

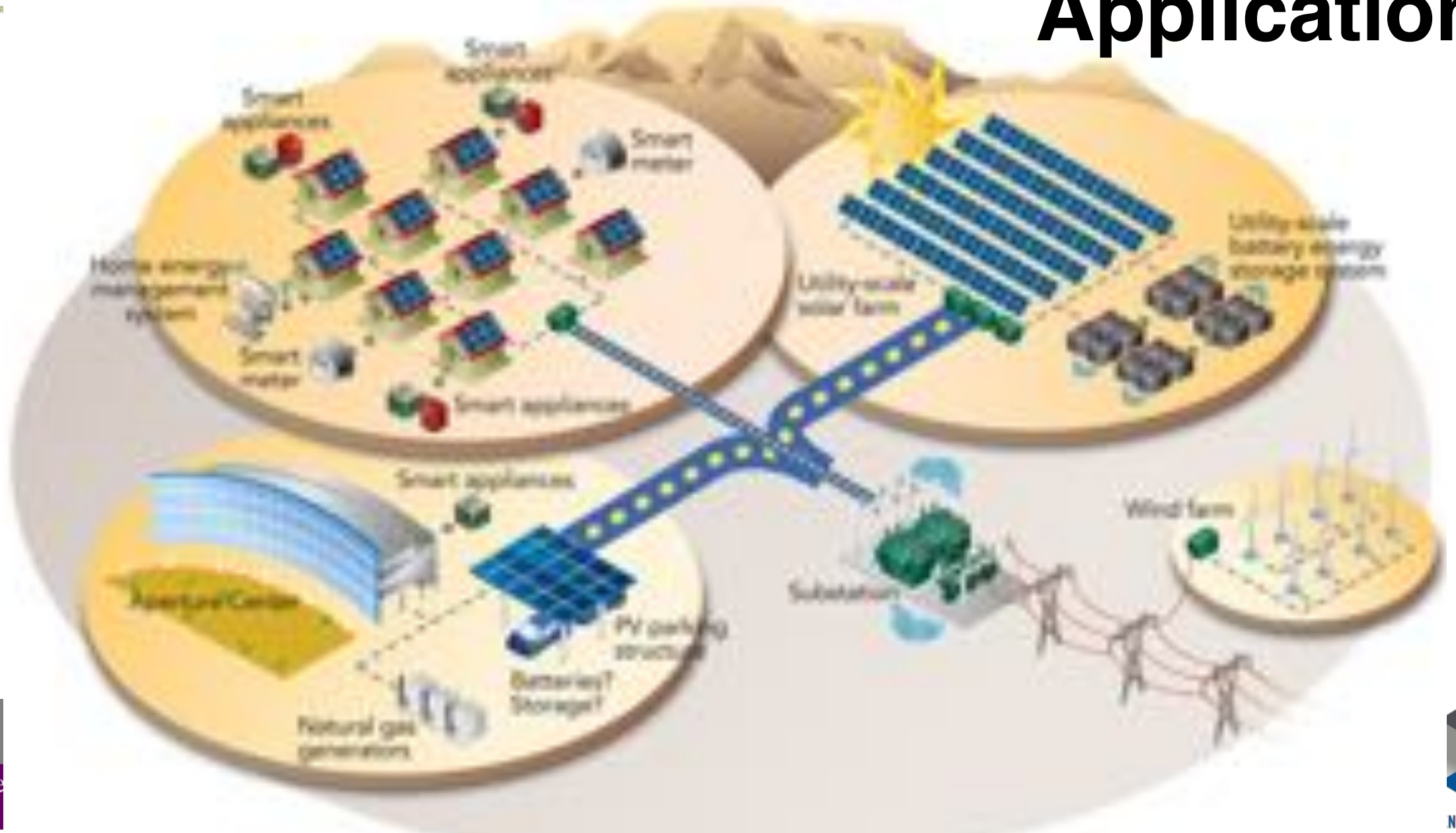
# **Commercialization of the Rechargeable Manganese Dioxide - Zinc Alkaline Battery Chemistry: A Story of Scale Up**

**Alexander Couzis  
Department of Chemical Engineering  
The City College of New York  
New York, NY 10031  
[acouzis@ccny.cuny.edu](mailto: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)

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



# Levelized Cost of Energy Storage:(LCOS)

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

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

$$LCOS = \frac{500 \frac{\$}{kWh_{in}}}{1000cycles * 0.80 \frac{kWh_{out}}{kWh_{in}}} = 0.625 \frac{\$}{kWh_{out}}$$

So the cost of using stored electricity to the customers would be the LCOE+LCOS which is way too expensive by current standards.

# Energy Storage Technology Options

<b>Compressed Air</b>	<b>Uses electricity to compress air into confined spaces</b>	<b>Site specific</b>
<b>Pumped Hydro</b>	Makes use of two vertically separated water reservoirs, using low cost electricity to pump water from the lower to the higher reservoir	Site specific
<b>Fly Wheel</b>	Mechanical devices that spin at high speeds, storing electricity as rotational energy, which is released by decelerating the flywheel's rotor, releasing quick bursts of energy	High power, short duration, low energy density, high cost per kWh
<b>Electrical Energy Storage</b>	Battery storage devices which use electrochemical processing for storing energy	Cost, limited cycle life, hazardous materials



# Insight into Battery Technology

## Lead Acid

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.

## Lithium Ion

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.

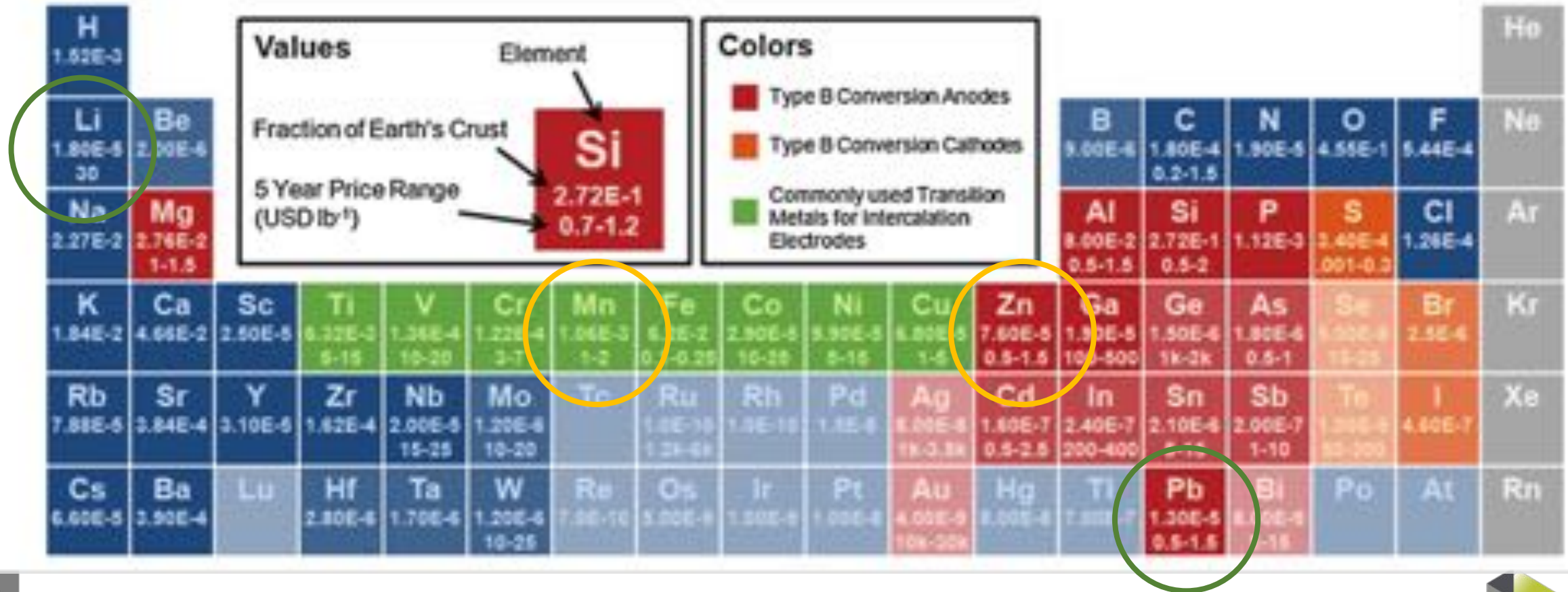
## Alkaline

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.



