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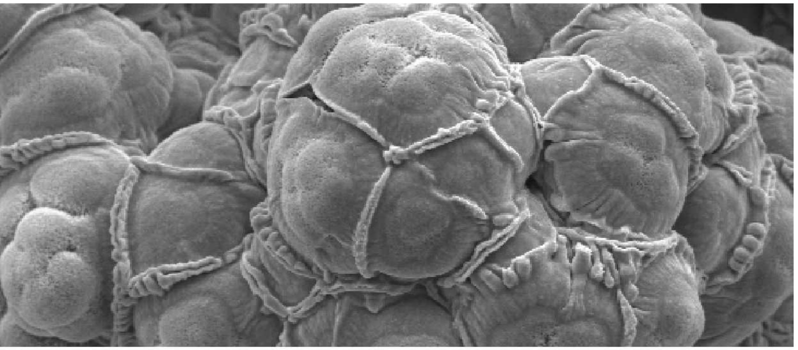

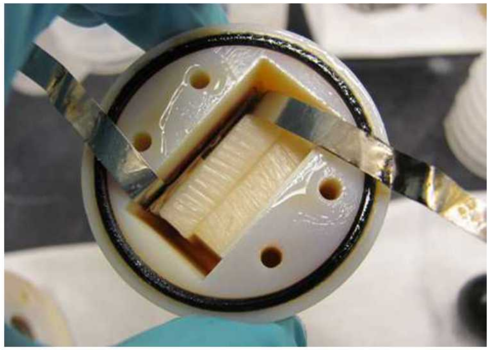

Improving Alkaline Zn/MnO_2 Battery Cycle-ability Under Limited Depth of Discharge Conditions with a Triethanolamine Additive

Maria Kelly, Timothy Lambert, Jonathon Duay, and Ruby Aidun

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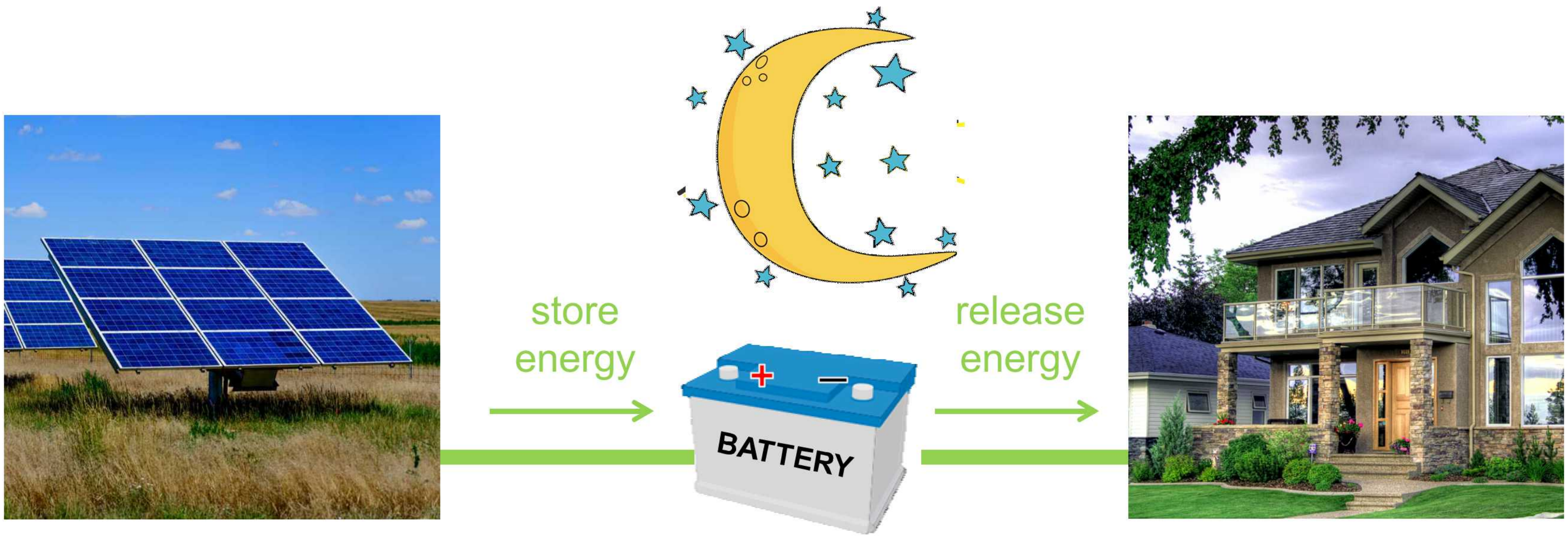
Grid Energy Storage



- Grid-level energy storage technologies will enable intermittent renewables
- Battery systems (Li-ion, Pb-Acid) have been implemented but pose safety and environmental risks
- Successful grid storage must be safe, reliable, and low-cost

