NANO-ENGINEERED MATERIALS FOR ENERGY
STORAGE AND CONVERSION APPLICATIONS:
FUEL CELLS AND ULTRACAPACITORS

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Greenhouse gases\(^1\) and declining world oil production\(^3,4\)

\(^1\)Intergovernmental Panel on Climate Change (2007)
\(^2\)Energy Information Administration (2004)
\(^3\)2005 Annual Energy Outlook, US DOE
\(^4\)BP Statistical Review of World Energy, June 2008
**Electrochemical Devices**

**Meeting perennial energy demand using Sustainable Green Technology**

**Polymer Electrolyte Membrane Fuel Cell**

- Membrane conducts protons from anode to cathode

**Electric Double Layer Capacitor**

- Ionic migration towards oppositely charged electrodes

<table>
<thead>
<tr>
<th>Properties</th>
<th>PEM Fuel Cell</th>
<th>EDLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency (%)</td>
<td>35-60</td>
<td>&gt; 90</td>
</tr>
<tr>
<td>Emissions</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Noise level</td>
<td>60 dB</td>
<td>None</td>
</tr>
<tr>
<td>Operating temperature</td>
<td>60-90°C</td>
<td>RT</td>
</tr>
<tr>
<td>Scalability</td>
<td>1-10^6 W</td>
<td>Modular</td>
</tr>
</tbody>
</table>
Challenges for PEM Fuel Cells

Many issues need to be overcome before fuel cells are commercialized

1. **Cost**: Platinum catalyst, bipolar plates\(^1\), Nafion\(^\text{®}\) membrane etc.

2. **Durability/Lifetime**: Material degradation – upon extended operation\(^1,\,^2\)

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\(^1\)S. Satyapal, *DOE H\(_2\)* Program & Vehicle Technologies Program, Annual Merit Review (Arlington, VA) 2009

Platinum Monolayer Electrocatalysts for O$_2$ Reduction: Pt Monolayer on Carbon-Supported PdIr Nanoparticles$^{1, 2}$

Stable nanoparticles resistant to oxidation and Pt dissolution (Core/shell)

$^1$Ph.D. Thesis: Seth Knupp, CNSE, 2010. $^2$In Collaboration with Brookhaven National Laboratory
Nano-engineering of $\text{Pt}_{\text{ML}}\text{Pd/C}$ via introduction of Ir sublayer to enhance ORR activity

- Pd surface modification via introduction of smaller atoms (Ir) leading to:
  - Creation of a compressive strain on Pd and hence the Pt
  - Lowering the d-band center, $\varepsilon_d$, hence lowering ORR intermediate adsorption

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TEM: Pt\textsubscript{ML}PdIr/C

EDS of nanocatalyst

EDS confirms presence of Pt, Ir, and Pd within metallic nanoparticles

Continuous lattice fringes at interface
Enhancement in ORR kinetics for $\text{Pt}_{\text{ML}}\text{PdIr/C}$ vs. Pt/C and $\text{Pt}_{\text{ML}}\text{Pd/C}$

$\text{Pt}_{\text{ML}}\text{PdIr/C}$ shows delayed oxidation vs. Pt/C and $\text{Pt}_{\text{ML}}\text{Pd/C}$ (ECSA)

First to demonstrate use of $\text{Pt}_{\text{ML}}\text{PdIr/C}$ as a cathode catalyst showing a 5x improvement in mass activity – meeting DOE target

**Specific activities**
Calculation based on ECSA

**Pt-mass activity**
Pt determined from $Q_{\text{H-Des}}$

**Price adjusted mass activity**
5 yr. avg.  Pt  Pd  Ir
$\text{oz}^{-1}$  1250  309  375

<table>
<thead>
<tr>
<th>ID</th>
<th>$j_s$ (mA cm$^{-2}$)</th>
<th>$i_m$ (A mg$^{-1}_{\text{Pt}}$)</th>
<th>$i_{\text{PGM}}$ (A mg$^{-1}_{\text{Pt}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.30</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>$\text{Pt}_{\text{ML}}\text{Pd/C}$</td>
<td>0.72</td>
<td>1.64</td>
<td>0.37</td>
</tr>
<tr>
<td>$\text{Pt}_{\text{ML}}\text{PdIr/C}$</td>
<td>0.94</td>
<td>2.17</td>
<td>0.43</td>
</tr>
<tr>
<td>DOE Target 2010</td>
<td>0.72</td>
<td>N/A</td>
<td>0.44</td>
</tr>
</tbody>
</table>

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Development of Durable Titanium Nitride Based Electrocatalysts for PEM Fuel Cells

Schematic of Pt/C

Before cycling

After cycling

Electrode degradation by Pt agglomeration, Pt dissolution, and carbon support corrosion under corrosive operating conditions