# Availability of Materials

(a) Availability



# The Zn Anode Advantage

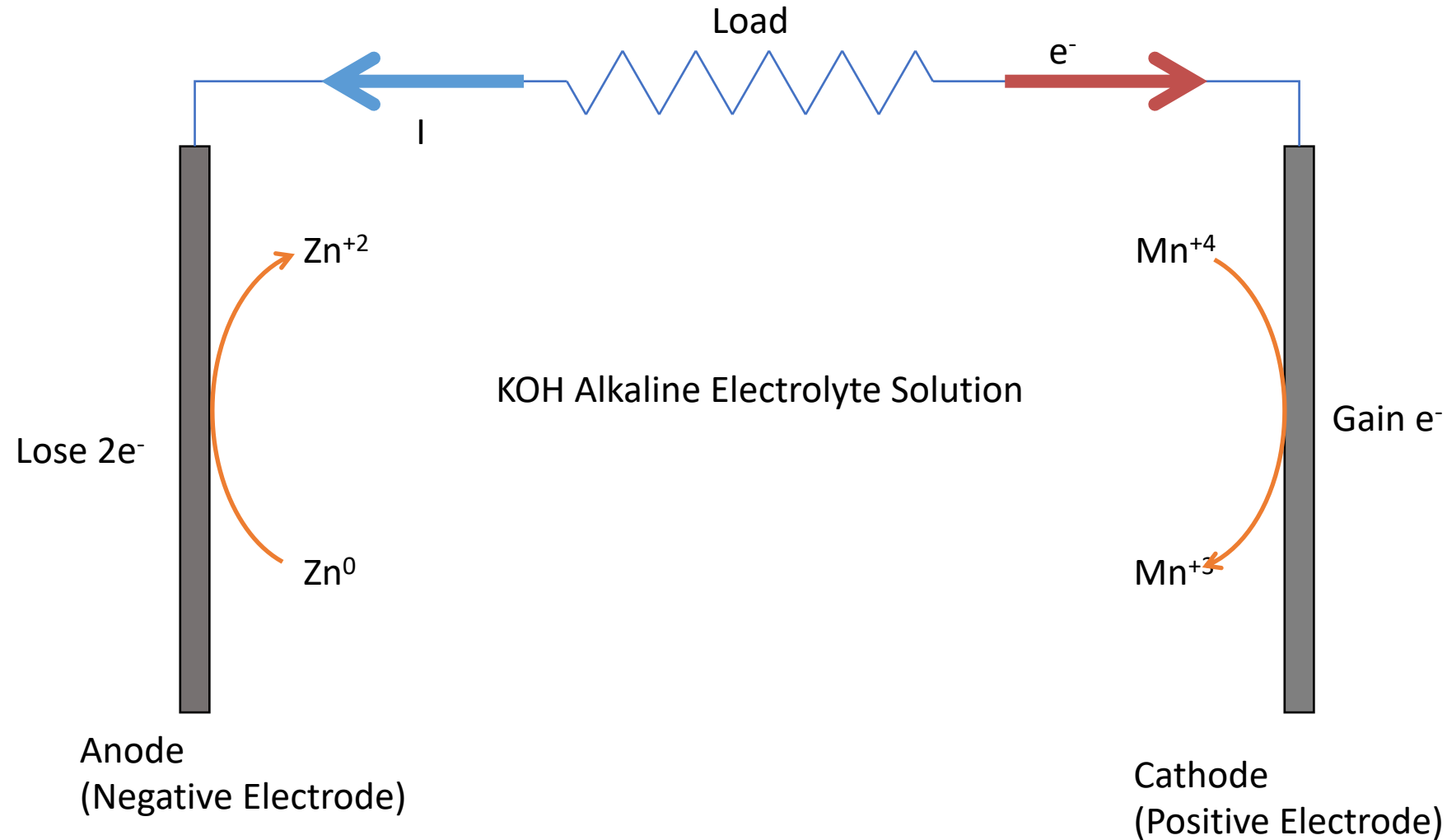
Material	\$/kg	Atomic Mass	Electron Change	kAh/kg	\$/kAh	Cell Voltage (V)	kWh/kg	\$/kWh
Lead	\$2.20	207	2	0.259	\$8.50	2	0.518	\$4.25
Lithium	\$60.00	6.9	1	3.884	\$15.45	3.3	12.818	\$4.68
MnO <sub>2</sub> (1e <sup>-</sup> )	\$1.60	86.9	1	0.308	\$5.19	1.4	0.432	\$3.71
Zinc	\$2.09	65.4	2	0.820	\$2.55	1.4	1.147	\$1.82

Battery Type	Reaction	Mass of Reactants (g)	Number of electrons	Theoretical mAh/g	Cell Voltage	Theoretical Wh/kg
Lead Acid Battery	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O} + 2\text{e}^-$	642.0	2	83.5	2.000	167
Li-Ion Battery (Lithium Ferrous Phosphate)	$\text{LiC}_6 + \text{FePO}_4 \rightarrow \text{LiFePO}_4 + 6\text{C} + \text{e}^-$	229.8	1	116.7	3.300	385
Sodium Sulfur	$2\text{Na} + 4\text{S} \rightarrow \text{Na}_2\text{S}_4 + 2\text{e}^-$	174.0	2	308.1	2.000	616
NiZn	$\text{Zn} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + 2\text{Ni(OH)}_2 + 2\text{e}^-$	284.8	2	188.2	1.730	326
ZnMnO <sub>2</sub> (1 electron)	$2\text{MnO}_2 + \text{Zn} + \text{H}_2\text{O} \rightarrow 2\text{MnOOH} + \text{Zn(OH)}_2 + 2\text{e}^-$	257.3	1	104.2	1.430	149
ZnAir	$2\text{Zn} + \text{O}_2 \rightarrow 2\text{ZnO}$	113.4	2	472.7	1.65V	780

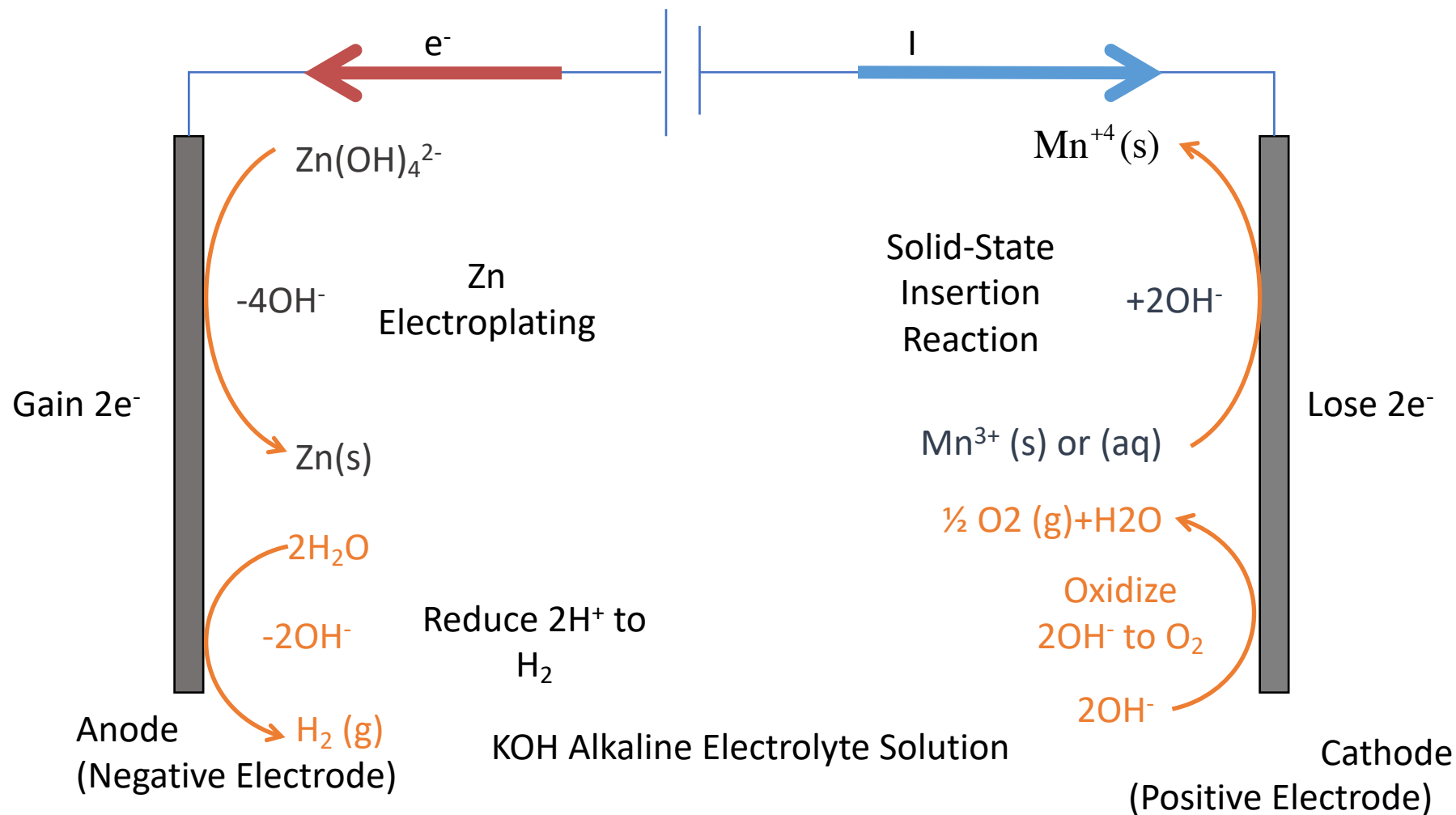
# How to Make Electrical Energy Affordable

- 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<sub>2</sub>-Zn Battery Discharge Cycle



