NAATBatt Workshop on Zinc Battery Technology

Rechargeable Aqueous Zn Batteries for Large-Scale Stationary Grid Storage

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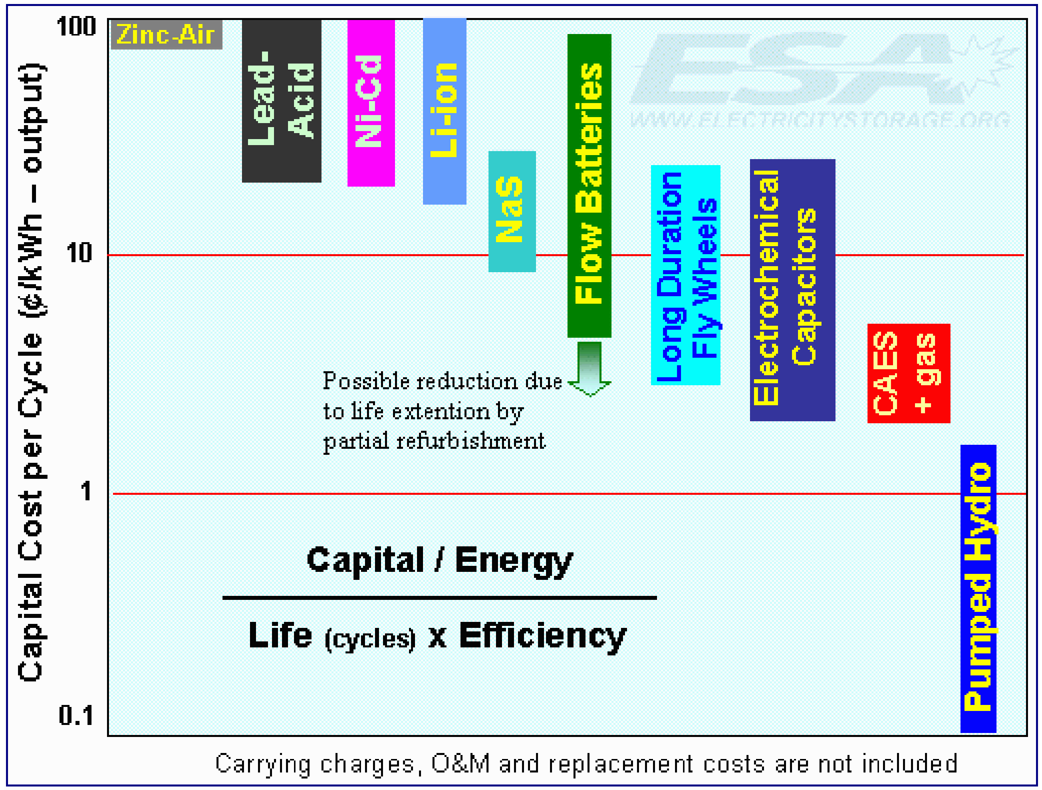
Performance, Life, Cost Metrics For Grid Storage

- ❑Cost
- ❑Cycle life
- ❑Reliability
- ❑Flexibility
- ❑Safety



CHANGING WHAT'S POSSIBLE

$$\$0.025 \text{ per kWh}_e = \frac{\$100 \text{ per kWh}}{5000 \text{ cycles} \cdot 80\% \text{ RTE}}$$

Aqueous Zn Battery

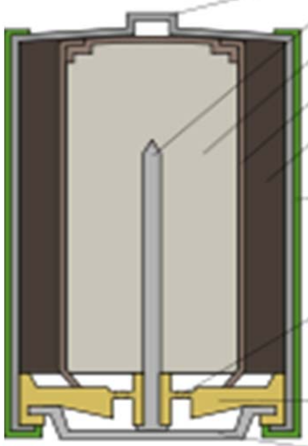
Among the aqueous rechargeable batteries, Zn^{2+}-based batteries exhibit a series of attributes for large-scale energy storage

- ❑ Low-cost Zn metal anode with a high theoretical specific capacity of 819 mAh g^{-1}

- ❑ Replacement of the traditional alkaline electrolytes by mild neutral electrolytes, mitigating the environmental disruption and recycling costs

- ❑ Low redox potential of Zn/Zn^{2+} (–0.76 V *vs.* standard hydrogen electrode) and two-electron transfer mechanism during cycling responsible for the high-energy density

