Multifunctional Electrodes for Structural Energy & Power

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It is not sufficient to solely design a material for its capacity or electrochemical performance for structural energy and power. One must consider *mechanical* properties as well.
Flexible for Electronics

Multifunctional Energy and Power

Structural for Aircraft and Ground Transportation

Stretchable and Elastic Biometrics

An, Lutkenhaus Scientific Reports 2015.
Not One Battery Can Fulfill All Requirements

LiCoO$_2$

LiFePO$_4$

LiNiMnO

Q: How do the radar charts change when mechanical properties are considered?
A: Not much, because transition metal oxides are inherently brittle
How does this plot change when mechanical properties are one of the axes?
Where are the Opportunities?

• Opportunities for structural enhancement exist at the electrode and the electrolyte.
• Current approach relies on external packaging, adding unnecessary weight.

Hyosung An (Lutkenhaus Lab)
Electrochemical vs. Mechanical Properties for Electrodes

![Graph showing specific energy vs. toughness for different materials]

- V$_2$O$_5$ wire
- V$_2$O$_5$/poly LiCoO$_2$
- Buckypaper (MWNT)
- LiCoO$_2$
- Graphene
- TiO$_2$/carbon fabric
- SnO$_2$/CNT + cellulose
- Buckypaper (SWNT)
- Graphite/CNT


Structural Materials for Mechanical Enhancement

In the Electrode:
- Carbon Nanotubes
- Carbon Fibers
- Functionalized Graphene Sheets
  - Ruoff et al. *Nano Lett.* 2008

In the Electrolyte:
- Glass Fiber
Towards a Quantitative Metric of Multifunctionality

\[ \eta_{mf} \equiv \eta_s + \eta_e > 1 \]

<table>
<thead>
<tr>
<th>Multifunctional Efficiency</th>
<th>Structural Efficiency</th>
<th>Energy Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical Property of M.F</td>
<td>Electrical Property of M.F</td>
<td>Energy, Power, Capacity, Capacitance (per mass)</td>
</tr>
<tr>
<td>Mechanical Property of Norm</td>
<td>Electrochemical Property of Norm</td>
<td></td>
</tr>
</tbody>
</table>

When \( \eta_{mf} > 1 \), mass-savings is possible

On-going Projects in Structural Energy and Power in the Lutkenhaus Lab

• Kevlar® aramid nanofiber – modified electrodes

• Electroactive, mechanically enhancing polymeric electrode binders

• Spray-on electrodes for high-surface area application
Kevlar® aramid nanofiber – modified electrodes

- Research question: Will Kevlar® aramid nanofibers, discovered recently in 2011, expand our structural materials portfolio?

**Kevlar® Thread**
- Famously used in bullet-proof vests
- High tensile modulus and strength (185 GPa and 4 GPa, respectively)

**Kevlar® Aramid Nanofibers**
- Nanoscale version of Kevlar®
- Made by treatment of Kevlar® thread with base
- Potential nanocomposite filler


Kevlar® Aramid Nanofiber (ANF)/Functionalized Graphene Sheet Paper Supercapacitors

Vacuum filtration

ANF
Graphene Oxide

0 wt% ANF (100 wt% GO)

1 um

In Preparation
Multifunctional Efficiency

- Multifunctional efficiency increases with increasing aramid nanofiber content

- (Structural efficiency scaled against 13.5 GPa)

- (Energy efficiency scaled against RGO capacitance)

$\eta_{mf} > 1$, mass-savings is possible

In Preparation
The Promise of V$_2$O$_5$

- Layered metal oxide
- Stores charge by Li$^+$ intercalation
- High initial capacity (340-1240 mAh/g)

\[ V_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xV_2O_5 \]

...And Its Problems

- Volume expansion
- Low ionic and electronic conductivity

Verduzco and Lutkenhaus et al. Scientific Reports 2015.
A Polymer Binder with Both Ionic and Electronic Conductivity

- Domains of ionic conductivity – PEO
- Domains of electronic conductivity – P3HT

Poly(3-hexylthiophene)-block-poly(ethylene oxide) - P3HT-b-PEO

And more from the Balsara group.
Scanning Electron Microscopy

- Layered structure, very similar in appearance to Bucky paper and graphene paper

Verduzco and Lutkenhaus et al. Scientific Reports 2015.
Mechanical Performance: Bending Test

- Pristine V$_2$O$_5$ is brittle, hybrid electrodes are flexible
- Flexibility is attributed to the interlocking V$_2$O$_5$ “brick” and polymer “mortar” structure
P3HT-\(b\)-PEO Enhances \(V_2O_5\)’s Flexibility and Toughness

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength(^a)(\sigma) (MPa)</th>
<th>Ultimate strain(^b)(\varepsilon) (m/m)</th>
<th>Normal strain(^b)(\varepsilon_{\text{f}}) (m/m)</th>
<th>Young’s modulus(^b)(E) (GPa)</th>
<th>Toughness(^a)(W) (kJ/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_2O_5)</td>
<td>27±2</td>
<td>0.0048±0.0004</td>
<td>0.8±0.3</td>
<td>6.0±0.7</td>
<td>70±8</td>
</tr>
<tr>
<td>P5</td>
<td>25±1</td>
<td>0.011±0.002</td>
<td>3.4±1.3</td>
<td>3.7±0.9</td>
<td>171±5</td>
</tr>
<tr>
<td>P10</td>
<td>26±2</td>
<td>0.017±0.003</td>
<td>5.6±0.6</td>
<td>3.5±0.3</td>
<td>293±73</td>
</tr>
<tr>
<td>PVdF10(^c)</td>
<td>24.1±0.3</td>
<td>0.0078±0.0006</td>
<td>1.0±0.1</td>
<td>2.9±0.6</td>
<td>99±9</td>
</tr>
</tbody>
</table>

P10: 7x more flexible, 4x tougher than pure \(V_2O_5\)

P3HT-\textit{b}-PEO Halts Volume Expansion in \(V_2O_5\)

After cycling:

- Only 5 wt% polymer is needed to stop electrodes from cracking
- Hybrid electrodes have better long-term cycling behavior
- Capacity is not as high as other reports, but mechanical properties and stability are bonuses

(CR2032 coin cell, lithium metal anode, 1 M LiClO_4 in propylene carbonate, Celgard separator)

Verduzco and Lutkenhaus \textit{et al.} Scientific Reports 2015.
Electrochemomechanical Tradeoffs

- All electrodes are additive free (no PVdF or carbon black)
- P3HT-\textit{b}-PEO imparts significant toughness (and flexibility)

Verduzco and Lutkenhaus \textit{et al.} \textit{Scientific Reports} 2015.
Paintable Batteries: Seamless Integration of Multifunctional Capabilities

- Imagine spray-painting or air-brushing batteries onto any surface
- Sequentially spray the cathode, electrolyte, and anode

Ajayan et al. Scientific Reports 2012.
Spray-on Polyaniline/Graphene Oxide Electrodes

- Follow by electrochemical reduction to reduced GO

Number of cycles

- 20
- 40
- 60
- 80
- 100

1.5 V vs Li/Li$^+$ for 10 h

GO Sheets

67 wt% polyaniline
33 wt% graphene
74 v% void
Challenges and Opportunities

• Simulation models have not adequately captured structural energy and power
• Electrochemical – mechanical coupling not developed
• Structural materials are limited in choice
• Cycling, fatigue, and failure must be considered
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