1Ph.D. Thesis: Bharat Avasarala, CNSE, 2010-11

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Surface Oxidation of Carbon During Potential Cycling

Potential cycling of carbon electrode (no Pt)

Surface Oxide Peak

\[ \text{C}=\text{O} + \text{e}^- + \text{H}^+ \rightarrow \text{C} \text{-OH} \]

Surface charge density vs. time

Increase in O$_2$ for different potential cycling conditions

<table>
<thead>
<tr>
<th>Carbon Black Electrode</th>
<th>O/C Ratio (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.01</td>
</tr>
<tr>
<td>Potentially Cycled</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Need a novel support capable of withstanding corrosive & repeat cyclic conditions

Novel Catalyst Support Material: Titanium Nitride

TiN Crystal structure
Crystal lattice (NaCl type)
● = N; O = Ti

50 nm

TiN Nanoparticles

Anodic Corrosion Curve for C and TiN

- Av. TiN particle size: 20 nm
- Sp. surface area: 55 m²/g
- TiN more resistant to oxidation than C
- Highly inert: triple bond, strong interaction between Ti 3d – N 2p
- Metallic nature: Electrical conductivity (4000 S/cm vs. 1150 S/cm for C)

Inert and conductive, oxidation resistant ➔ good catalyst supports (TiN NP)

1Oyama, The Chemistry of Transition Metal Carbides & Nitrides (1996)
3NanoAmor, Inc (USA)
Kinetics and Catalytic Activity: Pt/C vs. Pt/TiN

Pt/TiN Synthesis: Organo-metallic polyol process

CV curve for Pt/C and Pt/TiN

ORR curve for Pt/C and Pt/TiN

Enhancement in ECSA for Pt/TiN (88.2 m²/gₚt vs. Pt/C (66.1 m²/gₚt))

Pt/TiN shows delayed oxidation vs. Pt/C


Surface Characterization of Pt/C and Pt/TiN

### XPS of Pt/C

![Graph of Pt/C XPS]

### XPS of Pt/TiN

![Graph of Pt/TiN XPS]

<table>
<thead>
<tr>
<th>Pt groups</th>
<th>Binding Energy, eV 4f_{7/2} (At % in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt/TiN</td>
</tr>
<tr>
<td>Pt</td>
<td>71.90 (86%)</td>
</tr>
<tr>
<td>PtO or PtOH</td>
<td>73.20 (13.8%)</td>
</tr>
<tr>
<td>PtO₂ or Pt(OH)$_2$</td>
<td>-</td>
</tr>
<tr>
<td>Surface Pt At%</td>
<td>10.5 %</td>
</tr>
</tbody>
</table>

Higher catalytic performance in TiN due to (i) greater % of Pt(0), (ii) absence of Pt oxides, and (iii) minimal support corrosion

B. Avasarala and P. Haldar, Comparison of Pt/TiN and Pt/C electrocatalysts, *in preparation*
Electric Double Layer Capacitor Development

Novel High Voltage Window Electrodes* (Porous Silicon with tailored porosity) and Electrolytes* (high conductivity Room Temperature Ionic Liquids) for High Energy Density EDLCs

Electrolyte Development

- Parent Compound: Spirobipyridinium
- Modifications to Parent Compound

Electrode Development

- p-type wafer nano pores
- n-type wafer micro pores

* Work of Thamarai selvi Devarajan and Seiichiro Higashiya
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Novel Ionic Liquid Electrolyte Development

Novel Ionic liquids synthesized in-house (white)

<table>
<thead>
<tr>
<th>Salt</th>
<th>X</th>
<th>R2</th>
<th>R4</th>
<th>R5</th>
<th>A-</th>
</tr>
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<tbody>
<tr>
<td>SBP BF₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>BF₄</td>
</tr>
<tr>
<td>OP BF₄</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>BF₄</td>
</tr>
<tr>
<td>OP BF₃C₂F₅</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>BF₃C₂F₅</td>
</tr>
<tr>
<td>OP NTf₂</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>NTf₂</td>
</tr>
<tr>
<td>2MOP BF₄</td>
<td>CH₂</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>BF₄</td>
</tr>
<tr>
<td>2MOP BF₃C₂F₅</td>
<td>CH₂</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>BF₃C₂F₅</td>
</tr>
<tr>
<td>2MOP NTf₂</td>
<td>CH₂</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>NTf₂</td>
</tr>
<tr>
<td>2EOP BF₄</td>
<td>CH₂</td>
<td>Et</td>
<td>H</td>
<td>H</td>
<td>BF₄</td>
</tr>
<tr>
<td>4MOP BF₄</td>
<td>CH₂</td>
<td>H</td>
<td>Me</td>
<td>H</td>
<td>BF₄</td>
</tr>
<tr>
<td>5MOP BF₄</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>BF₄</td>
</tr>
<tr>
<td>5MOP NTf₂</td>
<td>CH₂</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>NTf₂</td>
</tr>
<tr>
<td>SBO BF₄</td>
<td>O</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>BF₄</td>
</tr>
</tbody>
</table>