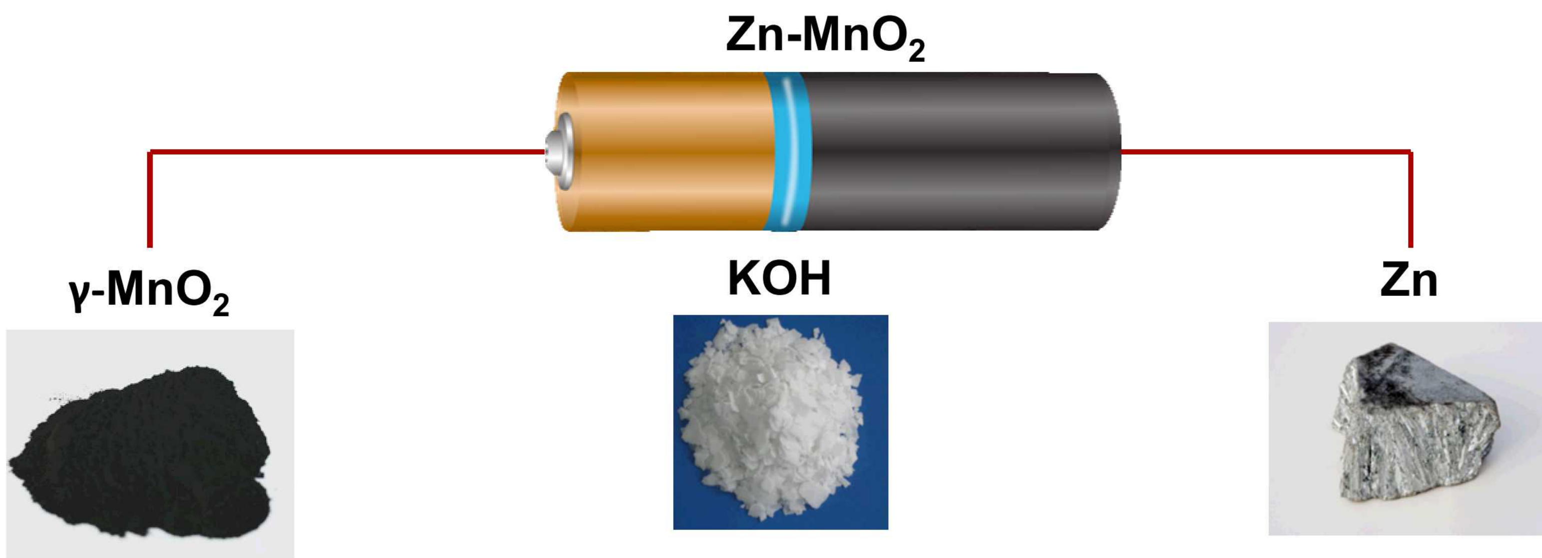
Center for Sustainable Systems, University of Michigan. 2016. "U.S. Energy Storage Factsheet." Pub. No. CSS15-17.
Energy Sage. n.d. “Ground Mount Solar Panels: Top 3 Things You Need to Know.”

Alkaline Zn/MnO_2 Batteries

- **Cost**
  - Traditional primary batteries - $18 per kWh
  - Established supply chain
  - Low-cost materials and manufacturing
- **Safety**
  - Aqueous chemistry
  - Non-flammable
  - EPA certified for landfill disposal
- **Reliability**
  - Long shelf-life
  - Limited thermal management required