# MnO<sub>2</sub>-Zn Battery Charge Cycle

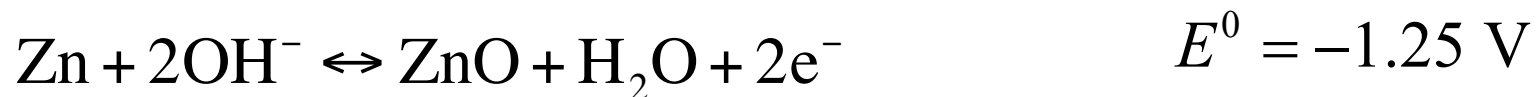


# Zn-MnO<sub>2</sub> Battery Chemistry

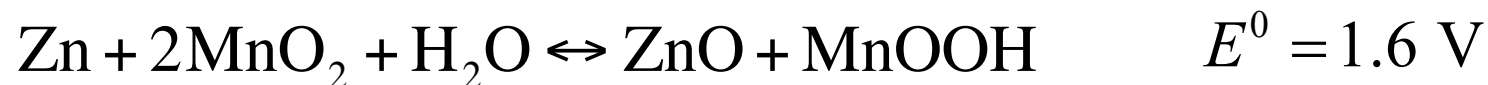
## At the Cathode



## At the Anode

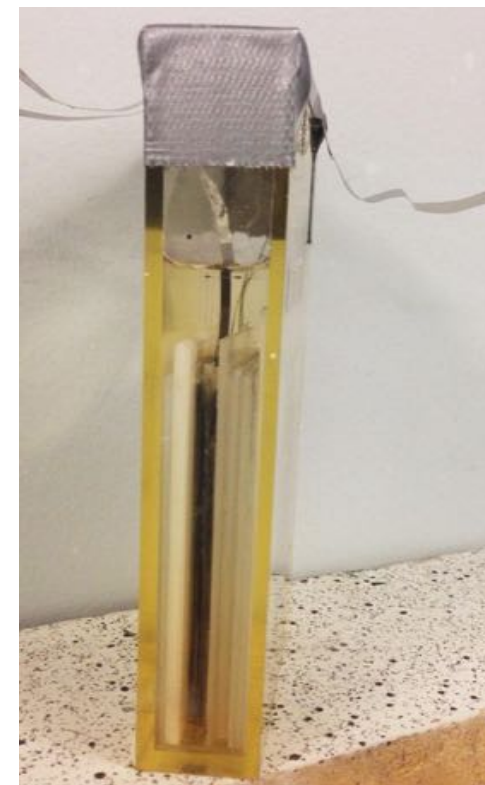
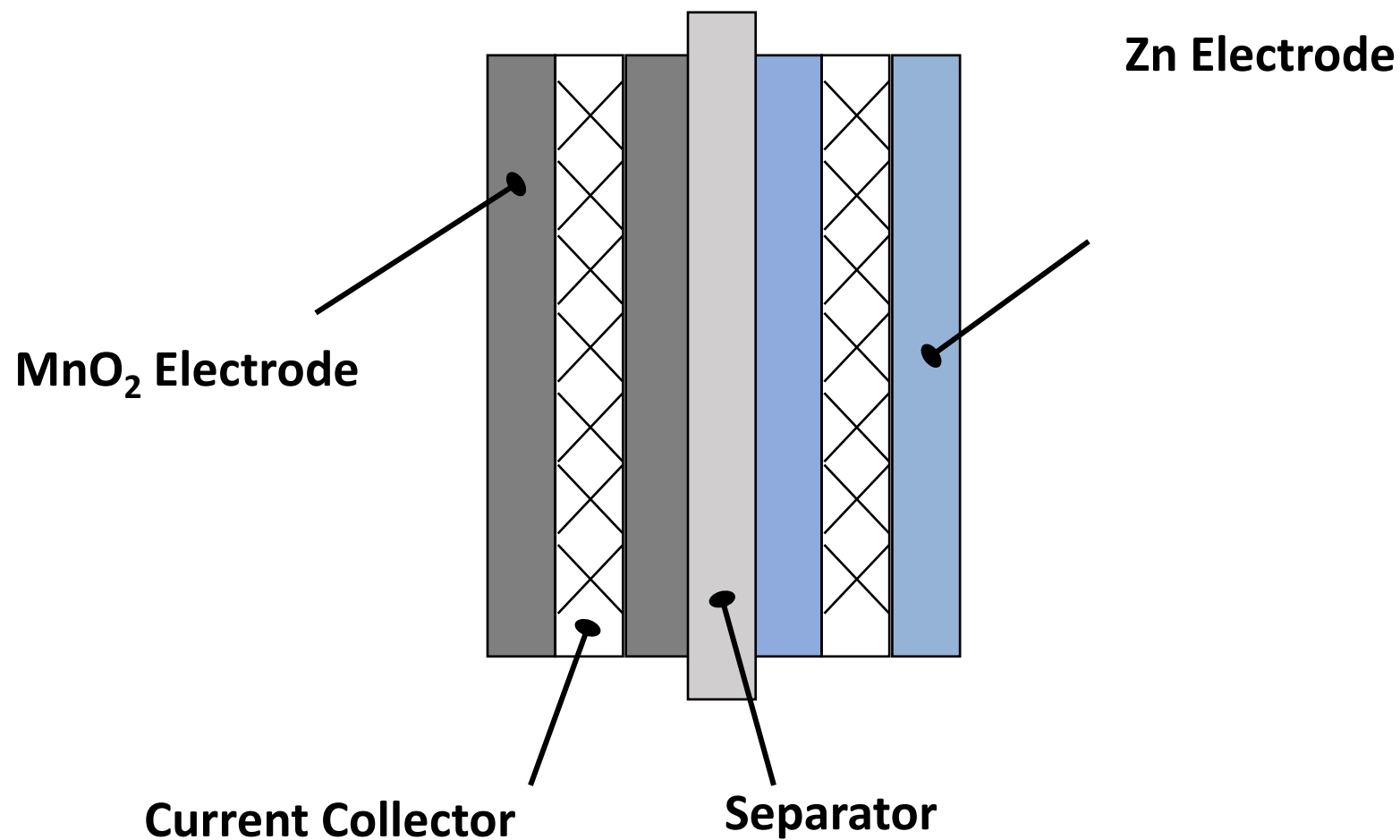


## Overall Reaction

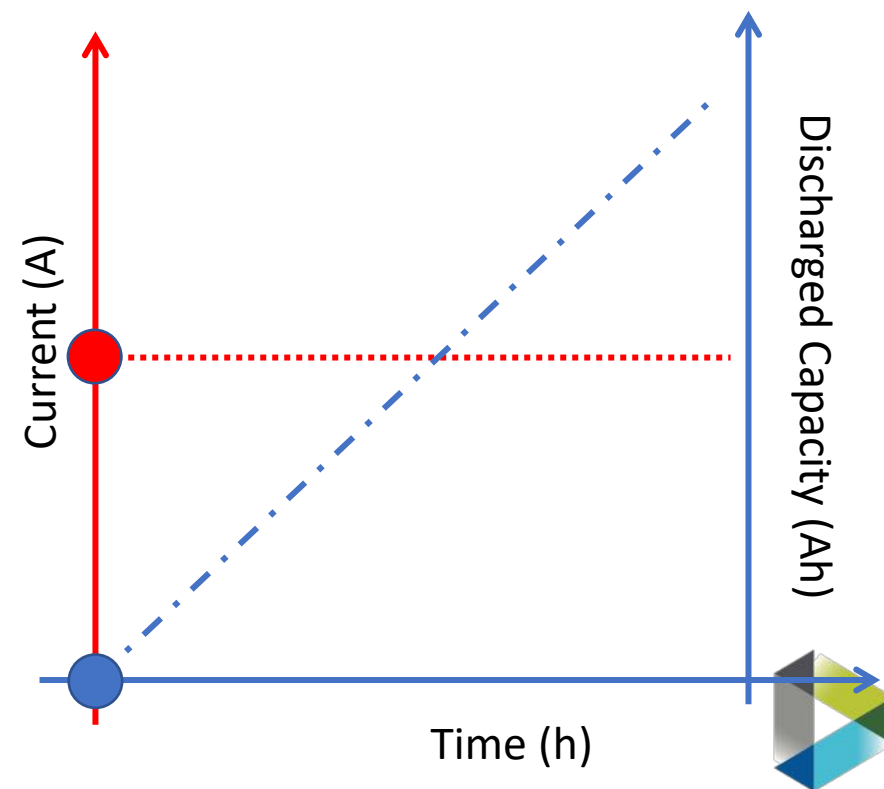
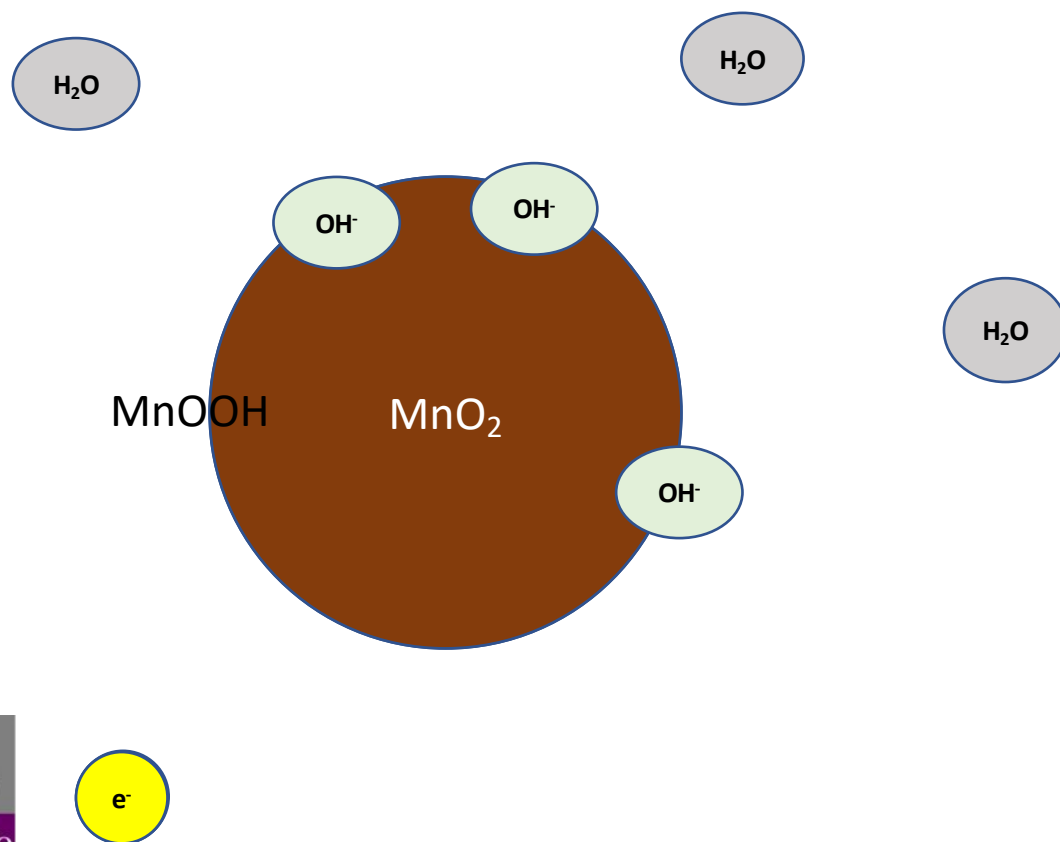