- 6/11 with MP < 100°C
- VW ≥ 7V in 7/11 (LSV)
- Temperature stability range: RT to 300-400°C
- Solubility range: in acetonitrile up to 4 M

MP: Melting point, VW: Voltage window, LSV: Linear Sweep Voltammetry
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Limitations of Activated Carbon Electrode

- Energy and Power density of EDLC\(^1\) is mainly dependent on cell potential
  \[ E = \frac{1}{2} CV^2 \text{ and } P = \frac{V^2}{4 \times ESR} \]

- Carbon EDLC breakdown voltage \( \geq 2.7 \text{ V} \)
- Numerous surface functionalities
- Un-optimized pore structure of carbon limits the capacitance

\[ \begin{align*}
E &= \text{Energy Density, } C = \text{Capacitance} \\
V &= \text{Cell Potential, } P = \text{Power Density} \\
ESR &= \text{External Series Resistance}
\end{align*} \]

Require an electrode capable of withstanding high voltage, and tailorable pore size that matches with ion size in electrolyte

\(^1\)EDLC: Electric Double Layer Capacitor
Benefits of Porous Silicon

- Simple fabrication process
  - Imparts nanoscale control over microstructure
  - Chemical inertness imparts higher voltage window

### Anticipated energy density with porous silicon electrode

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Activated Carbon</th>
<th>Porous Silicon*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>2.7 V</td>
<td>5 V</td>
</tr>
<tr>
<td>Capacitance</td>
<td>125 F/g</td>
<td>300 F/g</td>
</tr>
<tr>
<td>Energy Density</td>
<td>0.126 KWh/Kg</td>
<td>1.04 KWh/Kg</td>
</tr>
</tbody>
</table>

* Anticipated values for porous Silicon.

8X Improvement in energy density using porous silicon electrode
Summary and Future Directions

Core Shell Structures
- Introduced Ir into the Pd substrate to fine-tune the Pt-Pd interactions, and to improve stability under operating conditions of a fuel cell
- Observed enhanced ORR kinetics on Pt\textsubscript{ML}PdIr surfaces in comparison with Pt/C and Pt\textsubscript{ML}Pd/C surfaces.
- Reduced oxidation of Pt\textsubscript{ML}PdIr/C compared to Pt/C and Pt\textsubscript{ML}Pd/C is the cause of enhanced activity

TiN Catalyst Support
- Identified TiN nano particle as a potential catalyst support for PEMFC
- Higher catalytic performance due to higher % of Pt(0), absence of Pt oxides & minimal support corrosion
- Enhancement in ECSA for Pt/TiN (88.2 m\textsuperscript{2}/g\textsubscript{Pt} vs. Pt/C(66.1 m\textsuperscript{2}/g\textsubscript{Pt})
- Pt/TiN shows delayed oxidation vs. Pt/C

Novel Ionic Liquid Electrolytes and Porous Silicon Electrodes
- Developed 11 novel ionic liquid electrolytes with high voltage window
- Optimized 8X Improvement in energy density using porous silicon electrode

Future Directions
- Creation of Core-shell Pt nano catalysts on TiN support
- Development of high temperature EDLC using p-SI electrodes and ionic liquid electrolyte
• CNSE is the first college (established 2004) in the world dedicated to nanotechnology with constellations in:
  ◦ Nanoscience
  ◦ Nanoengineering
  ◦ Nanobioscience
  ◦ Nanoeconomics

Leveraging resources to establish effective partnerships that will enable realization of *industry* technology commercialization and pioneering nanoscale research.

Faculty: 55+
Students: 150+
Staff: 300+
Degrees: B.S., M.S., Ph.D.
Patents: 200+
Reports directly to SUNY Chancellor
$60M + in Research Contracts
- 800K Sq Ft cutting-edge facilities (with 80,000 Sq Ft -300 mm Cleanrooms)
- Partners include SEMATECH, IBM, AMD, Micron, Infineon, Tokyo Electron, and ASML, US Army, NIST and others
- AMD (Global Foundries to build new fab in Saratoga, NY)
- Over $5.0 B in assets, 2,500 + employees within the complex
Energy & Environmental Technology Applications Center

- Created in 1998 as an active expansion of CNSE
- Leverages CNSE’s intellectual power base and state-of-the-art infrastructure to integrate new technologies to advanced energy and environmental applications through:
  - Technology Development
  - Education and Outreach
  - Business Acceleration

- E2TAC focuses on developing clean energy and environmentally-friendly technologies
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