Opportunity: Rechargeable Zn/MnO_2 batteries for grid storage

Alkaline Zn/MnO_2 Batteries

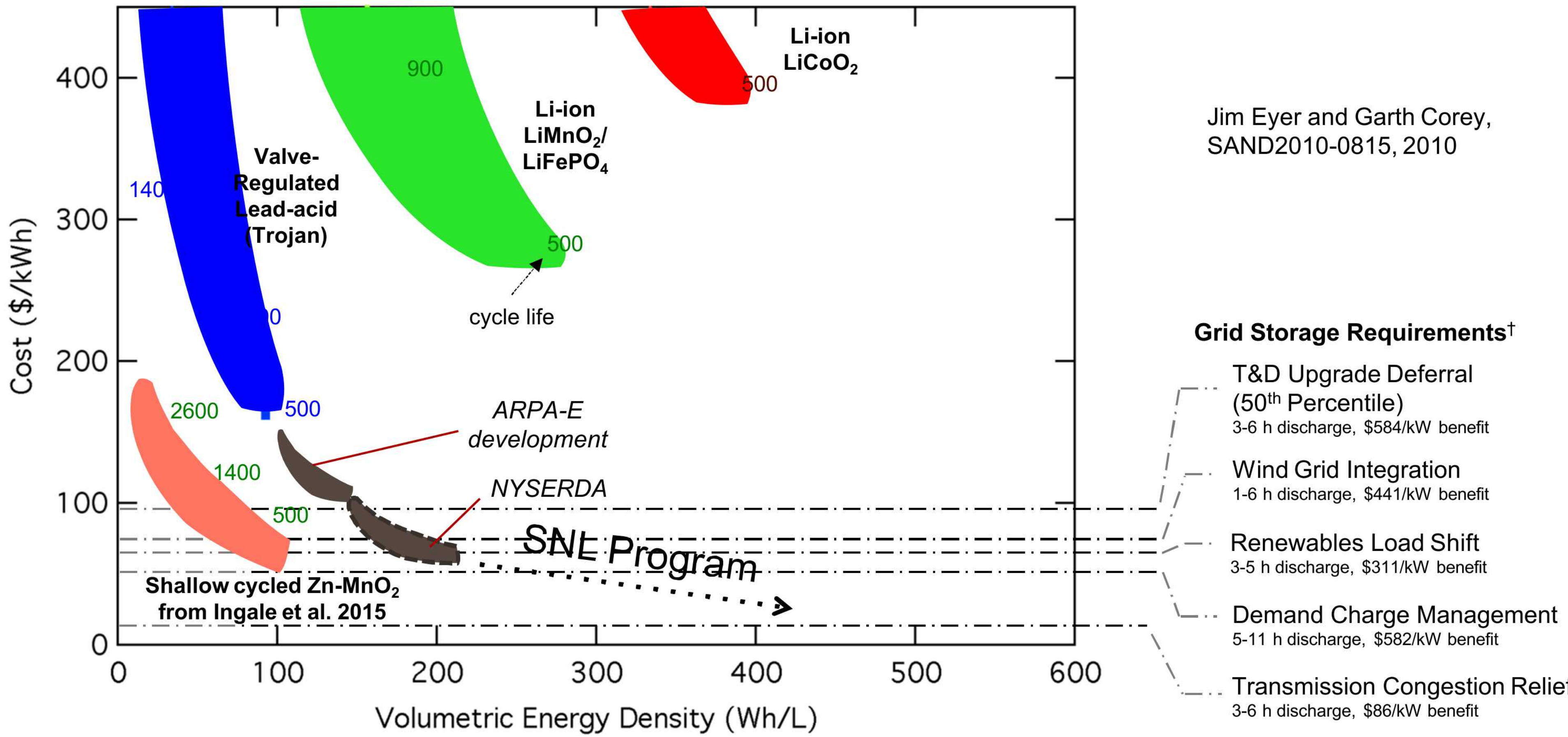


$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^- \qquad [E^0 = +0.15\,V]$$

$$Zn + 2OH^- \rightarrow ZnO + H_2O + \ 2e^- \qquad [E^0 = +1.28\,V]$$

$$\boldsymbol{Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3 \quad [E^0 = +1.43\,V]}$$

Grid Storage Landscape



Jim Eyer and Garth Corey, SAND2010-0815, 2010

- New materials development to increase usable capacity
- Control Ion distribution
- Full mechanistic understanding of battery chemistry
- Support US Industry *(limited DOD 1 e^-)*

Alkaline Zn/MnO_2 Batteries

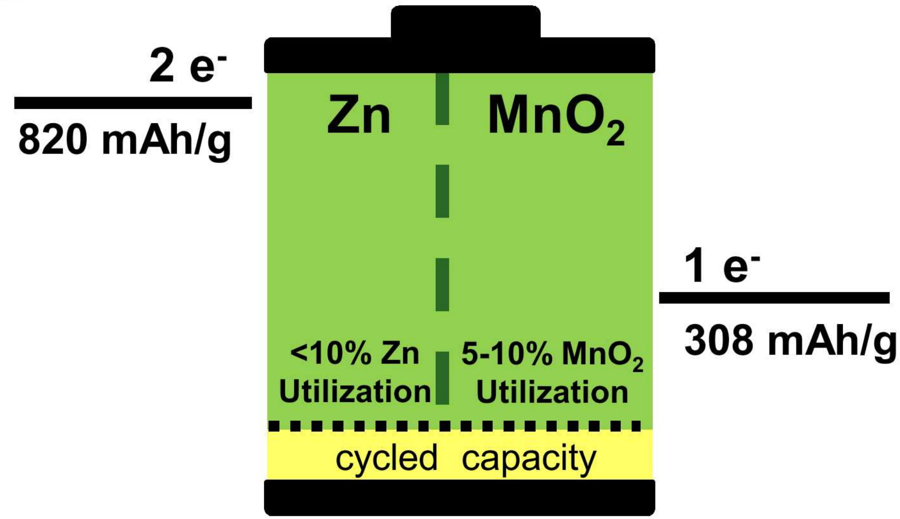
Two classes of rechargeable Zn/MnO_2 batteries:

- One Electron
  - 308 mAh/g-MnO_2
  - Historically limited cycle-ability
  - > 3000 rechargeable cycles shown under limited depth of discharge conditions
  - \$100 - \$150 per kWh

- Two Electron
  - 616 mAh/g-MnO_2
  - Historically limited cycle-ability
  - Recently stabilized with Cu, Bi, CNT additives
  - Extended cycling versus Zn anode not reported

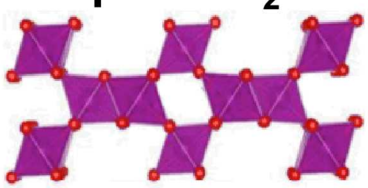
N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).
G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nat. Commun., 8, 14424 (2017).

Limited DOD Cycling



Reversibility can be maintained when only *a fraction of the first* e^- *step is cycled.*

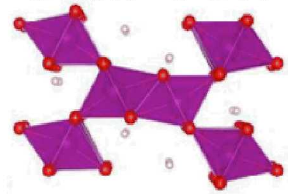
γ-$Mn^{IV}O_2$



Ramsdellite-like (2x1 channels)
Pyrolusite intergrowths (1x1 channels)

Intercalation Regime
$n = {}^{1}/_{x}\ e^-$

α-$Mn^{III}OOH$



Volume expansion
Mn^{3+} (0.645 Å) > Mn^{4+} (0.530 Å)

Mn_3O_4
$ZnMn_2O_4$
Mn_2O_3
$Mn(OH)_2$

Formation of undesirable phases from soluble Mn^{3+}

Cathode issues

- Only 5-10% of total capacity
- Crystal Structure Breakdown
- Inactive Phase(s) formed
- Zinc poisoning