Alkaline battery Zn/MnO_2



The half-reactions are:

$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
$[E_{oxidation}^\circ = +1.28\ V]$

$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$
$[E_{reduction}^\circ = +0.15\ V]$

Overall reaction:

$Zn_{(s)} + 2MnO_{2(s)} \rightleftharpoons ZnO_{(s)} + Mn_2O_{3(s)}\ [e^\circ = +1.43\ V]$

- **The primary Alkaline batteries (over 10 billion individual units produced worldwide) account for**
  - **80% of manufactured batteries (US)**
  - **46% of all primary battery sales (Japan)**
  - **68% (Switzerland), 60% (UK), and 47% (EU) of all battery sales including secondary types.**

Question/Motivation

Can we make alkaline battery rechargeable?

Attributes – low cost, safe, environmentally benign constituents, and relatively high energy density

nature energy

ARTICLES

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Reversible aqueous zinc/manganese oxide energy storage from conversion reactions

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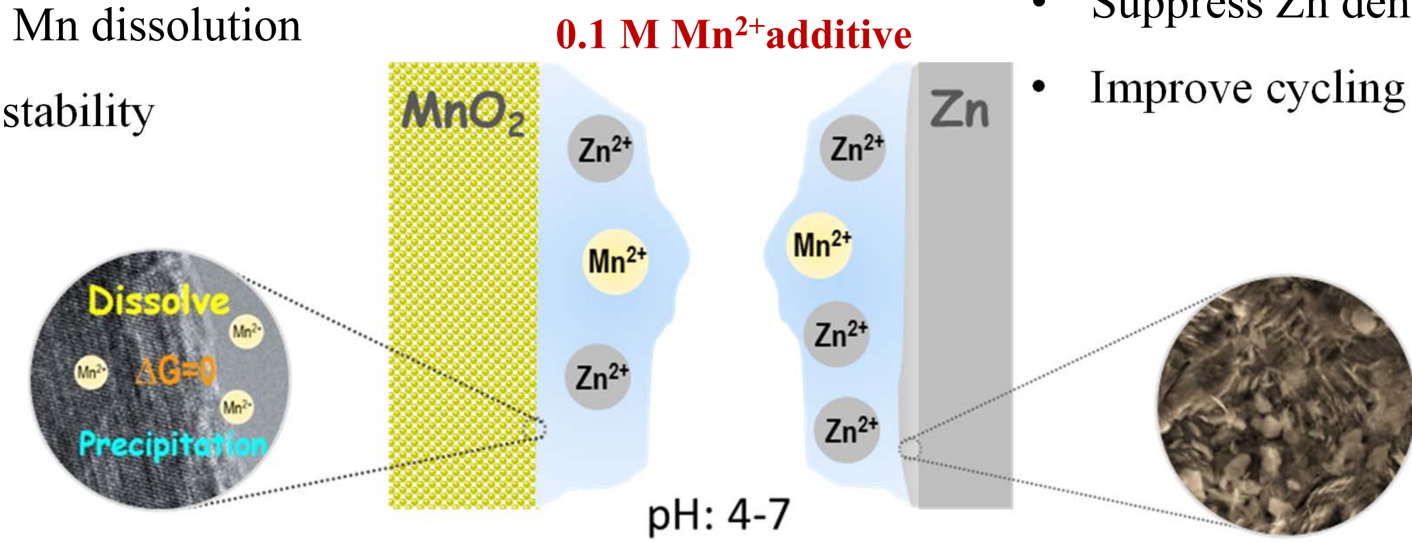
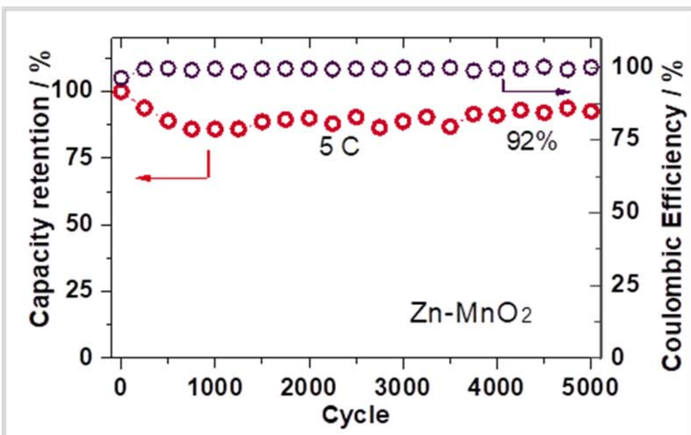
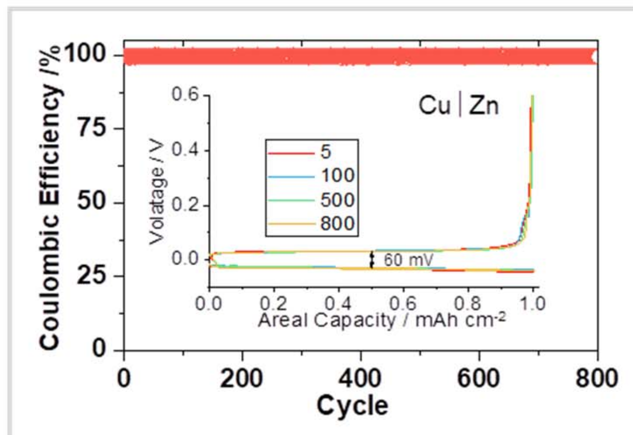
- Stabilize MnO_2/Electrolyte interface
- Suppress Mn dissolution
- Improve stability

