Commercialization of the Rechargeable Manganese Dioxide - Zinc Alkaline Battery Chemistry: A Story of Scale Up

Alexander Couzis
Department of Chemical Engineering
The City College of New York
New York, NY 10031
acouzis@ccny.cuny.edu
Electrical Energy Storage: Should we care?

- We store most of our important commodities for use on demand
  - Water, food, air, minerals, etc.
- We maintain an energy stockpile by storing wood, oil, coal, gas, etc.
  - Carbon based fuels are a type of energy storage that took millions of years of achieve. **Extremely slow restocking process.**
  - Carbon based fuels can only produce heat directly. The heat is then converted to mechanical work or electrical energy. **Inefficient (~35-40% efficient)**
- Electrical energy can be stored directly into batteries and capacitors but they are expensive and don’t last long (batteries) or don’t store a lot of energy (capacitors)...
Electrical Energy Storage Applications
Urban Electric Power (UEP)

- Founded in 2012
- Originally Headquartered in West Harlem, NY
  - Special Economic Zone (SEZ)
- Currently in the Pfizer Campus in Pearl River
- Developed at the City University of New York (CUNY) Energy Institute
  - Funded in part by DOE / ARPA-E
  - NYSERDA
- Developed proprietary integrated Battery Management System (BMS)
- Targeting grid-scale/renewables stationary energy storage applications
Definitions

- Typical Power Plants generate power – MW, or GW by burning fuels at a given rate (kg/hr) that is converted to heat, steam, and then electricity using turbine generators.
  - 1 year at 1000MW yields 8.5TWh of energy.
  - A typical house uses 500-1000 kWh/month on average With a max power rating of 12kW (120V@100A)
- Customer demands energy at a minimum rate, but pays for energy, kWh, MWh, GWh
- Utilities must have the infrastructure to provide the customer the power required, even when its not needed.
- Customers typically pay for energy, $/kWh
- Customers in some cases pay for power, demand charges, in order to support the utility companies infrastructure,, $/kW (eg in NYC the summer time demand charges can reach over $50/kW)
### Levelized Cost of Energy: (LCOE)

<table>
<thead>
<tr>
<th>Energy Plant Type</th>
<th>Lifetime Cost</th>
<th>$ per kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Offshore Wind</td>
<td></td>
<td>0.1380</td>
</tr>
<tr>
<td>Coal with 30% CCS</td>
<td></td>
<td>0.1300</td>
</tr>
<tr>
<td>Coal with 90% CCS</td>
<td></td>
<td>0.1190</td>
</tr>
<tr>
<td>Biomass</td>
<td></td>
<td>0.0950</td>
</tr>
<tr>
<td>Advanced Nuclear</td>
<td></td>
<td>0.0926</td>
</tr>
<tr>
<td>Nat Gas Combined Cycle with CCS</td>
<td></td>
<td>0.0746</td>
</tr>
<tr>
<td><strong>PV SOLAR</strong></td>
<td></td>
<td><strong>0.0632</strong></td>
</tr>
<tr>
<td>Hydro-electric</td>
<td></td>
<td>0.0617</td>
</tr>
<tr>
<td>Land Based Wind</td>
<td></td>
<td>0.0591</td>
</tr>
<tr>
<td>Natural Gas Combined Cycle</td>
<td></td>
<td>0.0501</td>
</tr>
<tr>
<td>Geothermal</td>
<td></td>
<td>0.0446</td>
</tr>
</tbody>
</table>

*US Energy Information Administration (EIA-March 2018)*
Levelized Cost of Energy Storage: (LCOS)

\[ \text{LCOS} = \frac{(\text{Total cost of Project} + \text{Cost of Operation})}{\left( \frac{\text{total amount of energy delivered}}{\text{over the life of the project}} \right) \cdot \left( \frac{\text{Storage}}{\text{Efficiency}} \right)} \]

Assume that system deliver 1000 cycles at rated capacity with a 80% efficiency and the cost of the batteries is $500/kWh

\[ \text{LCOS} = \frac{500 \ \$}{1000 \text{cycles} \times 0.80 \frac{\text{kWh}_{\text{out}}}{\text{kWh}_{\text{in}}}} = 0.625 \frac{\$}{\text{kWh}_{\text{out}}} \]

So the cost of using stored electricity to the customers would be the LCOE+LCOS which is way too expensive by current standards.
<table>
<thead>
<tr>
<th>Energy Storage Technology Options</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compressed Air</strong></td>
</tr>
<tr>
<td><strong>Pumped Hydro</strong></td>
</tr>
<tr>
<td><strong>Fly Wheel</strong></td>
</tr>
<tr>
<td><strong>Electrical Energy Storage</strong></td>
</tr>
</tbody>
</table>
**Insight into Battery Technology**