Anode issues

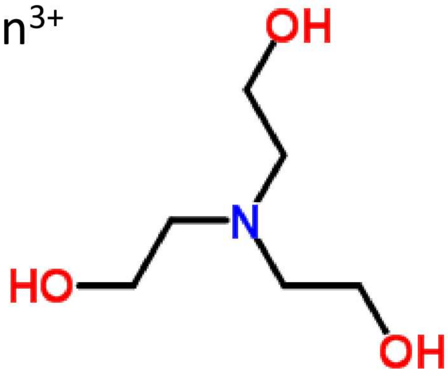
- < 10% of total capacity
- Shape Changes
- Passivation
- Dendrite Formation

Improving Performance

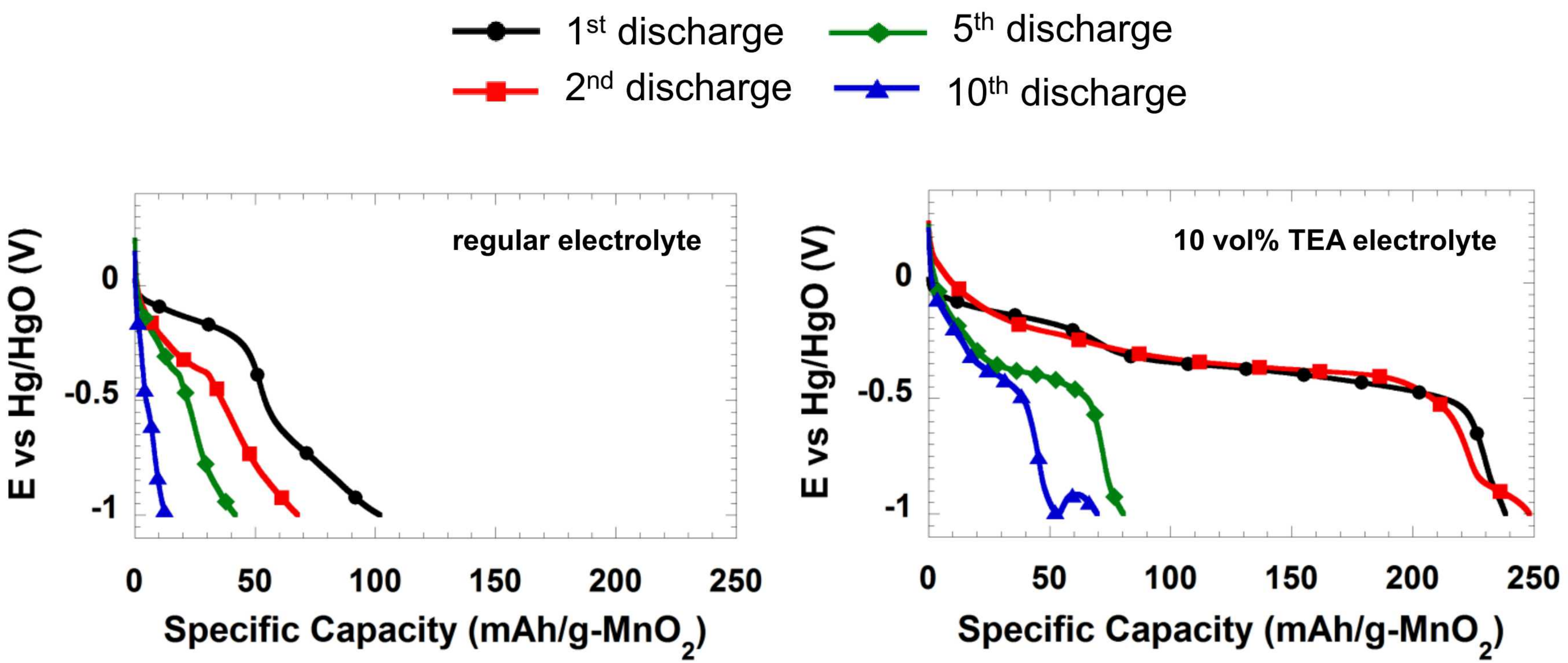
Sandia National Laboratories

- Chemical additives often used to improve battery performance
  - Cathode Additives: Bi_2O_3, MgO, Sr-, Ba-, and Ti-based compounds
  - Anode Additive: In, Bi, Pb, $Ca(OH)_2$, carboxymethyl cellulose
  - No reports on additives in limited DOD Zn/MnO_2 systems

- Triethanolamine (TEA)
  - Known to form stable complexes with Mn^{2+} and Mn^{3+}
  - *Hypothesis*: Adding triethanolamine will bind solubilized Mn^{2+} and Mn^{3+}, thereby mitigating the formation of irreversible species