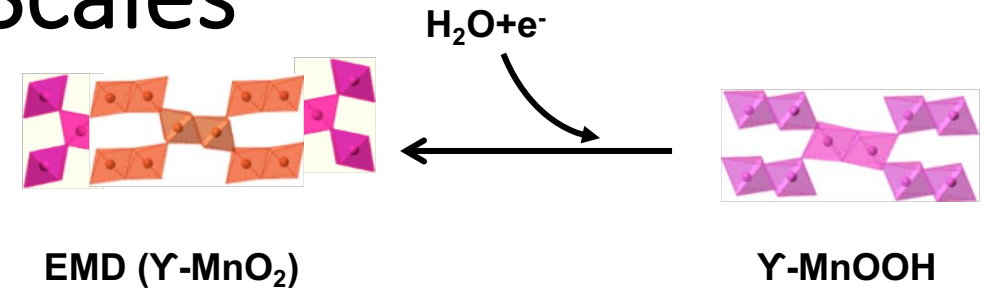
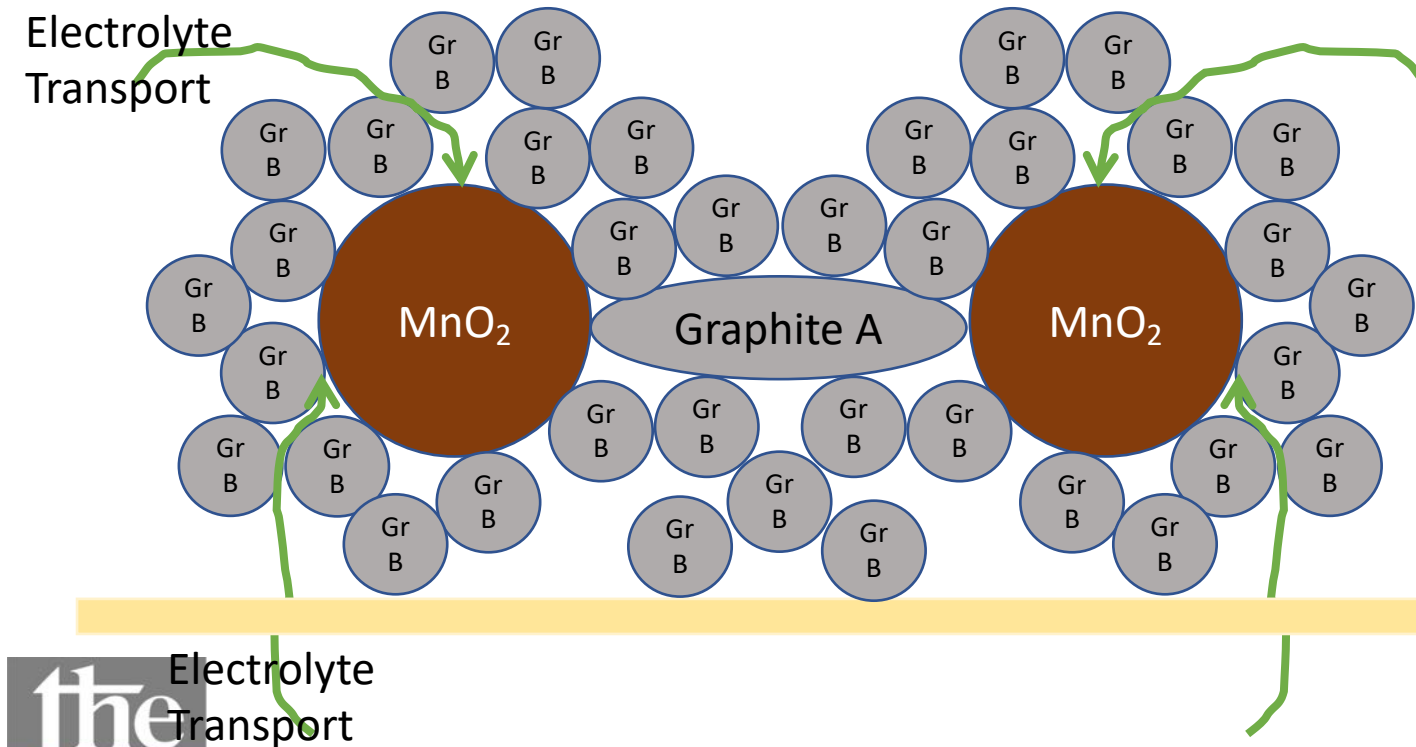
# Basic Architecture of the Cell



# Microscopy View of the Events on the Cathode During Discharge



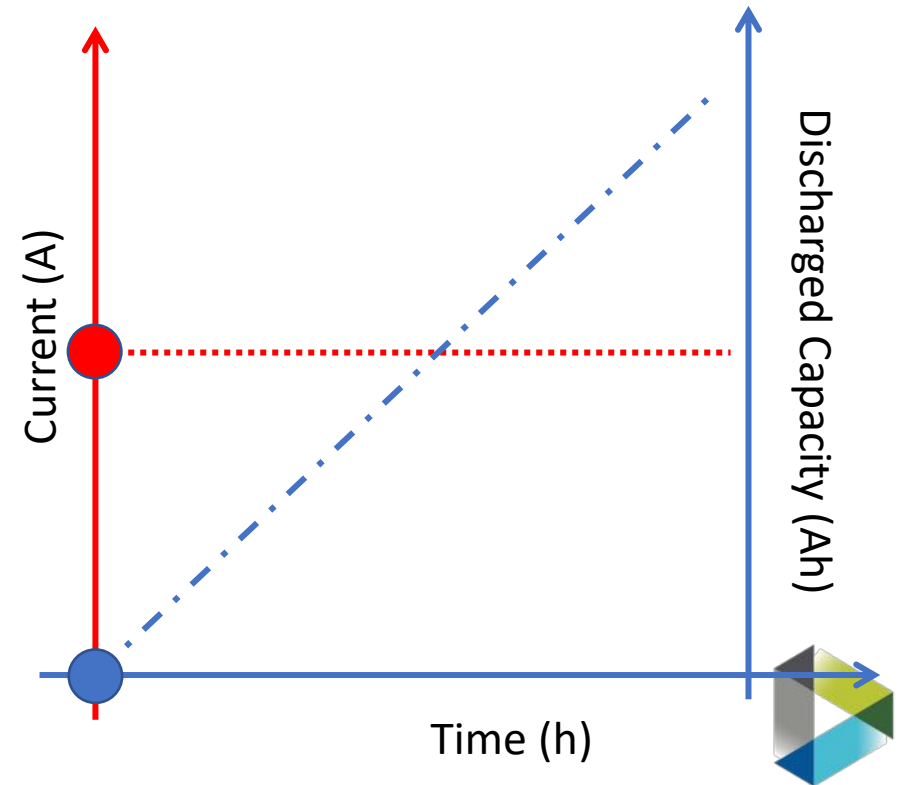
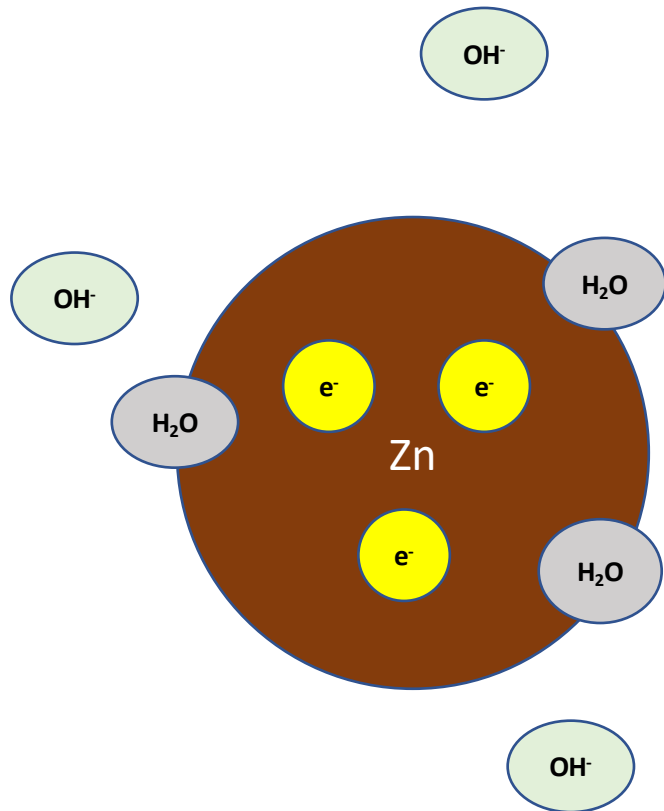
# Cathode: Heterogeneous Reactions at Many Scales