- Improve Zn rechargeability
- Suppress Zn dendrite
- Improve cycling



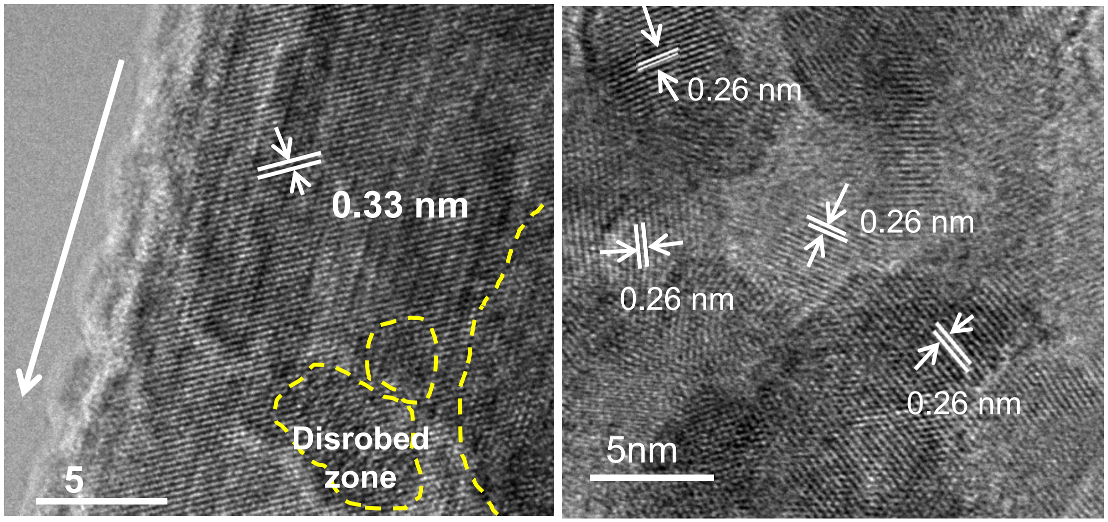




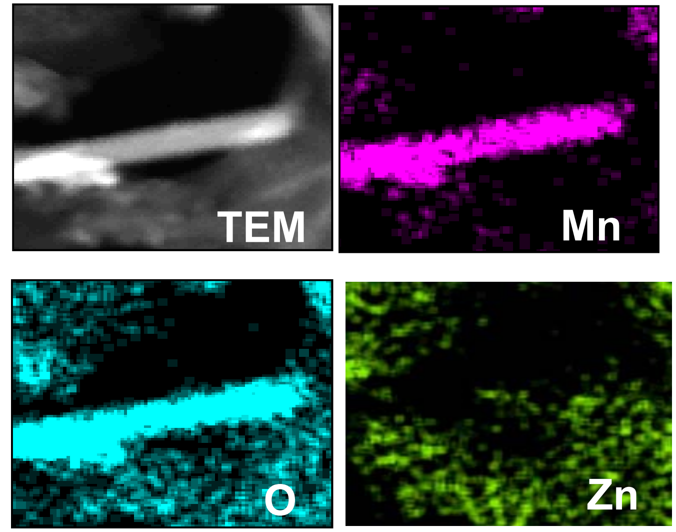
- 5000 cycles stable cycling
- CE of Zn metal >99.5%, low over potential