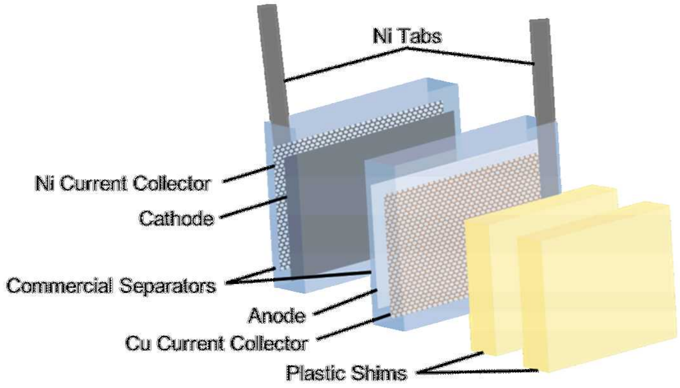


Cathode Discharge Studies

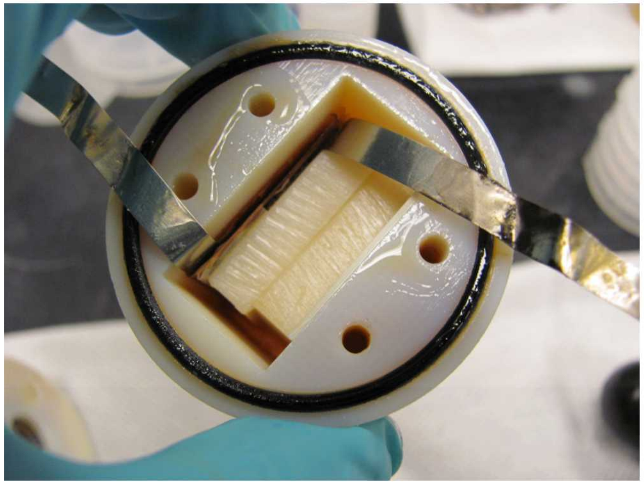


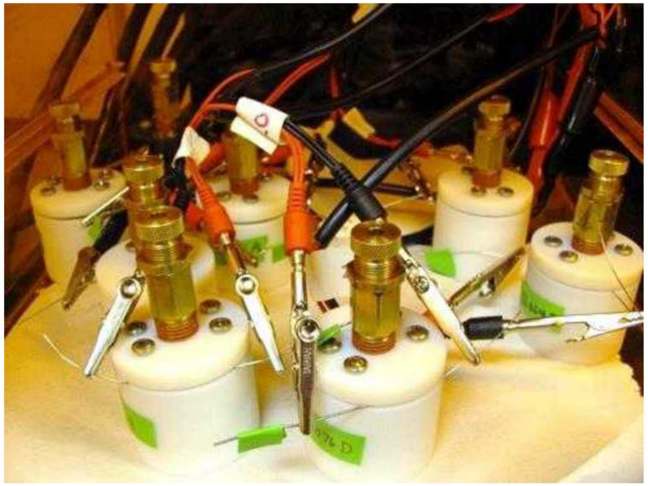
- Examine effect of TEA on Mn^{3+} and Mn^{2+}
- Local deep discharge zones due to electrode heterogeneity
- More capacity accessed when cycled with TEA

Battery Fabrication



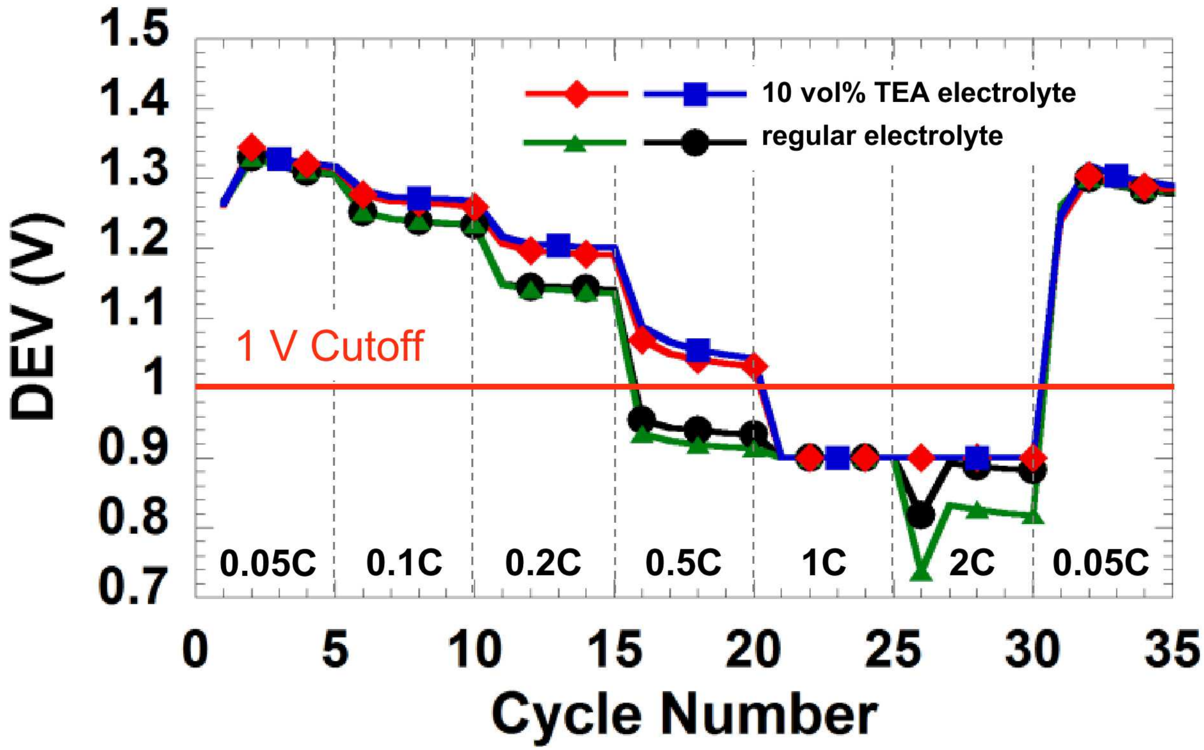
- COTS materials
- 10 vol% TEA added to electrolyte
- 3D printed cells with pressure relief valve
- Cathode-limited cells (< 1.5% DOD on Zn)
- ~ 200 mAh capacity





