Fundamentals & Applications of Electrochemical Capacitors

Veronica Augustyn (vaugust@ncsu.edu)
Assistant Professor
Dept. of Materials Science & Engineering
North Carolina State University

~

Advances, Challenges, and Long-Term Opportunities for Electrochemistry
A Chemical Sciences Roundtable
Washington, DC, November 18, 2019
Key Points

**Energy Storage at Electrochemical Interfaces**
- Electrosorption & chemisorption of ions
- Excellent electrochemical reversibility
- No solid state mass transfer limitations

**Devices & Applications**
- High power
- High reliability
- Complementary to batteries; take advantage of batteries for hybrid devices

**Emerging Materials & Concepts**
- New materials & advanced characterization challenge traditional views of surface storage
- Insertion/intercalation processes critical for obtaining simultaneous high energy + high power
- Understanding confinement is crucial
What are electrochemical capacitors? (ultracapacitors, supercapacitors)

**Electric Double Layer Capacitor**
- Capacitance: 3200 F
- Voltage: 2.85 V
- Specific Energy: 6.82 Wh/kg
- Specific Power: 32 kW/kg
- Cycles: 1,000,000
- Weight: 530 g
- Source: Skeleton SCA 3200

**Hybrid Li-ion Capacitor**
- Capacitance: 3300 F
- Voltage: 2.2 - 3.8 V
- Specific Energy: 13 Wh/kg
- Specific Power: 11 kW/kg
- Cycles: 600,000
- Weight: 350 g
- Source: JM Energy 3300F Prismatic

Electrochemical Capacitor Applications

Electrochemical capacitors offer:

• high power densities
  → deliver & accept large currents, quickly
• excellent kinetics
  → high energy efficiency at high power
• intermediate energy densities
  → store energy and power devices
• reliability
  → long lifetime, > 500,000 cycles

Examples of Manufacturers:

Maxwell Technologies
Panasonic
KEMET
muRata
TAIYO YUDEN

Source: Hy-Cap/VinaTech

Market Size: ~ $1 billion (LIBs: ~ $40 billion)
1954: 1st Patent for Electric Double Layer Capacitors (EDLCs) Granted to GE

July 23, 1957

H. I. BECKER

LOW VOLTAGE ELECTROLYTIC CAPACITOR

Filed April 14, 1954

Fig. 1.
Energy Storage Mechanism of EDLCs

Electrosorption of ions (reversible potential-induced adsorption) at a high surface area electrode


Not limited by faradaic charge transfer or solid state mass transfer!
Storing Charge at the Electric Double Layer

Capacitance:

\[
C = \varepsilon \varepsilon_0 \frac{A}{d} = \frac{Q}{V} = \frac{[\text{Coulomb}]}{[\text{Volt}]} = [\text{Farad}]
\]

- **A**: electrode surface area
- **d**: distance b/w electrode & electrolyte, ~ few Å
- **C**: 5 – 20 µF/cm², < 100 F/g

Electrochemical Features of Carbons in EDLCs

Why carbon?
- Relatively high conductivity
- Large surface areas
- Low density
- Good corrosion resistance
- Inexpensive

For EDLCs:
- Surface area ~ 1000 m²/g
- Good intra- & inter-particle conductivity
- Good electrolyte wetting
- Surface free of impurities to prevent self-discharge


### Energy Storage of Batteries vs. EDLCs

<table>
<thead>
<tr>
<th>Battery</th>
<th>EDLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideally constant discharge curve</td>
<td>Intrinsically sloping discharge curve</td>
</tr>
<tr>
<td>May not have good state-of-charge indication</td>
<td>Good intrinsic state-of-charge indication</td>
</tr>
<tr>
<td>Higher energy density</td>
<td>Lower energy density</td>
</tr>
<tr>
<td>Lower power density</td>
<td>Higher power density</td>
</tr>
<tr>
<td>Cycle life limited by redox irreversibility &amp; phase changes</td>
<td>Electrosorption leads to excellent cyclability</td>
</tr>
</tbody>
</table>

**Capacitance** of an ideal EDLC is constant:

$$E = \frac{1}{2} CV^2$$

Energy Storage of Batteries vs. EDLCs

- Thin film Li-ion battery: 70 Wh/kg
- EDLC: 4 Wh/kg

Hybrid Devices: Combining EDLCs with Faradaic Electrodes


Increasing the Energy without Decreasing Power

\[ Energy = \int_0^Q Vdq = \frac{1}{2}QV = \frac{1}{2}CV^2 \]

The energy can be increased by:

- **the capacitance/capacity (electrode)**
  - higher surface area carbons; pseudocapacitive materials (charge transfer via chemisorption, intercalation); pre-lithiated graphite
- **the voltage (electrolyte)**
  - wide potential window ionic liquids

Pseudocapacitance

Reversible faradaic surface reactions (chemisorption) can significantly increase the areal, and thus gravimetric, capacitance.

