNi [26]</td>
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<td>Pt&lt;sub&gt;80&lt;/sub&gt;Pd&lt;sub&gt;20&lt;/sub&gt; aerogel [22]</td>
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<td>PtNi nanowires [69]</td>
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<td>PtCo nanowires [31]</td>
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<td>PICu aerogel [24]</td>
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<td>Nanoporous Pt&lt;sub&gt;Ni&lt;/sub&gt; [80]</td>
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<td>Double gyroid PtNi [62]</td>
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<td>Pt&lt;sub&gt;3&lt;/sub&gt;Ni aerogel [23]</td>
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<td>Hollow PtFe nanocapsules [33]</td>
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<td>PtCu nanowires [30]</td>
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<td>Double gyroid Pt [28]</td>
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<td>NSTF PtCoZr [25]</td>
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<td>Pt nanotubes [64]</td>
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<td>NSTF Pt&lt;sub&gt;Co&lt;/sub&gt;Ni [25]</td>
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<td>Pd aerogel [22]</td>
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<td>PtPdCo nanosponge [51]</td>
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From Model to PEFC Studies: PtNi Aerogel as Example

I. Synthesis & Characterization

II. RDE Test

III. FC Test

Novel unsupported ORR catalysts

“Rigorous MEA testing and characterization must be included early in the development process, as was demonstrated in the past decade with the Pt alloy catalysts.”

Moving from C-supported to unsupported catalysts changes the catalyst layer properties.

- **Pt/C**
  - Thickness: \(\approx 30 \, \mu\text{m/mg}_{C}\)
  - Hydrophilicity: Hydrophobic (C-support) & hydrophilic (Pt nanoparticles)
  - Porosity/Pore size distribut.: Porosity provided by C-support

- **Pt\(_3\)Ni aerogel**
  - Thickness: \(\approx 4 \, \mu\text{m/mg}_{Pt}\)
  - Hydrophilicity: hydrophilic (Pt\(_3\)Ni nanochain)
  - Porosity/Pore size distribut.: Porosity through self-supportability

Different electrical & proton conductivity and mass transport efficiency (reactants & water) anticipated for these systems.

FC performance of aerogels was enhanced by adding removable porosity increasing filler.

**FC performance Pt₃Ni aerogel cathodes**

![Graph showing FC performance of Pt₃Ni optimized cathodes compared to Pt/C and Pt₃Ni cathodes.](image)

- **Potential [V_RHE]**
  - Pt₃Ni optimized
  - Pt/C
  - Pt₃Ni

- **H₂/crossover-free current density [A cm²]**
  - Pt₃Ni optimized
  - Pt/C
  - Pt₃Ni

- **N₂-potential [mV]**
  - Pt₃Ni optimized
  - Pt/C
  - Pt₃Ni

**Preparation procedure Pt₃Ni optimized cathodes**

- Ink prep. (incl. K₂CO₃ and Na⁺-exchanged Nafion)
- Spraying on Nafion XL membrane
- CCM washing in 1 M H₂SO₄
- Drying & MEA prep.

**Porosity from cross section SEM images**

- Pt/C
- Pt₃Ni optimized
- Pt₃Ni

FIB SEM tomography indicates shift in pore size distribution for Pt$_3$Ni optimized CLs

- Shift to larger pore sizes for Pt$_3$Ni optimized vs. Pt$_3$Ni
- Majority of porosity present in macroporous regime > 50 nm (molecular diffusion)

Instrument: Zeiss NVision 40
Experiment parameters: Ga$^+$ ion milling at 30kV accelerating voltage, slice thickness ~ 5 nm, SEM acceleration voltage of 1 kV
Pt$_3$Ni aerogel MEAs show superior durability in start-stop durability test

**Start-stop durability test conditions**

- 10,000 potential cycles between 1.0 and 1.5 V at 500 mVs$^{-1}$
- 80°C, 100 % RH, ambient pressure, H$_2$/N$_2$

**Evolution of mass-specific activity and ECSA**

- Retention of MA and ECSA for Pt$_3$Ni aerogel (vs. 50 % loss for Pt/C)

**Beginning & end-of-life I/E curves**

- No decrease of high current density performance for Pt$_3$Ni aerogel

In load-cycle stress tests, Pt₃Ni aerogel mass activity is more severely affected.

**Load-cycle durability test conditions**

- 10,000 potential cycles between 0.6 and 1.0 V at 50 mVs⁻¹
- 80°C, 100 % RH, ambient pressure, H₂/N₂

**Evolution of mass-specific activity and ECSA**

- Severe MA reduction for Pt₃Ni aerogel is related to significant Ni leaching from the alloy
- Particle size effect can explain smaller MA vs. ECSA loss for Pt/C catalyst

**Beginning & end-of-life I/E curves**

- Minor decrease of high current density performance for Pt₃Ni aerogel and Pt/C

Conclusions (2)

**Summary**

- Optimized catalyst layers for Pt$_3$Ni aerogel match Pt/C benchmark mass activity and high current density performance in H$_2$/air I/E curves
- Addition of K$_2$CO$_3$ to catalyst inks leads to shift of pore size distribution towards larger pores
- Pt$_3$Ni aerogel MEAs show superior durability vs. Pt/C benchmark in start-stop stress test

**Outlook**

- Tuning of Pt$_3$Ni aerogel structure to minimize Ni dissolution
- Explore lower loading limits for catalyst layers
- Implementation of aerogels as anode catalysts (≤ 0.05 mg$_{Pt}$/cm$^2$) in the PEFC and anode fuel starvation tests
Overall Summary

• Designing transition-metal oxide supports with flat-band potentials > 0.9 V might be a way to protect Pt-nanoparticle dissolution

→ Electrochemical Transistor Switching

• Unsupported metallic Aerogels are very durable cathode and anode catalysts, specifically under high potential excursions (Start/Stop operation and gross fuel starvation)
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