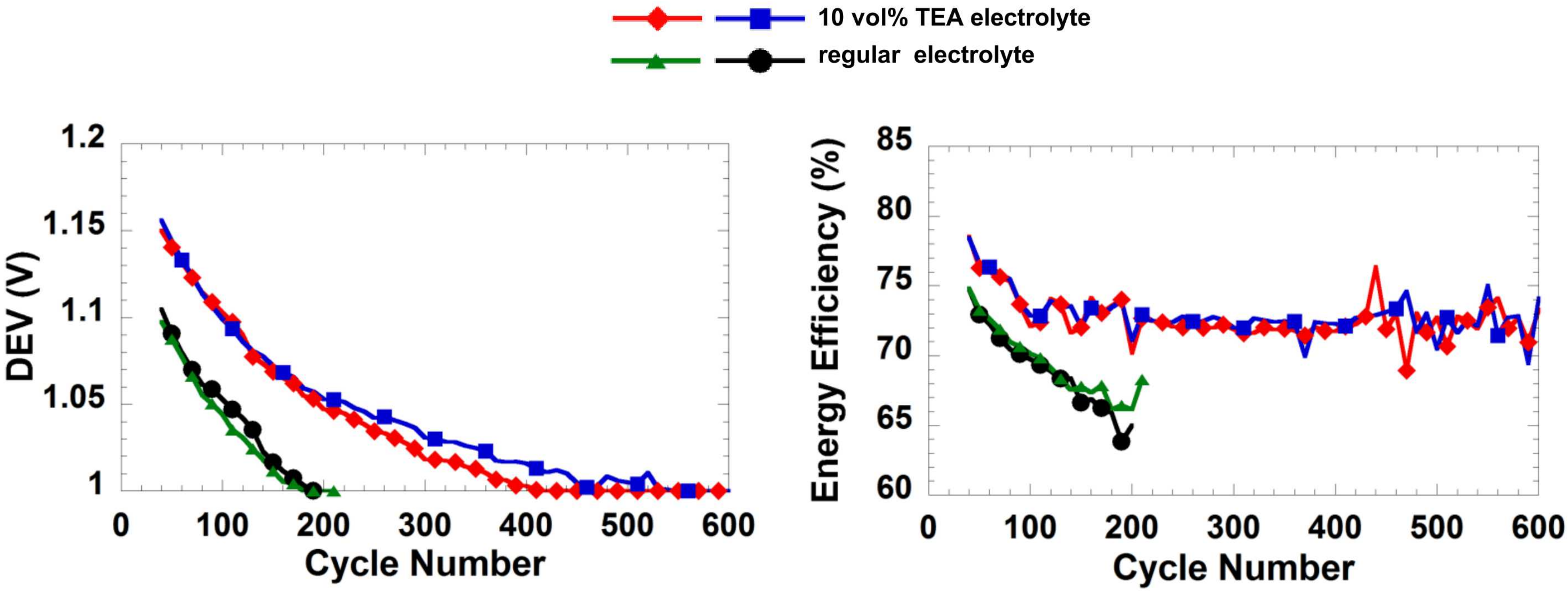
N. D. Ingale, J. W. Gallaway, M. Nyce, A. Couzis and S. Banerjee, J. Power Sources, 276, 7 (2015).

Rate Performance



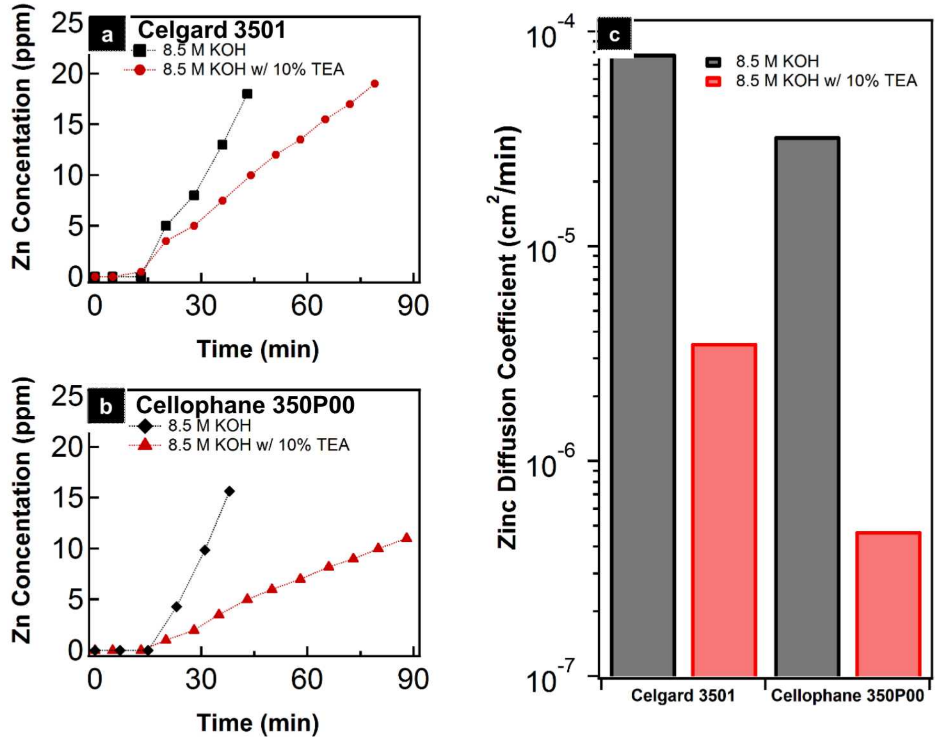
- 5 cycles each of C/20, C/10, C/5, C/2, 1C, 2C
- Cells prepared with TEA exhibit 29, 58, and 121 mV higher DEV at C/10, C/5, C/2
- All cells drop below 1V at 1C and 2C rates – high resistivity of MnO_2

