Materials Design and Diagnosis for Rechargeable Battery Energy Storage

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# The Challenge of Power vs. Energy

<table>
<thead>
<tr>
<th>Power</th>
<th>1</th>
<th>10³</th>
<th>10⁶</th>
<th>10⁹</th>
<th>10¹²</th>
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<tbody>
<tr>
<td>W</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>kW</td>
<td>10³</td>
<td>10⁶</td>
<td>10⁹</td>
<td>10¹²</td>
<td>1</td>
</tr>
<tr>
<td>MW</td>
<td>10⁶</td>
<td>10⁹</td>
<td>10¹²</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>GW</td>
<td>10⁹</td>
<td>10¹²</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>TW</td>
<td>10¹²</td>
<td>1</td>
<td>1</td>
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</tr>
</tbody>
</table>

- **1nJ ~ pWh**
  - 16 hr = 16 Whr
  - 1/60 hr = 16.7 Whr

- **Energy**: 1J = 1W x 1s = 1/3600 Whr

- **1mJ ~ 1uWh**
  - 100kJ (20W*2hr)

- **MJ ~ kWh**
Why No Batteries Last Forever?

Chemical Energy ↔ Electric Energy

Moving Ions (Chemical Bond)
Dynamic Phenomena
Strain - Fatigue
Electrolyte Stability
Cell - Module - Pack (1/2 1/2 rule)

Physics, Chemistry, Materials Science and Various Engineering Disciplines - ALL MUST CONTRIBUTE

Review – Meng and Arroyo Accounts of Chemical Research 2012
The initial discovery of fast ionic transport in solids has started a revolution in battery technology.

... 44 years later the Li-ion technology is still under development.
Negative Press in Media


Positive News from Market

Li Ion Battery Pricing

From Sam Jaffe

Monday, September 8, 14
Li Ion Technology for Transportation

Cost $/kWh
Safety
Cycle Life 10 yr

Novel Materials and Better Engineering to Remove the Barriers

Reduce Cost, Enhance Safety and Extend Cycle-life
Battery Structural Change Often Correlates With Life

Most desirable

ΔG

Li-Ion

Ni-MH

Ni-Cd

Pb-acid

Capacitor

Low energy Li-ion

Structural Change

Long Life

Courtesy of Dr. Ping Liu and Dr. Paul Albertus
Electrolyte Stability Windows – Aqueous

Thermodynamic stability (at pH=0)

Potential vs. NHE (V)

O₂ evolution

H₂ evolution

0 7 14

pH

Solids

Liquids

PbO₂

Ni(OH)₂

Pb

MH

Cd(OH)₂

V⁴⁺/V⁵⁺

Br₂

V²⁺/V³⁺

Quinone

H₂ evolution

O₂ evolution

Courtesy of Dr. Ping Liu and Dr. Paul Albertus
Recent Development – MWh Li Ion Storage

- Increasing grid efficiency, solar and wind means increasing energy storage

**Efficiency > 90%**
Lithium-ion: $500-600/kWh  We Need $100/kWh

AES – U.S.

BYD – China

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http://www.calit2.net/newsroom/ (Oct. 2012)

Real-Time Market vs. Day-Ahead Market

Source: Mnyshenko & Elliott UCSD, 2012
The BEST Na Ion Battery will have the same Energy density as the low-energy Li Ion Battery.