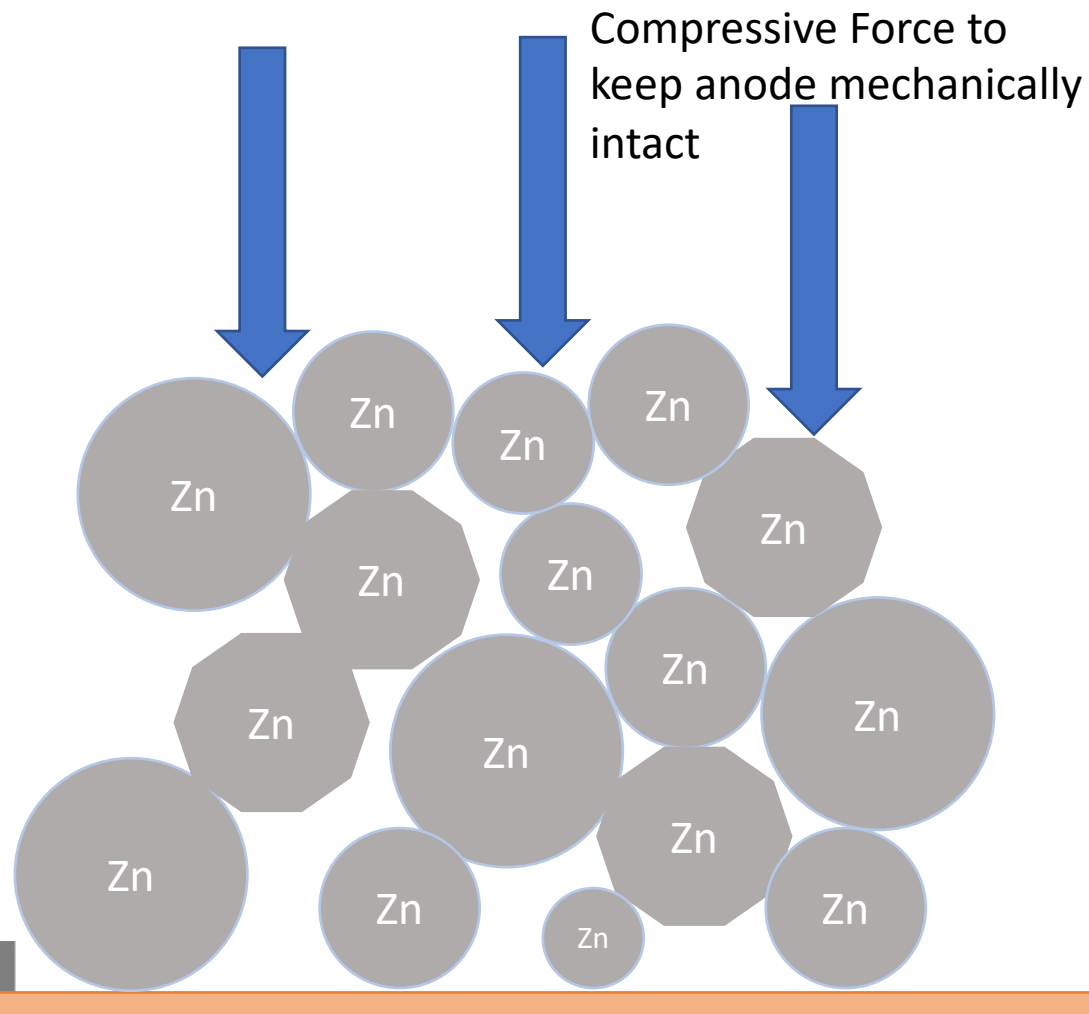
Performance is effected by

- 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



# Anode: Heterogeneous Reactions at Many Scales



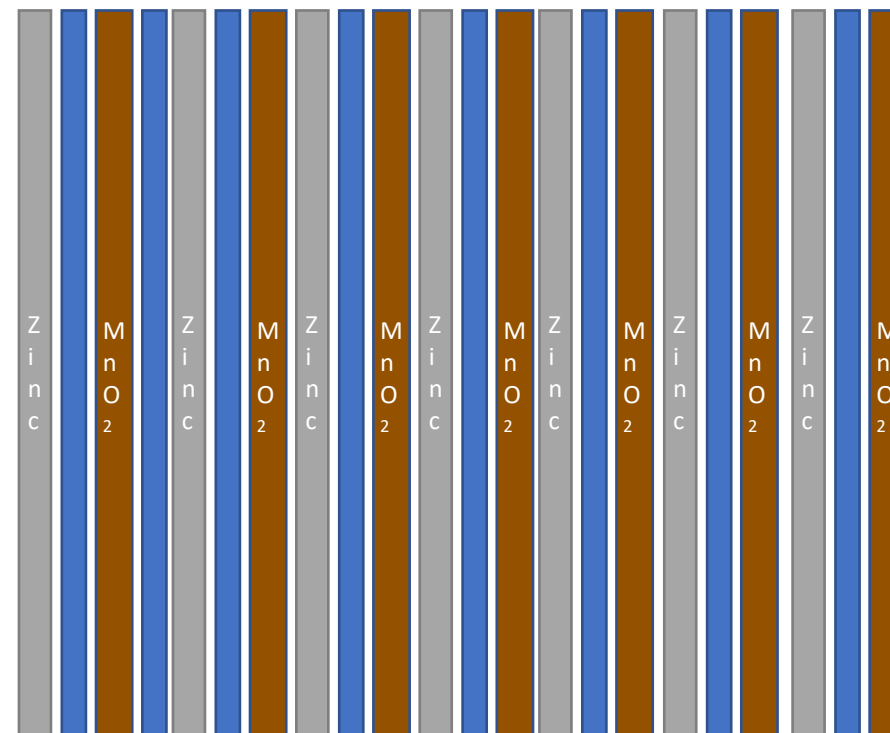
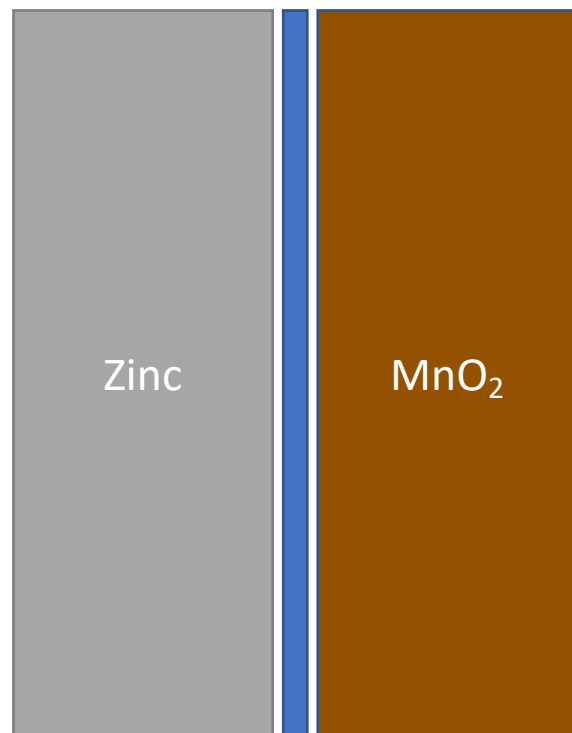
Performance is effected by

- Specific Surface areas of Zn particle
- Availability of  $\text{OH}^-$  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

# Design Considerations in Batteries: Power Battery vs an Energy Battery

- The geometric area of the anode/cathode interface defines the reaction area that is use 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)