Extended Cycling



- Cycled at C/5 rate, 10% DOD until 80% capacity remained
- Baseline Cells: 183 to 198 cycles, TEA Cells: 483 to 653 cycles
- TEA extends cycle lifetime by 297%

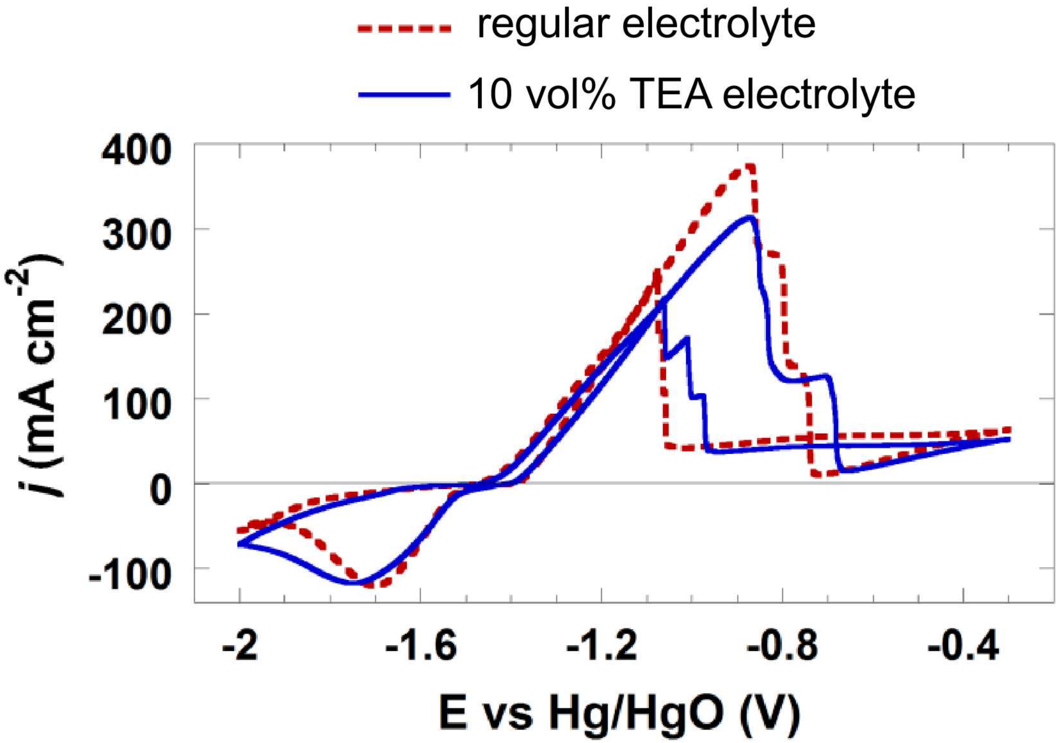
Anodic Stripping Voltammetry



- Provides *real-time* determination of zincate diffusion across commercial membranes
- LOD: 1.6±0.6 ppm

J. Duay, T. N. Lambert, R. Aidun, Electroanal., 29, n/a (2017).

Zn Electrodeposition



- Reduction peak of Zn shifted to more negative potentials by 50 mV
- May be due to complexing ability of TEA

Conclusions

- Cells prepared with TEA show:
  - Higher rate DEV at C/10, C/5, and C/2 rates
  - 297% increase in cycle lifetime
  - More crystalline Zn formation on the cathode after 100 cycles
- More accessible cathode capacity in the presence of TEA
- TEA decreases Zn mobility across Celgard and cellophane separators
- TEA shifts the Zn reduction potential to more negative potentials by 50 mV and produces lower surface area Zn

Acknowledgements

- **Sandia National Laboratories**
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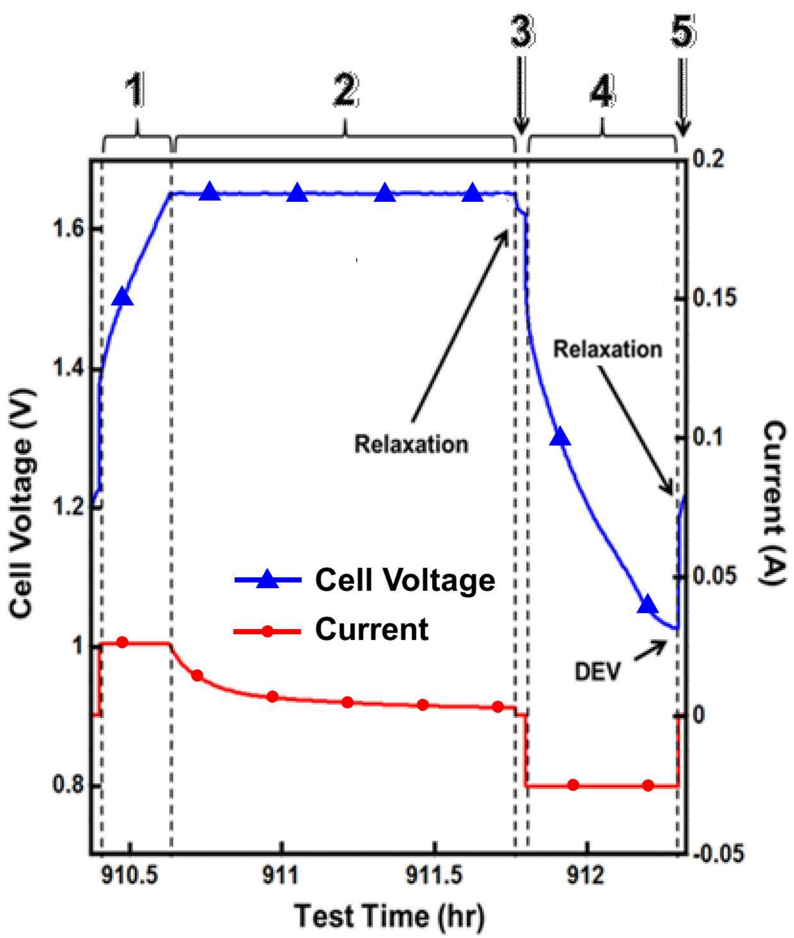
- **Julian Vigil**
- **Ruby Aidun**