<table>
<thead>
<tr>
<th>Battery Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lead Acid</strong></td>
<td>Oldest and most common batteries; low-cost and adaptable (e.g., electric vehicles, uninterruptible power supplies). “Advanced” lead-acid battery technology combines standard lead-acid battery technology with ultra-capacitors; increase efficiency and lifetimes though are more costly.</td>
</tr>
<tr>
<td><strong>Lithium Ion</strong></td>
<td>Lithium-ion batteries are relatively established, used in the electronics and advanced transportation industries. Lithium-ion batteries are increasingly replacing lead-acid batteries with higher energy density, low self-discharge and high charging efficiency.</td>
</tr>
<tr>
<td><strong>Alkaline</strong></td>
<td>Zinc battery systems are non-toxic, non-combustible and low-cost due to the abundance of the primary metal; however, this technology remains unproven in widespread commercial deployment to date.</td>
</tr>
</tbody>
</table>
Availability of Materials
## The Zn Anode Advantage

<table>
<thead>
<tr>
<th>Material</th>
<th>Reaction</th>
<th>Mass of Reactants (g)</th>
<th>Number of electrons</th>
<th>Theoretical mAh/g</th>
<th>Cell Voltage (V)</th>
<th>kWh/kg</th>
<th>$/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>Pb+PbO2+2H2SO4---2PbSO4+2H2O+2e-</td>
<td>642.0</td>
<td>2</td>
<td>83.5</td>
<td>2.000</td>
<td>0.518</td>
<td>$4.25</td>
</tr>
<tr>
<td>Lithium</td>
<td>LiC6 + FePO4---LiFePO4 + 6C+e-</td>
<td>229.8</td>
<td>1</td>
<td>116.7</td>
<td>3.300</td>
<td>12.818</td>
<td>$4.68</td>
</tr>
<tr>
<td>MnO2(1e⁻)</td>
<td>2Na + 4S ---Na2S4 +2e-</td>
<td>174.0</td>
<td>2</td>
<td>308.1</td>
<td>2.000</td>
<td>0.432</td>
<td>$3.71</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn+2NiOOH+2H2O---Zn(OH)2+2Ni(OH)2+2e-</td>
<td>284.8</td>
<td>2</td>
<td>188.2</td>
<td>1.730</td>
<td>0.432</td>
<td>$3.71</td>
</tr>
<tr>
<td>ZnMnO2 (1 electron)</td>
<td>2MnO2+Zn+H2O---2MnOOH+Zn(OH)2+2e-</td>
<td>257.3</td>
<td>1</td>
<td>104.2</td>
<td>1.430</td>
<td>1.147</td>
<td>$1.82</td>
</tr>
<tr>
<td>ZnAir</td>
<td>2Zn+O2----2ZnO</td>
<td>113.4</td>
<td>2</td>
<td>472.7</td>
<td>1.65V</td>
<td>780</td>
<td></td>
</tr>
</tbody>
</table>

### Material Costs

<table>
<thead>
<tr>
<th>Material</th>
<th>Cost/$kg</th>
<th>Atomic Mass</th>
<th>Electron Change</th>
<th>kAh/kg</th>
<th>$/kAh</th>
<th>Cell Voltage</th>
<th>kWh/kg</th>
<th>$/kWh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>$2.20</td>
<td>207</td>
<td>2</td>
<td>0.259</td>
<td>$8.50</td>
<td>2</td>
<td>0.518</td>
<td>$4.25</td>
</tr>
<tr>
<td>Lithium</td>
<td>$60.00</td>
<td>6.9</td>
<td>1</td>
<td>3.884</td>
<td>$15.45</td>
<td>3.3</td>
<td>12.818</td>
<td>$4.68</td>
</tr>
<tr>
<td>MnO2(1e⁻)</td>
<td>$1.60</td>
<td>86.9</td>
<td>1</td>
<td>0.308</td>
<td>$5.19</td>
<td>1.4</td>
<td>0.432</td>
<td>$3.71</td>
</tr>
<tr>
<td>Zinc</td>
<td>$2.09</td>
<td>65.4</td>
<td>2</td>
<td>0.820</td>
<td>$2.55</td>
<td>1.4</td>
<td>1.147</td>
<td>$1.82</td>
</tr>
</tbody>
</table>

### Additional Information

- **Material Cost**: Cost of the material per kilogram.
- **Atomic Mass**: Atomic mass of the material.
- **Electron Change**: Number of electrons involved in the reaction.
- **kAh/kg**: Theoretical energy stored in kA hours per kilogram.
- **$/kAh**: Cost of energy stored per kA hour.
- **Cell Voltage**: Voltage of the cell.
- **$/kWh**: Cost of energy stored per kilowatt-hour.
How to Make Electrical Energy Affordable