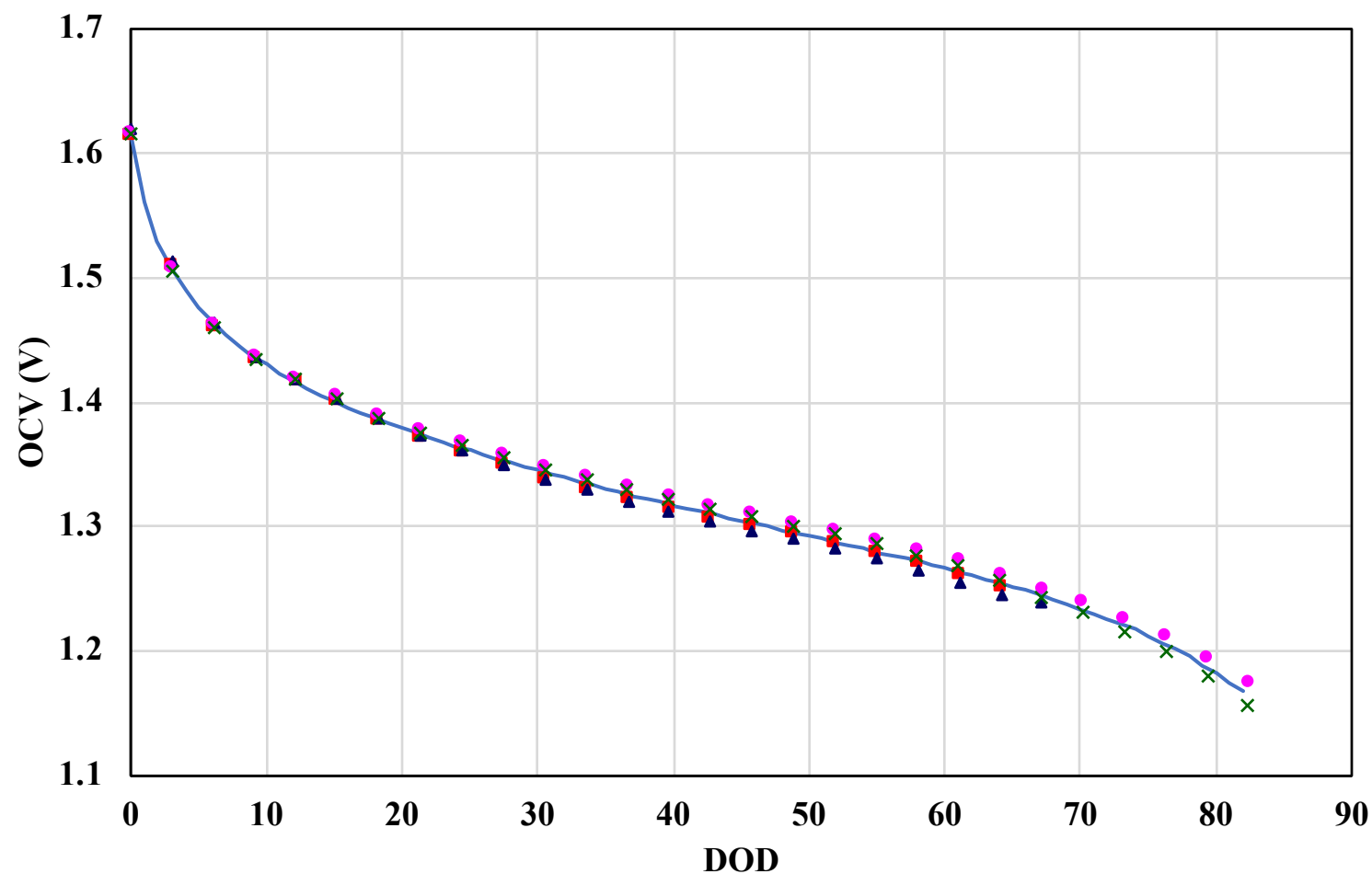
# Design Variations



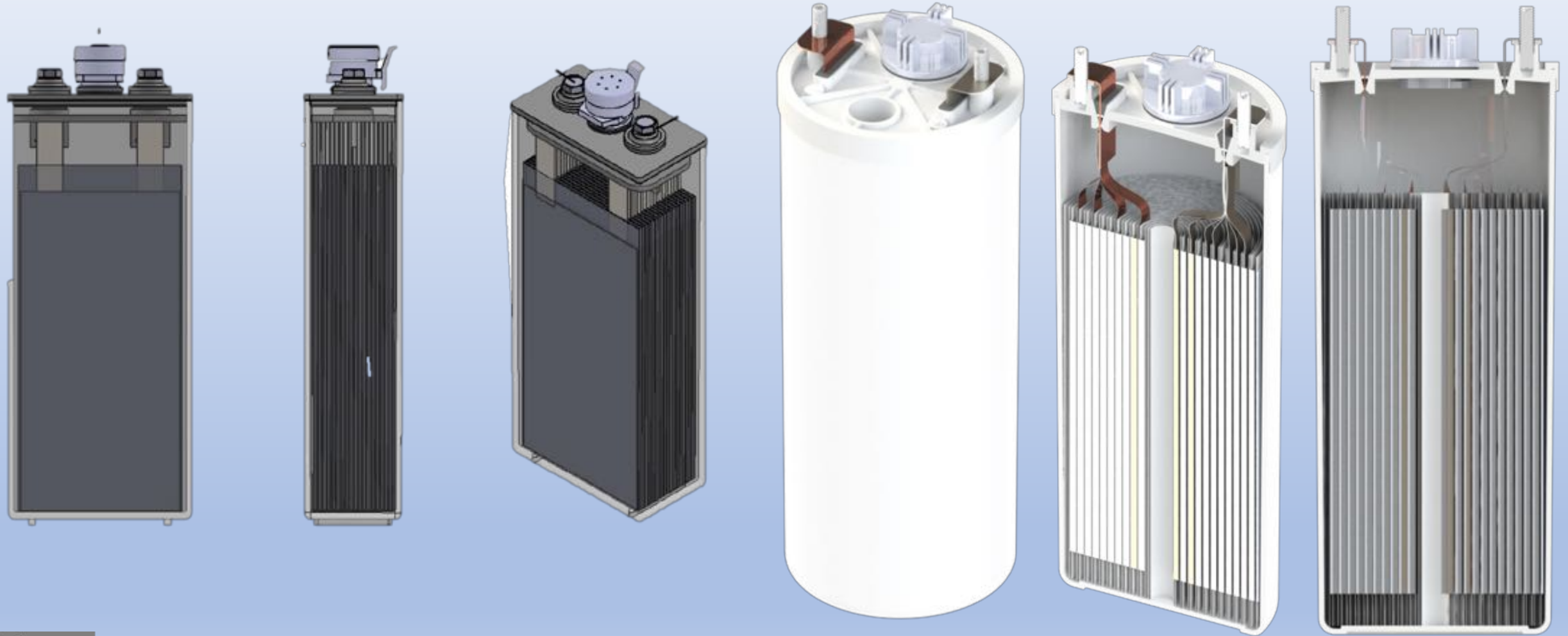
Same Capacity, battery on the right has much higher power rating. Especially true if the brown electrode is not very conductive