Questions?

Thank You!

Cycling Protocol



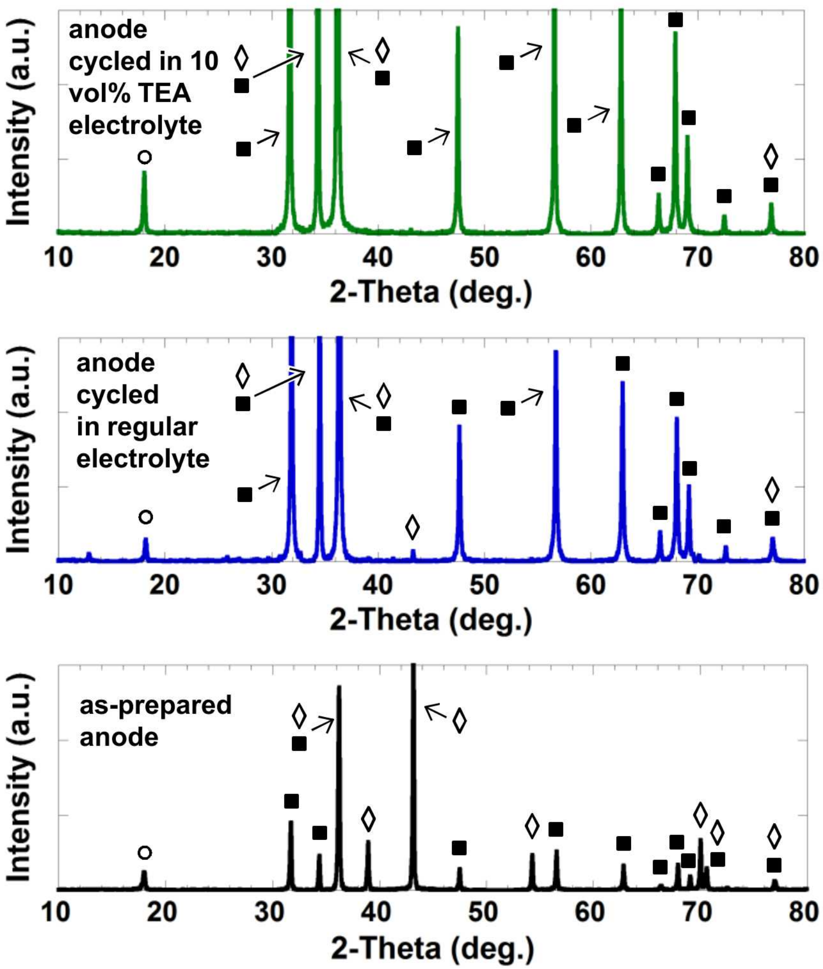
DOD controlled by *time* and *C-rate*

1. Constant current charge
2. Constant voltage charge
3. Rest step
4. Constant current discharge
5. Rest step

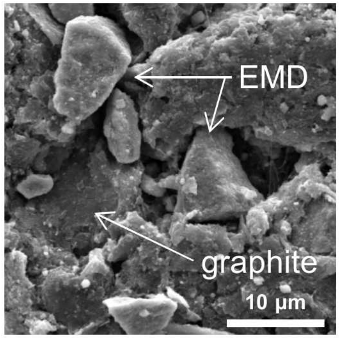
$$M \times T \times C = Discharge\ Current$$

M: Mass of Active Material (g)
T: Theoretical Capacity of Material (mAh/g)
C: C-rate (h^{-1})

XRD After 100 Cycles

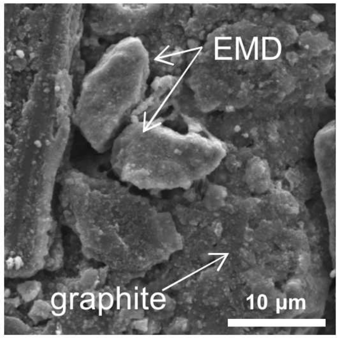


γ-MnO_2 □PTFE ○ $ZnMn_2O_4$ ♦
graphite ●ZnO ■ Mn_3O_4 ◊
PTFE ○ Zn ◊ ZnO ■



Cathode cycled in regular electrolyte

5-6% Zn



Cathode cycled in 10 vol% TEA electrolyte

8-9% Zn

Cathode changes with cycling