Electrochemical Supercapacitors in F.E.E.Lab

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Supercapacitors and Applications

Energy Density (Wh/kg)

Power Density (W/kg)

0.01 0.1 1 10 100 1000

Ultracapacitors

Capacitors

Batteries

Fuel cells

From Maxwell Web

From Prof. K. Noai US DOE workshop

1. Modification of Carbon electrodes
   1. Activated Carbon, CNT, graphite nanofibers and onion-like carbon characterization and chemical modification (Prof. Gogotsi, Drexel)
   2. Direct formation of TiNx

2. Solid Polymer Electrolytes
   1. Solid proton conducting electrolytes for thin, flexible devices
   2. Ionic liquid/polymer for high voltage window.

3. Hybrid Device & System
   1. Super thin and flexible symmetrical and asymmetrical EC cells
   2. ANN battery and hybrid cycle life prediction (Prof. Weigert, MST)
   3. Simulation of devices life and thermal properties (Prof. Dawson, ECE, UT)
   4. Hybrid EC with battery, photovoltaic for “self-power” and for extending power/energy efficiency (Prof. Kherani, ECE, UT)
New Advances in Proton Conducting Polymer Electrolytes and their Applications in Ultrahigh Rate Solid Electrochemical Capacitors

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Outline

• Background
  – Ultra-high-rate Solid Electrochemical Capacitors (EC)
  – Heteropolyacid (HPA) as proton conducting electrolytes

• Solid Proton Conducting Polymer Electrolytes

• Solid symmetric ECs
  – Metallic ECs
  – Double Layer ECs
  – Pseudocapacitive ECs

• Expansion of Cell Voltage
  – Alternative Electrolytes
  – Asymmetric
  – Multicell-in-one package

• Summary

• **Key words: high rate, solid/flexible**
State-of-the-Art High Rate ECs

Fast device response, small time constant, high power density

Onion-like carbon

Graphene nanosheets

Reduced graphene oxide

Laser scribed graphene

Advanced electrodes

Liquid electrolytes

Our goal
Flexible/rollable EC devices

Battery – Capacitor Hybrid System

- The thin and flexible ultracapacitor can have various form factor
- It can be readily combined with the energy sources

**2.5 A Pulse, Peak Power > 2.25 W**

- EC+Battery hybrid
- Battery only

**3.6 A Pulse, Peak Power > 3.4 W**

- EC+Battery hybrid
- Battery only
Solid State ECs – polymer electrolytes

To eliminate metal cans and separators to form flexible dry ECC

multicell in one package
Solid Electrochemical Capacitors

RuO$_2$ based solid 10-cell EC
10 V/s


Yuan et.al, ACS Nano 6(1) 656 (2012)


Polymer Electrolytes: PVA-H$_3$PO$_4$
Heteropolyacid (HPA)

- High ionic conductivity at solid state
- Low cost
- Less aggressive chemistry
- Have been considered in fuel cells and sensors

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}<em>3\text{PW}</em>{12}\text{O}_{40} \cdot 29\text{H}_2\text{O} )</th>
<th>( \text{H}<em>3\text{PMo}</em>{12}\text{O}_{40} \cdot 29\text{H}_2\text{O} )</th>
<th>( \text{H}<em>4\text{SiW}</em>{12}\text{O}_{40} \cdot 28\text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton conductivity (S/cm)</td>
<td>0.17</td>
<td>0.18</td>
<td>0.027</td>
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</table>

![Graph showing E (V) vs. Ag/AgCl and I (A*cm⁻²) for different samples.](image)

1. Bare MWCNT
2. Single PMo12
Dependence of the 1\textsuperscript{st} one - e\textsuperscript{-} reduction potentials on the negative charge: 1) \(XW_{12}O_{40}^{n^-}\) and 2) \(XV_{12}O_{40}^{n^-}\)

Graphite cell with H$_2$SO$_4$, PWA and SiWA (EDLC)

0.3 M solution; Sweep Rate = 100 mV/s


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## Issues and Approaches

### Issues of HPAs:
- Poor film forming
  - Often, HPA are pressed as pellets
- Soluble in water
- Sensitive to moisture and temperature

### A good solid electrolyte should possess:
- High ionic conductivity at all temperature range
- High stability and shelf life

### Our Approach:
- Composite with polymer to immobilize the HPAs
- Additives
Composition of Polymer Electrolytes

Our polymer electrolytes are comprised of 3 functional components:

- **Polymer matrix:** Polyvinyl alcohol (PVA)
- **Ionic conductor:** Heteropoly acid, Silicotungstic acid
- **Additives:** Glutaraldehyde, Silica oxide, Phosphoric acid

![Polyvinyl Alcohol Structure]

![Heteropoly Acid Structure]

![Silicotungstic Acid Structure]

\[ H_4SiW_{12}O_{40} \cdot 28H_2O \text{ (SiWA)} \]

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HPA - Polymer Systems

HPA + additives + Polyvinyl alcohol
(>90 wt.%) (<10 wt.%)  

- Lower HPA sensitivity on environment  
- Form thin film electrolyte  
- Achieve better electrode/electrolyte contact

Gen I

- SiWA + PVA

Gen II

- SiWA + H₃PO₄ + PVA

Gen III

- SiWA + H₃PO₄ + Crosslinked-PVA (XL-PVA)

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Cell Assembly

Electrode (Stainless steel foils or RuO₂ on Ti foils)