These processes are not limited by solid state mass transfer!

2D electrochemical chemisorption modeled as Langmuir or Frumkin isotherm:

Formalism developed by Conway, Gileadi, & others in early 1960s

\[
\Au + x\H^+ + xe^- \rightarrow \Au \cdot x\H_{\text{ads}}
\]

\[
\frac{\theta}{1 - \theta} = KC_{H^+}e^{\frac{VF}{RT}} \quad C_P = q_1 \frac{d\theta}{dV}
\]


Pseudocapacitance for Energy Storage: Hydrous RuO$_2$

- First discovered by Trasatti & Buzzanca in 1971 when studying thin film and single crystal RuO$_2$ electrodes in acidic electrolyte. 
- Appears capacitive but with huge surface area normalized capacitance.
- Kinetics not limited by solid state mass transfer.

\[
\text{RuO}_2 \cdot 0.5\text{H}_2\text{O}
\]
Specific capacitance: 720 F/g
Areal capacitance: \(~1,000 \ \mu\text{F/cm}^2\) (activated carbon: 3 – 70 \ \mu\text{F/cm}^2)


Intercalation Pseudocapacitance: Intercalation as Adsorption

- Similarity between ion "sorption" into a bulk intercalation host and 2D adsorption at a surface
- Allows calculation of intercalation capacitance, analogous to pseudocapacitance
- Kinetics not considered "capacitive" due to sluggish solid state diffusion or phase transformations

\[
X - X_0 = \frac{VF}{RT} e\left[-g(X-0.5)\right]
\]

Frumkin intercalation isotherm

\[ M_2 + xLi^+ + xe^- \rightarrow Li_xM_2 \]


Li\(^+\) intercalation into thin-film LiCoO\(_2\)
Concept of intercalation pseudocapacitance is important for achieving simultaneous high power + high energy density:

- Intercalation is a unique mechanism amongst batteries
- Recognizes mechanistic similarity between intercalation and surface adsorption
- Gives pathway for “bulk” energy storage with surface-like kinetics
Solid-Solution Intercalation into a Conductive Host: $\text{Li}_x\text{Nb}_2\text{O}_5$

Importance of Structural Stability for High Power: Proton Intercalation into $\text{WO}_3 \cdot n\text{H}_2\text{O}$

Operando AFM dilatometry shows significant differences in intercalation-induced electrode deformation.

Importance of Structural Stability for High Power: Proton Intercalation into WO$_3$·$n$H$_2$O

At 10 mV/s (70 sec)
- WO$_3$·2H$_2$O exhibits rapid, reversible phase transition as a function of proton intercalation
- WO$_3$ does not completely transform, 2 phases present

At 100 mV/s (7 sec)
- WO$_3$·2H$_2$O still exhibits clear & reversible phase transition
- WO$_3$ appears “frozen,” structure not responding at this rate

Discriminating between Capacitive Mechanisms: Fundamental Nature of Nonfaradaic vs. Faradaic Processes

Nonfaradaic: Capacitance in Sub-nm Pores

Faradaic: Capacitance in Sub-nm Layers


Blurring the Line Between the Electrolyte and the Electrode: Capacitive Mechanisms Under Confinement

Simulated induced charges on carbon walls confining monolayer of ionic liquid:
- **blue**: -0.01 eV
- **red**: 0.01 eV
- **cyan**: intermediate charge

Blurring the Line Between the Electrolyte and the Electrode: Proton Intercalation into Ti$_3$C$_2$T$_x$ MXene

10,000 mV/s = 120 msec

Key Points

Energy Storage at Electrochemical Interfaces

- Electrosorption & chemisorption of ions
- Excellent electrochemical reversibility
- No solid state mass transfer limitations

Devices & Applications

- High power
- High reliability
- Complementary to batteries; take advantage of batteries for hybrid devices

Emerging Materials & Concepts

- New materials & advanced characterization challenge traditional views of surface storage
- Insertion/intercalation processes critical for obtaining simultaneous high energy + high power
- Understanding confinement is crucial


Acknowledgements

Graduate Students
Shelby Boyd
Matthew Chagnot
Ishita Kamboj
James Mitchell
Saeed Saeed
Michael Spencer
Ruocun (John) Wang

Collaborators
Nina Balke, ORNL
Bruce Dunn, UCLA
Yury Gogotsi, Drexel
De-en Jiang, UC Riverside
Jeff Long, NRL
Alexander Kolesnikov, ORNL
Eugene Mamontov, ORNL
Matt Pharr, Texas A&M
Volker Presser, INM Leibniz
Patrice Simon, Université Paul Sabatier
Mike Toney, SLAC

Postdoctoral Fellows
Simon Fleischmann
Alisa Paterson