• Decrease the cost of the battery on per kWh basis
• Increase its lifetime of operation (increase deliverable cycles)
• Increase efficiency
• Other important factors (energy density, operating temperature, safety, fire suppression, transportable)
MnO$_2$-Zn Battery Discharge Cycle

Load

I

Lose 2e$^-$

Zn$^0$

Zn$^{+2}$

KOH Alkaline Electrolyte Solution

Gain e$^-$

Mn$^{+3}$

Mn$^{+4}$

Anode (Negative Electrode)

Cathode (Positive Electrode)
MnO$_2$-Zn Battery Charge Cycle

Anode (Negative Electrode):
- Gain 2e$^-$
- Zn(s)$\rightarrow$Zn(OH)$_4^{2-}$
- Reduce 2H$^+$ to H$_2$
- 2H$_2$O$ightarrow$2H$^+$ + 2OH$^-$

Cathode (Positive Electrode):
- Lose 2e$^-$
- Mn$^{4+}(s)\rightarrow$Mn$^{3+}(s)$ or (aq)
- Oxidize 2OH$^-$ to O$_2$
- $\frac{1}{2}$ O$_2$(g)+H$_2$O$ightarrow$2OH$^-$

Solid-State Insertion Reaction:
- Mn$^{3+}(s)$ or (aq)$\rightarrow$Mn$^{4+}(s)$ + 2OH$^-$

KOH Alkaline Electrolyte Solution:
- 2OH$^-$

Electroplating:
- Zn(s)$\rightarrow$Zn(OH)$_4^{2-}$
- Zn(OH)$_4^{2-}\rightarrow$Zn(s)
- Zn(s) + 4OH$^-$ $\rightarrow$ Zn(OH)$_4^{2-}$

Insertion Reaction:
- 2H$_2$O$ightarrow$2H$^+$ + 2OH$^-$

Reduction Reaction:
- 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$
Zn-MnO₂ Battery Chemistry

At the Cathode

\[ \text{MnO}_2 + \text{H}_2\text{O} + e^- \leftrightarrow \text{MnOOH} + \text{OH}^- \quad E^0 = 0.35 \text{ V} \]

At the Anode

\[ \text{Zn} + 2\text{OH}^- \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^- \quad E^0 = -1.25 \text{ V} \]

Overall Reaction

\[ \text{Zn} + 2\text{MnO}_2 + \text{H}_2\text{O} \leftrightarrow \text{ZnO} + \text{MnOOH} \quad E^0 = 1.6 \text{ V} \]
Basic Architecture of the Cell

- MnO$_2$ Electrode
- Current Collector
- Separator
- Zn Electrode
Microscopy View of the Events on the Cathode During Discharge

\[
\begin{align*}
\text{MnOOH} & \rightarrow \text{MnO}_2 + \text{H}_2\text{O} + \text{e}^- \\
\text{MnO}_2 & \rightarrow \text{MnOOH} + \text{H}_2\text{O} + \text{e}^-
\end{align*}
\]
Cathode: Heterogeneous Reactions at Many Scales

Performance is effected by
- Specific Surface areas of EMD crystals
- Porosity of Carbon Additive
- Macroscopic Porosity
- Conductivity of Carbons
- Concentration of Electrolyte
- Diffusion of electrolyte toward the interface with the active material.
Microscopy View of the Events on the Anode During Discharge

\[ \text{Zn} + 2\text{OH}^- \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + 2e^- \]
Anode: Heterogeneous Reactions at Many Scales

Zn + 2OH^- ↔ ZnO + H_2O + 2e^-

Performance is effected by
- Specific Surface areas of Zn particle
- Availability of OH^- for reaction on the zinc surface
- Macroscopic Porosity between particles
- Continuous Connection between the zinc particles determines electronic conductivity
- Concentration of Electrolyte
- Diffusion of electrolyte toward the interface with the active material.
- Insulating properties of binder used

Compressive Force to keep anode mechanically intact
Design Considerations in Batteries: Power Battery vs an Energy Battery

• The geometric area of the anode/cathode interface defines the reaction area that is used for energy storage and regeneration.

• The total mass of the anode/cathode define the total capacity of the electrochemical cell.

• The maximum rate of charge discharge is determined by the intrinsic kinetics of the reduction/oxidation reactions.