Pressure and temperature

Electrolyte coating

Hot-pressing 90 °C

Film lamination

Electrode area 0.8 cm²

Electrolyte thickness ≈ 50 μm

Cell thickness ≈ 0.2 mm

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Proton Conductivity of the Polymer Electrolytes

Stainless Electrodes
Conductivity of Polymer Electrolytes

- Stainless steel electrodes
- Measured in ambient condition

![Conductivity Graph]

- Gen I (SiWA-PVA)
- Gen II (SiWA-H$_3$PO$_4$-PVA)
- Gen III (SiWA-H$_3$PO$_4$-XL-PVA)

Day

Conductivity (S cm$^{-1}$)
0 °C to 50 °C at 50% RH

Arrhenius plot

-5.0
-4.8
-4.6
-4.4
-4.2
-4.0
-3.8
-3.6
-3.4
-3.2
-3.0
-2.8
-2.6

Proton hopping in crystalline material

Conductivity and Stability *(Comparison with Nafion®)*

![Graph showing conductivity and stability comparison between SiWA-H$_3$PO$_4$-PVA cell and Nafion cell over days.](image)

*SiWA-H$_3$PO$_4$-PVA cell*

*Nafion cell*

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Structural Analyses (XRD) (cont)

Hydration  Dehydration  Keggin crystal structure

HPA-PVA (solid)

HPA-XLPVA (solid)

HPA-XLPVA (gel)

No long range order & crystal structure

Solid ECs

- Metallic electrode: Stainless steel
- EDLC electrode: Graphite
- Pseudocapacitive electrode: RuO$_2$, Mo$_x$N
Solid Metallic EDLC

5,000 V/s

Current density (A cm\(^{-2}\))

Cell voltage (V)

- H\(_2\)SO\(_4\)  
- Nafion  
- HPA-XLPVA

Both solid EC devices are tested at an Ultra high Rate of 5000 V/s.

- Polymer electrolyte) have exceeded Nafion® in stability.

Solid Graphite EDLC

Current density (Acm$^{-2}$)
Cell voltage (V)

2.5 mF/cm$^2$

Graphite EDLC: Charge-discharge & EIS

10 ms

5 mA/cm², 2.6 mF/cm²
RuO₂ Solid pseudocapacitor

- Current density vs. cell voltage at 1 Vs⁻¹: 30 mF/cm²
- Current density vs. cell voltage at 5 Vs⁻¹: 10 mF/cm²
- Current density vs. time at 5 Vs⁻¹: 8.3 mA/cm², 32 mF/cm²
- C' and C'' vs. frequency at 100 ms: 10 mF/cm²
Solid vs. Liquid Mo$_x$N EC Cell

Sweep rate = 1 V/s

Sweep rate = 10 V/s

H. Gao, K. Lian, Journal of Power Sources, 222(15) 301 (2013)
Solid EC Cell at High Rates

Sweep rate = 50 V/s

Sweep rate = 100 V/s

H. Gao, K. Lian, Journal of Power Sources, 222(15) 301 (2013)
Solid vs. Liquid EC Cell – EIS Analyses

H. Gao, K. Lian, Journal of Power Sources, 222(15) 301 (2013)

(a) Mo\textsubscript{x}N liquid cell
Mo\textsubscript{x}N solid cell

(b) \[ \tau = 125 \text{ ms} \]
\[ \tau = 10 \text{ ms} \]
Mo\textsubscript{x}N solid cell

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Voltage Window Expansion

Organic or Ionic Liquid Polymer Electrolytes.
Asymmetric Cell
Multi-cell-in-One package
Asymmetrical Polymer-based Capacitor

① Electrode active materials coated on substrate
- Activated/modified carbon
- Mixed metal oxides
- Conductive polymers
- CNT

② Electrolyte coated on electrode active material
- Polymer/acid gel blends
- Thin film polymer electrolyte 30 to 50μm

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Fabrication of Solid Asymmetric Cell

Film conductivity 0.01 S/cm

Thickness 0.4 – 0.6 mm
Solid Asymmetric Ecs (graphite-RuO$_2$)

Solid multi-cell-in-one package ECs

- Multi-cell EC in single packag
  - Two ECs in series (bipolar plate)
  - Smaller device capacitance
  - Higher cell voltage window
Solid Metallic 2-cell-in-1 EC

At 5,000 V/s scan rate

- Increased voltage window and excellent cycle life

Solid Carbon Based 2-cell-in-1 EDLC

Single Cell

2-Cell-in-1 package

Electrodes: Graphite on Stainless Steel foils

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Solid Carbon Based 2-cell-in-1 EDLC

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Solid Carbon Based 2-cell EC (Impedance)

C' (mF cm$^{-2}$) vs. Frequency (Hz)
- Single cell
- Multi-cell

C'' (mF cm$^{-2}$) vs. Frequency (Hz)
- Single cell
- Multi-cell

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Latest: Alkaline based solid electrolyte

50°C to -10°C

Rate: 2000 V/s

Potential / V

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SiWA - H₃PO₄ – PVA electrolytes have been shown to:
1. perform equal or better than liquid aqueous electrolyte;
2. be applicable for both EDLC and pseudocapacitors.
3. store and deliver charge at ultrahigh rates;
4. retain its conductivity and ultrahigh rate capability over time, yielding excellent shelf and cycle life;
5. enable multi-cell ECs in single package without sacrificing rate capability.

Solid polymer electrolytes are viable for high rate and high power energy storage devices.

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Acknowledgement

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  - Han Gao, Sanaz Ketabi, Haoran Wu, Jak Li, Alex Dilio and Blair Decker

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