C-cp-Ag Composite Electrodes: A New Approach for Metal Air Batteries

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Metal-air batteries provide the opportunity for unprecedented energy density improvements.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Voltage (V)</th>
<th>Capacity (Ah/kg)</th>
<th>Energy (Wh/kg)</th>
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</thead>
<tbody>
<tr>
<td>Li / (CF)ₙ</td>
<td>3.1</td>
<td>860</td>
<td>2,180</td>
</tr>
<tr>
<td>Li / SOCl₂</td>
<td>3.7</td>
<td>450</td>
<td>1,470</td>
</tr>
<tr>
<td>Li / MnO₂</td>
<td>3.5</td>
<td>310</td>
<td>1,010</td>
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<tr>
<td>Li-ion</td>
<td>3.8</td>
<td>150</td>
<td>570</td>
</tr>
<tr>
<td>Li / O₂</td>
<td>3.4</td>
<td>3,860</td>
<td>13,000</td>
</tr>
<tr>
<td>Al / O₂</td>
<td>2.3</td>
<td>2,990</td>
<td>6,900</td>
</tr>
<tr>
<td>Mg / O₂</td>
<td>2.7</td>
<td>2,200</td>
<td>5,950</td>
</tr>
<tr>
<td>Zn / O₂</td>
<td>1.3</td>
<td>820</td>
<td>1,070</td>
</tr>
</tbody>
</table>

Conventional electrode fabrication

**Conventional electrode**
- silver = active material
- black = conductive additive
- yellow = insulating binder
- tan = metal foil current collector

**Novel composite electrode**
- black = conductive carbon
- red = conductive polymer
- silver = catalyst

planar (2D) — 3D
Our composite electrode strategy offers several advantages

Electrochemical deposition of layers ensures good electrical contact among composite electrode components and electrolyte.

This is a transferrable concept that can be extended to prepare 2D and 3D layered composite electrodes.

Depending on the nature of the current collector (cc), and conducting polymer (cp), morphology and porosity of the layered composite can be tuned.

Due to the conductive nature of the composite, even small quantities of catalyst (Ag) should exhibit high oxygen reduction activity.
Project objectives

i. Demonstrate new composite electrode based on carbon-conductive polymer-silver (C-cp-Ag) composite.

ii. Evaluate composite oxygen reduction activity.

iii. Assess roles of composite components.

iv. Investigate non-aqueous oxygen reduction mechanism.

v. Develop and investigate 3D C-cp-Ag composite.
Electrodeposition is desirable for fabrication.
C-cp-Ag prep can be quantitatively controlled

\[ \Delta f = \frac{-2f_0^2}{A\sqrt{\mu p}} \Delta m \]

- **cp deposition**
- **Ag deposition**

\[ q = n \cdot F \]

### cp deposition
- Current vs. potential
- Mass vs. cycle number

### Ag deposition
- Ag by charge vs. Ag by CP
- EQCM mass and Faraday mass
- Ag loading vs. scan rate

<table>
<thead>
<tr>
<th>EQCM mass (µg)</th>
<th>trial 1</th>
<th>trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19.0</td>
<td>5.94</td>
</tr>
<tr>
<td>Faraday mass (µg)</td>
<td>21.7</td>
<td>6.75</td>
</tr>
<tr>
<td>Δ (%)</td>
<td>12.5</td>
<td>12.0</td>
</tr>
</tbody>
</table>
C-cp-Ag compares favorably to benchmarks

C-cp-Ag composite shows activity
2.6x higher than C
1.4x higher than Pt
comparable to Au
C-cp-Ag composite shows catalytic activity

C-cp-Ag composite electrodes retain high oxygen reduction capability on multiple cycling.
Low Ag loading is required for optimization.

Response optimized at Ag loading of 0.08 mg/cm².

Activity in air was 20 – 40% of the activity in pure oxygen.

Using density of Ag metal, suggests that 80 nm is minimum Ag thickness required.
kinetics:

C-cp-Ag shows well behaved ORR
linear response to $[O_2]$, consistent with 1$^{st}$ order process

C-cp-Ag shows enhanced activity at all $[O_2]$ Ag loading of 0.3 mg/cm$^2$ for C-cp-Ag composite
C-cp-Ag and Au-cp-Ag show similar profiles

cp, then Ag deposition

cp coating mitigates impact of substrate
C-cp-Ag composites are robust

demonstrated macroscopic and microscopic Ag (and activity) retention after physical stresses

<table>
<thead>
<tr>
<th>number</th>
<th>12</th>
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<tbody>
<tr>
<td>average</td>
<td>73%</td>
</tr>
<tr>
<td>median</td>
<td>72%</td>
</tr>
<tr>
<td>st. dev.</td>
<td>8.7%</td>
</tr>
</tbody>
</table>
3D C-cp-Ag electrodes can be fabricated

Achieved successful cp and Ag-cp deposition on non-planar (3D) substrates of varying geometry and porosity.
3D C-cp-Ag electrodes can be fabricated

<table>
<thead>
<tr>
<th>electrode</th>
<th>electrode surface area (cm²)</th>
<th>electrode surface area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>reported</td>
<td>planar</td>
</tr>
<tr>
<td>C</td>
<td>0.071</td>
<td>0.069</td>
</tr>
<tr>
<td>Cfelt</td>
<td>121</td>
<td>1.0</td>
</tr>
</tbody>
</table>

estimated cp thickness ~4X greater for C than for Cfelt

electrochemically active surface area reduced 20% for C, > 40% for Cfelt
3D C-cp-Ag composite electrodes

For C-cp-Ag composites, use of 3D substrates provided 4X improvement over 2D substrates based on planar area.

There is opportunity to further improve homogeneity of the 3D composite.
3D C-cp-Ag composite electrodes

Cycle 1 – 2 peak Coulomb flux was unchanged for the planar C-cp-Ag electrode, while the 3D Cfelt-cp-Ag composite showed a significant decrease.

Difference is consistent with reduction on the surface and interior during cycle 1, with surface only on cycle 2.


4) “Three dimensional carbon-conductive polymer-silver (C-cp Ag) composite electrodes for metal-air batteries.” *J. Composite Materials.* **in press.**

5) “Secondary Battery Science: At the Confluence of Electrochemistry and Materials Engineering.” *Electrochemistry.* **in press.** (invited highlight)

6) “Mechanistic investigation of the oxygen reduction reaction on carbon-conductive polymer-silver composites.” **in preparation.**

7) “Activation energy of oxygen reduction on carbon substrates in nonaqueous media.” **in preparation.**

**Patent**

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