• Reaction rate are limited either by:
  • Transport of reactants in the electrolyte phase (porosity)
  • Transport of reactants in the solid phase (crystal structure, temperature)
  • Transport of products in the electrolyte phase (porosity)
  • Transport of products in the solid phase (crystal structure, temperature)
  • Intrinsic Reaction Rates (system thermodynamics)
  • Resistance in getting electrons in or out of the cell (tab and current collector design)
Same Capacity, battery on the right has much higher power rating. Especially true if the brown electrode is not very conductive.
OCV Curve for Zn-MnO2
UEP Cell Design Evolution
UEP Manufacturing Process:

- **Zinc Powder Super Sack Unloader**
- **Minor Component Addition**
- **Graphite A Unloader**
- **Graphite B Unloader**
- **MnO2 Powder Super Sack Unloader**
- **Anode Current Collector**
- **Coater**
- **Calendar**
- **Drying**
- **Slitting**
- **Cathode Current Collector**
- **Teflon**
- **Water**
- **Anode Paste Mixing**
- **Coater**
- **Oven Drying**
- **Calendar**
- **Slitting**
- **Cathode Paste Mixing**
- **Coater**
- **Electrode Cleaning at Tab Locations**
- **4 Ply Separator Package (Rolls)**
- **Tab to Terminal Welding**
- **Potting of Terminals**
- **Insert Roll into Box**
- **Tab To Terminal Welding**
- **Electrode Winding**
- **Tab to Terminal Welding**
- **Bending of Terminals**
- **Glue Lid On**
- **Seal/Leak Test**
- **Fill Cell**
- **Test Cell**
- **Record Cell Data**
- **KOH.aq**
UEP Manufacturing Process:
Part 1: Continuous Segment
UEP Manufacturing Process: Part 2: Discreet Segment

- Electrode Cleaning at Tab Locations
  - Tab To Terminal Welding
    - Electrode Cleaning at Tab Locations
      - 4 Ply Separator Package (Rolls)
        - Tab To Terminal Welding
          - Electrode Winding
            - 23

- Bending of Terminals
  - Potting of Terminals
    - Insert Roll into Box
      - Tab To Terminal Welding
        - 26

- Glue Lid On
  - Seal/Leak Test
    - Fill Cell
      - Test Cell
        - Record Cell Data
          - KOH.aq
Cathode Coating
Anode Coating
UEP Jellyroll Cell Design
Winding Process
## Battery project evolution

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>2008-2012</td>
<td>Early CUNY Energy Institute R&amp;D focused on innovations to the zinc anode.</td>
</tr>
<tr>
<td>2012-2013</td>
<td>UEP spun-out of CUNY in 2012 to productize the zinc anode battery. UEP rents facility in Harlem. May 2013 UEP executes a license agreement with CUNY for exclusive world wide rights to the CUNY IP. UEP provides royalties, fees, and ownership to CUNY.</td>
</tr>
<tr>
<td>2014-2015</td>
<td>UEP decides to focus on a Zn-MnO2 battery for stationary energy storage markets. Market trends and raw material pricing drive this decision.</td>
</tr>
<tr>
<td>2016</td>
<td>UEP moves into a pilot plant facility in Pearl River. Develops manufacturing process for the Zn-MnO2 battery. 35 residential systems are installed for field trials. CUNY develops materials for energy dense cathodes competitive with Li-ion for a Gen 2 UEP product.</td>
</tr>
<tr>
<td>2017</td>
<td>UEP continues to refine manufacturing process and increase production for market penetration. Conversion to the Cylindrical design is completed. Raw materials pipe line is established.</td>
</tr>
<tr>
<td>2018</td>
<td>UEP pilot scale manufacturing is stabilized. Cell Quality improving. UEP begins UL and FDNY certifications for US based installations.</td>
</tr>
</tbody>
</table>
Credits

• S. Banerjee (Founder of UEP)
• Valerio DeAngelis (Co-Founder of UEP)
• David Elliman (Early Investor)
• Tom Baruch (Early Investor)
• Jamshyd Godrej (Early Investor)
• Sunedison (Strategic Investor)
• Funding Agencies:
  • NYSERDA
  • NY BEST
  • NYSTAR
  • NSF SBIR
• J. W. Gallaway
• N. Ingale
• Michael Shmukler
• Xia Wei

• Ryan Camaratta
• Mike Nyce
• Kevin Galloway
• G. Yadav
• M. Menard
• D. Kaplin
• Sam Sefa
• Mehdi Omrani
• Tony Cartolano
• Ann Marie Scuderi
• Devon Branch Elliman
• Gabe Cowles
• John Santoleri
• Andy Naukam
THANK YOU!

Alexander Couzis

• acouzis@ccny.cuny.edu (https://www.ccny.cuny.edu/profiles/alexander-couzis)
• alex@urbanelectricpower.com (http://www.urbanelectricpower.com)