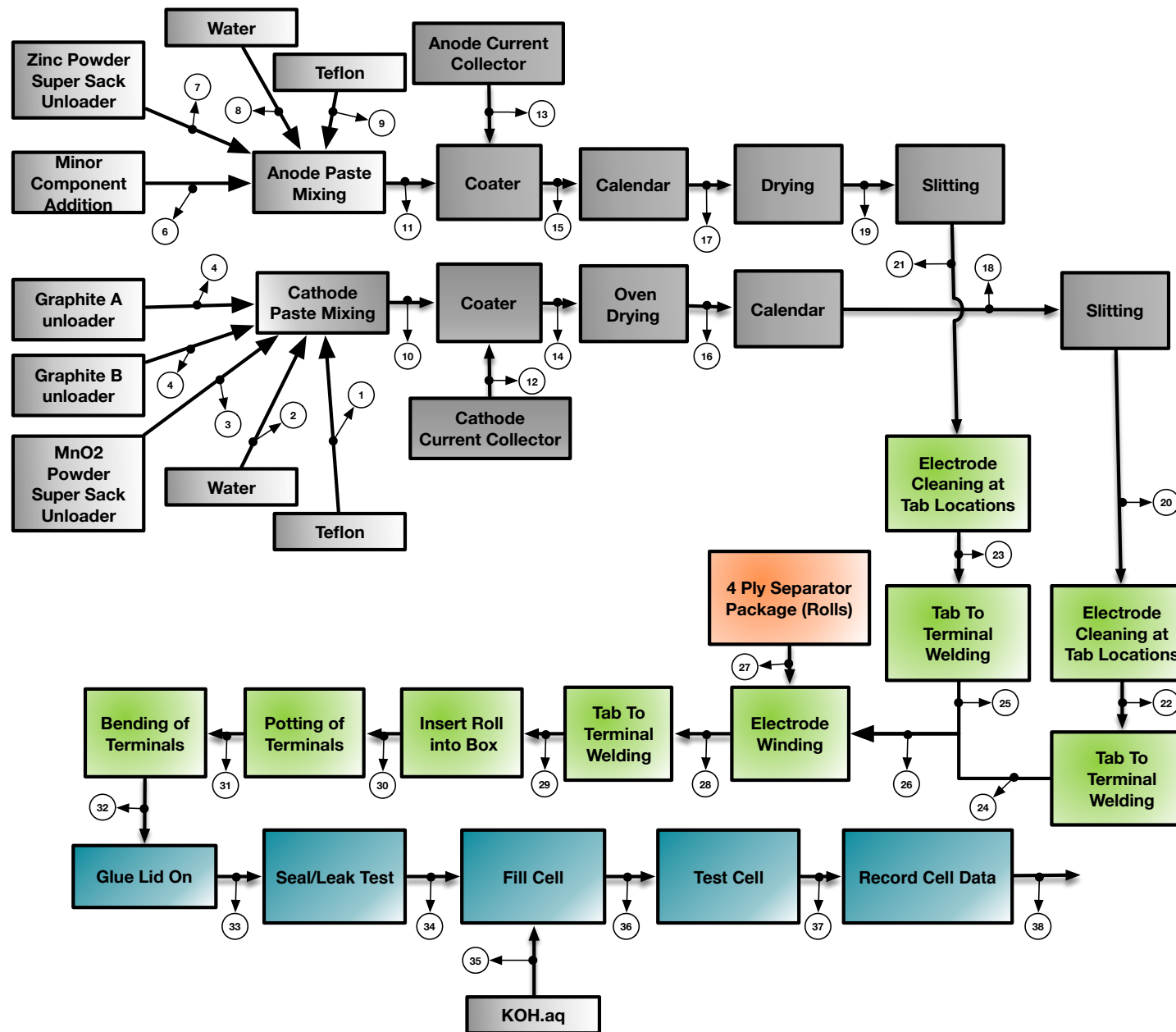
# OCV Curve for Zn-MnO<sub>2</sub>



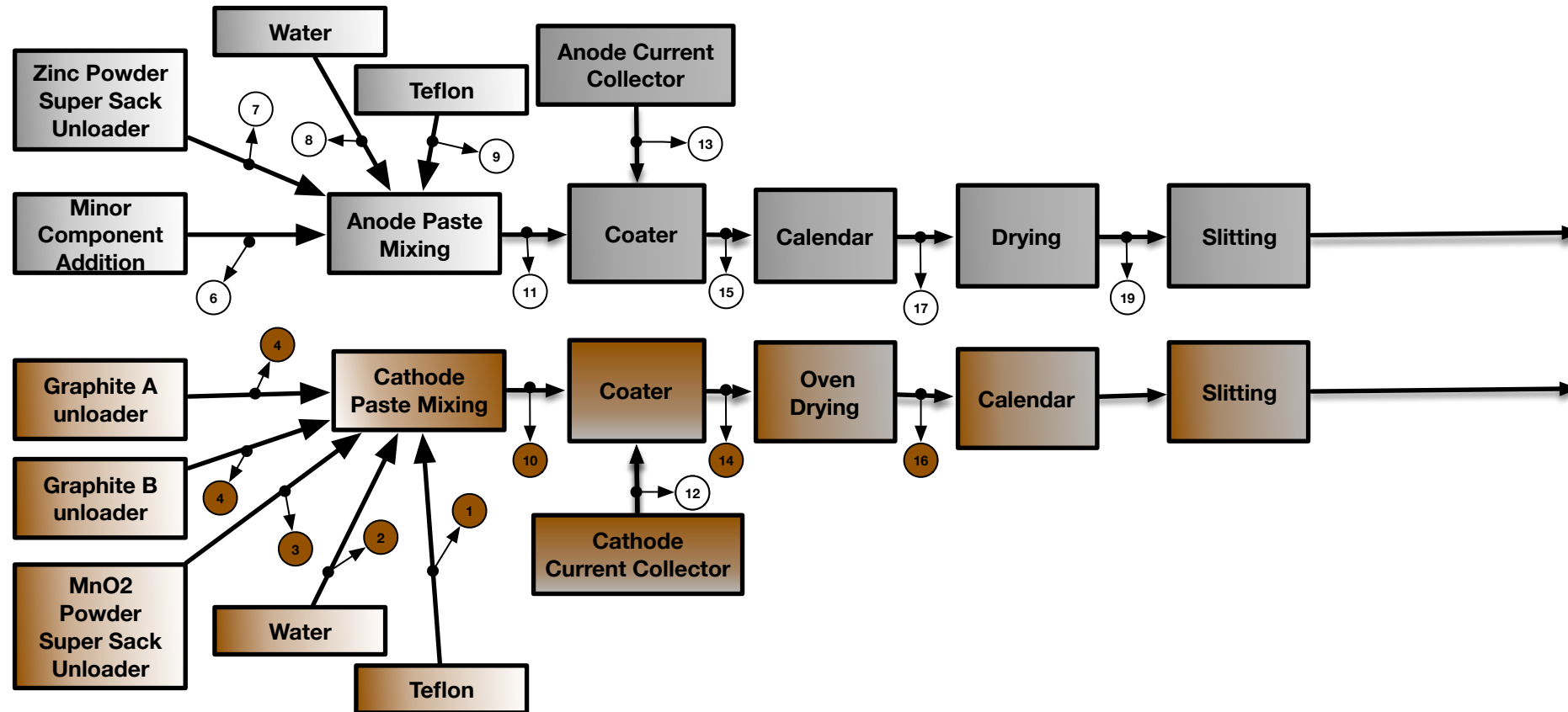
# UEP Cell Design Evolution



# UEP Manufacturing Process:

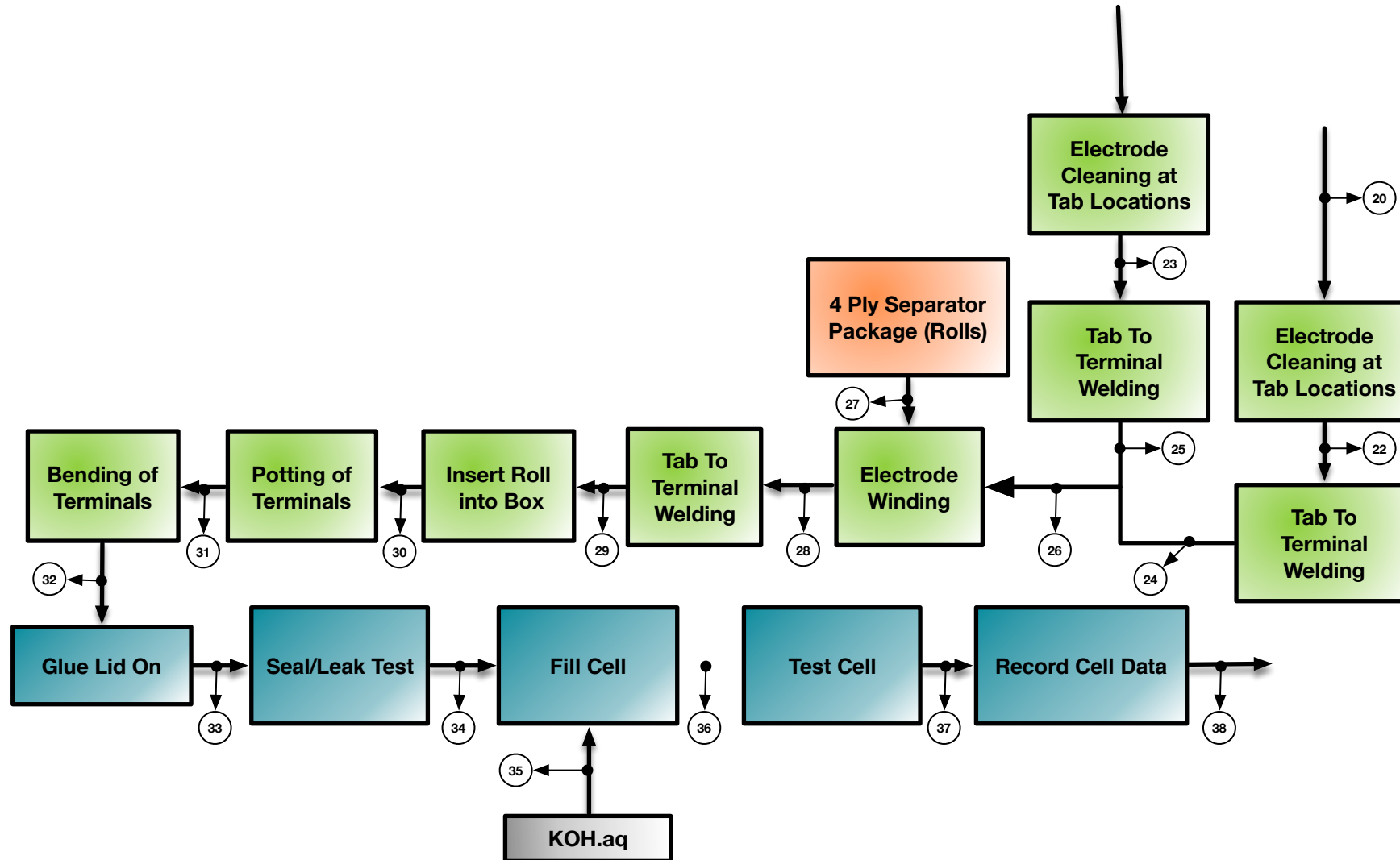


# UEP Manufacturing Process: Part 1: Continuous Segment

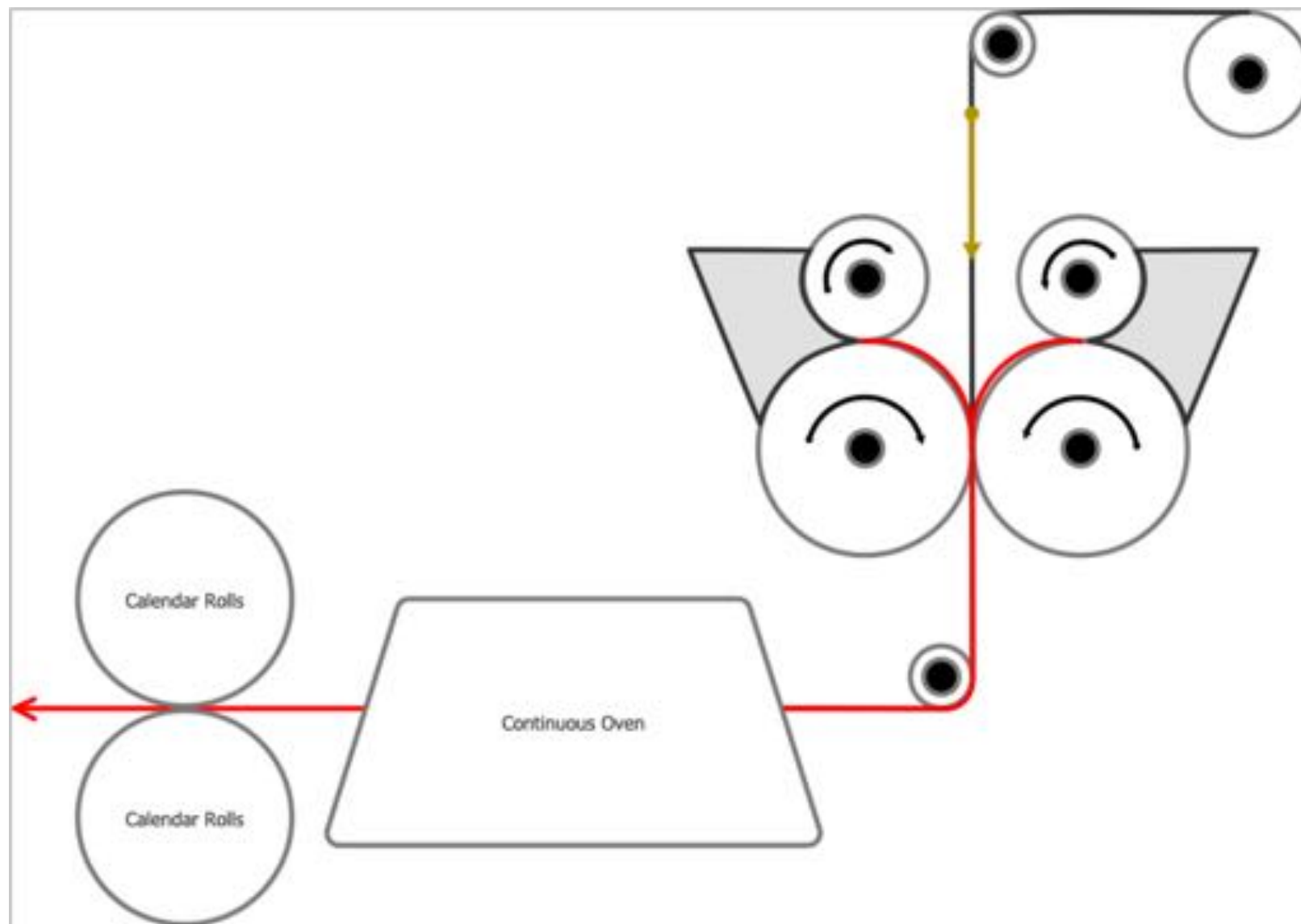


# UEP Manufacturing Process:

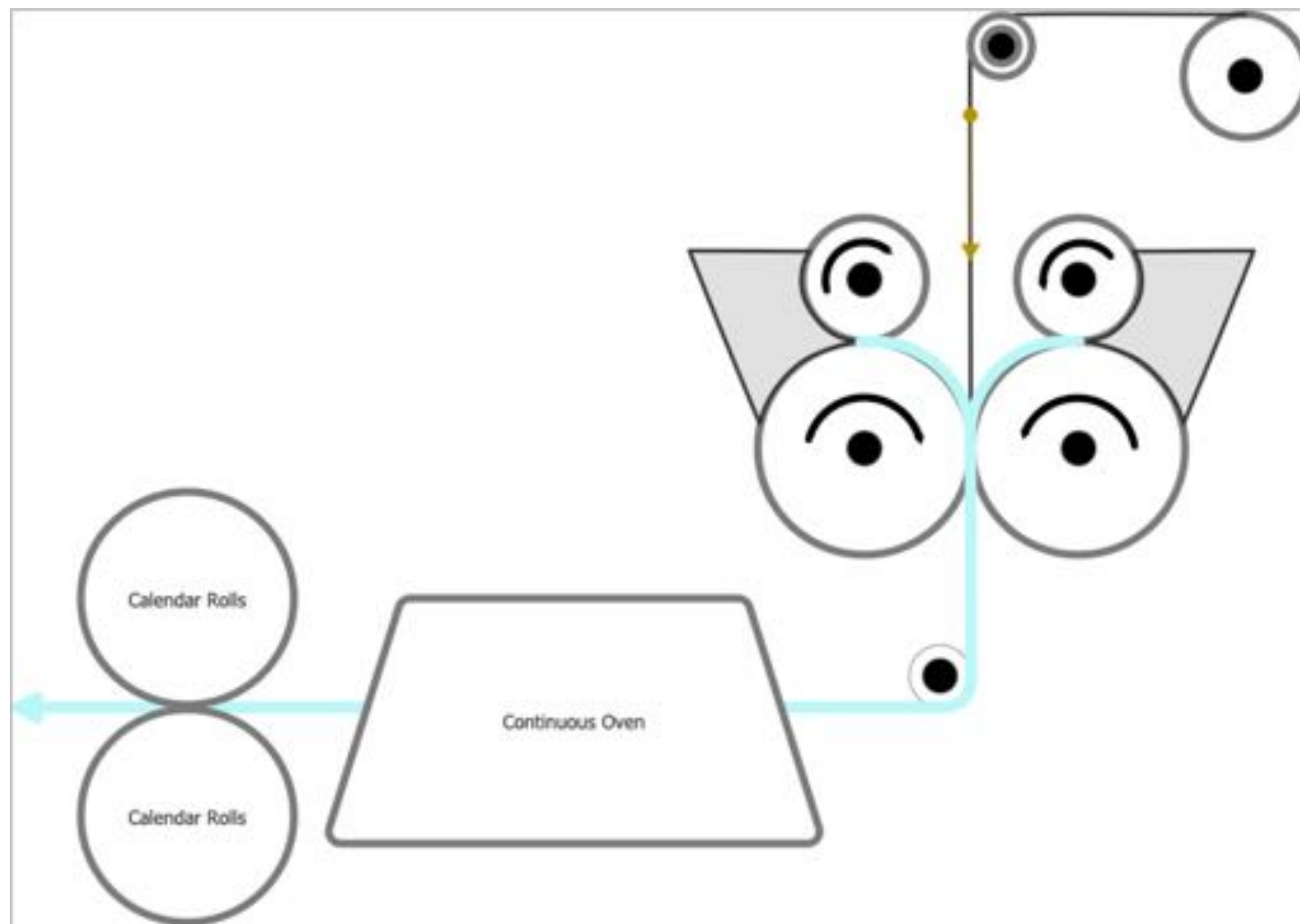
## Part 2: Discreet Segment



# Cathode Coating

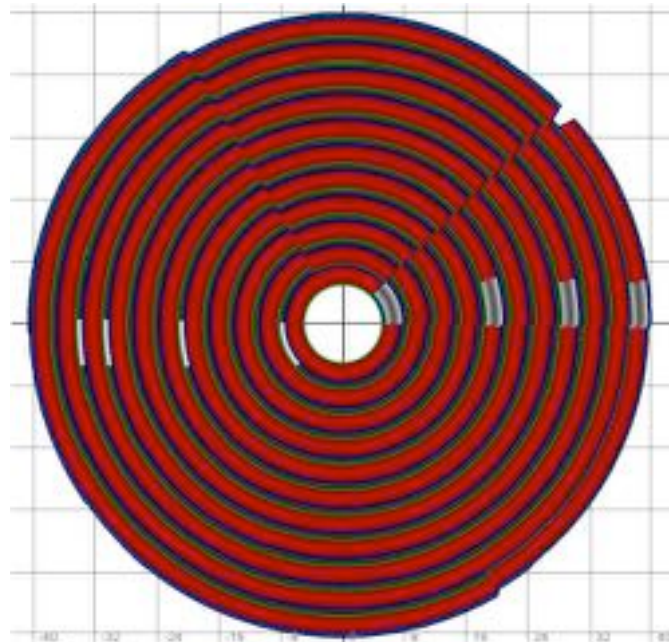


# Anode Coating

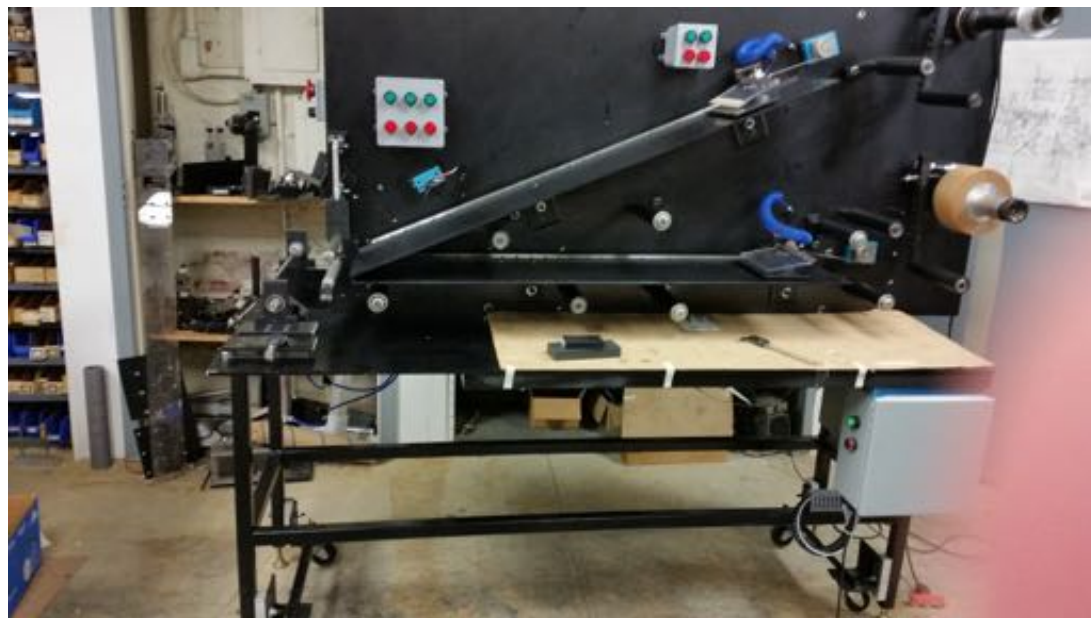




# UEP Jellyroll Cell Design



# Winding Process



# Battery project evolution

Early CUNY Energy Institute R&D focused on innovations to the zinc anode.

NY-STAR, NYSERDA EERE and ARPA-E fund dendrite and shape change prevention in zinc anodes with manganese dioxide and nickel cathodes.

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.

UEP decides to focus on a Zn-MnO<sub>2</sub> battery for stationary energy storage markets.

Market trends and raw material pricing drive this decision.

UEP moves into a pilot plant facility in Pearl River. Develops manufacturing process for the Zn-MnO<sub>2</sub> 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.

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.

UEP pilot scale manufacturing is stabilized. Cell Quality improving.

UEP begins UL and FDNY certifications for US based installations.

2008-2012

2012-2013

2014-2015

2016

2017

2018

# 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](mailto:acouzis@ccny.cuny.edu) (<https://www.ccny.cuny.edu/profiles/alexander-couzis>)
- [alex@urbanelectricpower.com](mailto:alex@urbanelectricpower.com) (<http://www.urbanelectricpower.com>)