Xu, Lee and Meng., Funct. Mater. Lett. DOI: 10.1142/S1793604713300016

Monday, September 8, 14
Na Ion Battery for MWh Grid Storage

Active material: 2 mg/cm²

High voltage

Excellent retention

Na₂Ti₃O₇ Anode

Al current collector

Na₀.₈₀[Li₀.₁₂Ni₀.₂₂Mn₀.₆₆]O₂ Cathode

Charge

Discharge
Duel Reservoir (traditional)  Soluble Lead (flow assist)


Metal Air Battery - Fuel Cell

**Diagram:**
- **Hydrogen flow field**
- **Air (oxygen) flow field**
- **Water and air**
- **Anode current collector**
- **Cathode current collector**
- **MEA**
- **Hydrogen outlet**
- **Pathways for gas access to electrode**
- **Polymer Electrolyte Membrane**
- **Backbone layer**
- **Membrane/electrode assembly**
- **Backing layer**

**Chemical Reaction:**
\[ \text{CO}_2 + \frac{1}{2}\text{H}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2e^- \]

**Electrodes:**
- **Positive Electrode**
- **Negative Electrode**

**Electrolyte:**
- **YSZ electrolyte**
- **LaMnO_3**

**Temperature:**
- **1000°C**

**Reactions:**
- \( \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{O}^2- \)
- **Excess Air**
A Challenge Since 1975

Can we solve the dendrite problem? Is characterization and theory up to it in 2014?
Battery Structural Change Often Correlates With Life

Most desirable

ΔG

Long Life

Structural Change

Metal Air

Low energy Li-ion

Capacitor

Li-Ion

Ni-MH

Ni-Cd

Pb-acid

Courtesy of Dr. Ping Liu and Dr. Paul Albertus
Ask Ourselves What is Different from 1970s?

- **1980.** LiCoO$_2$
- **1983.** LiMn$_2$O$_4$
- **1997.** LiFePO$_4$
- Mg Ion Electrolyte

**Na Ion Batteries?**

**Mg Ion Batteries?**

**Na Intercalation compounds**

**DISREGARDED**
- Phosphates/Silicates were banned (Poor electronic properties)
- Organic electrodes rapidly sink into oblivion

Arrival of Nano-materials

SUCCESS
- Phosphates are becoming the most praised electrode materials

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Understanding How Materials Function

*In situ* non-destructive analysis at the highest sensitivity, selectivity and spatial and temporal resolution, and detection limits

- **Spectroscopy**
  - photons, x-ray, electron, NMR

- **Microscopy**
  - SPMs, electrons, x-ray, near-field

- **Diffraction**
  - X-ray, electrons, ions, neutrons

**Novel Techniques and Methodologies**

Characterization ↔ Detection

**Materials**
- Crystals and artificial structures
- Electrolytes (disordered structures)
- Phase transitions
- Electronic and magnetic properties

**Target parameters**
- *In situ* sensing/monitoring
- Spatial resolution: sub-Å, below diffraction limit
- Time resolution: fsec
- Higher energy resolution

**Interface**
- Kinetics of surface phenomena
- (Meta)Stability of surface structures
- Competing processes, side-effects
- Transport and response functions
New Advanced Characterization Tools

Aberration Corrected Z-contrast Imaging by STEM
Unprecedented Spatial Resolution - 0.8 A

Source: Xu, Fell, Chi and Meng, Energy and Environmental Science 2011
Accelerating the Search for Novel Materials

Reducing the time 15 - 20 years

Average time from concept of new material to its commercialization

Properties
- Voltage / Capacity
- Structural stability
- Ionic diffusivity

Computables
- Total energies
- Lattice parameters
- Charge density / Electronic structure

Initial Input & Validation (experiments)

Translation

Computation

$H\Psi = E\Psi$
Advances in theory and computational methods, as well as understanding of relevant phenomena in battery materials lead to increased predictability of relevant electrode properties.
Go For Nano

- Minimize diffusion distance
- Phase stability change
- Defect tolerance
- Enable new chemistry

Need to Take Care of

- Stability due to interface
- Packing density (vol. density is key)
- Scalability
Priority Research Directions for Next Decade

Solid State Batteries
Conversion Type
Na & Mg Intercalation
Nano Structured
Safety
Energy
Cost
Power
Roadmap of Energy Storage

- Close the gap on intercalation
- Enable metal anode Li or Zn
- ORR will be the key for any metal air electrochemistry
Energy Storage for A Sustainable Future