2 M ZnSO4+0.1M MnSO4/H2O

Mild Aqueous system-Zn-MnO_2 reaction mechanisms



(210) and (020) planes from MnOOH



No Zn intercalation in α-MnO_2

Cathode: $H_2O \leftrightarrow H^+ + OH^-$

$MnO_2 + H^+ \leftrightarrow MnOOH$

$1/2Zn^{2+} + OH^- + 1/6ZnSO_4 + x/6H_2O \leftrightarrow 1/6ZnSO_4[Zn(OH_2)]_3 . xH_2O$

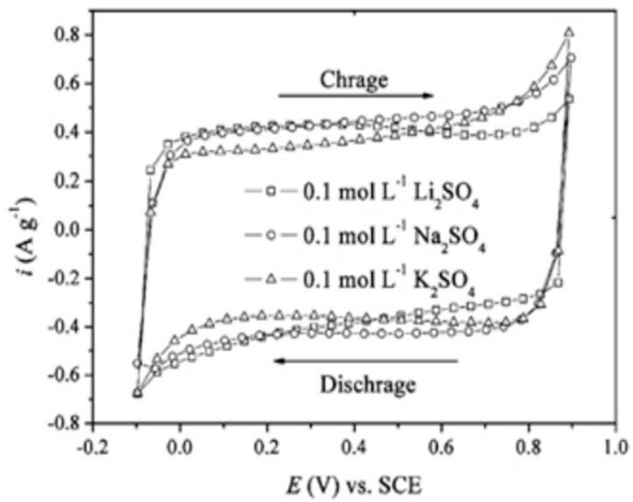
Anode: $1/2Zn \leftrightarrow 1/2\ Zn^{2+} + e^-$

Overall: $MnO_2 + 1/2Zn + x/6H_2O + 1/6ZnSO_4 \leftrightarrow MnOOH + 1/6ZnSO_4[Zn(OH_2)]_3 . xH_2O$

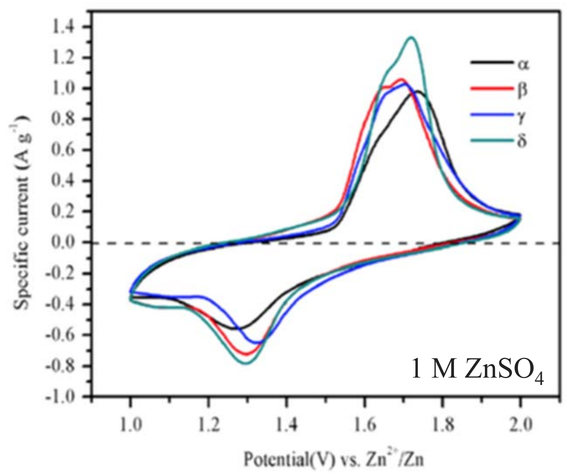
Energy density： 175 Wh/kg

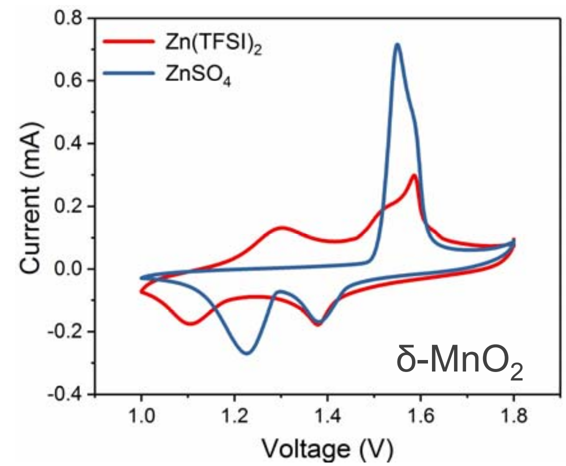
Nature Energy, 2016

Are Protons the Only Thing Active?



Journal of Power Sources 196.18 (2011): 7854-7859.





Unpublished results

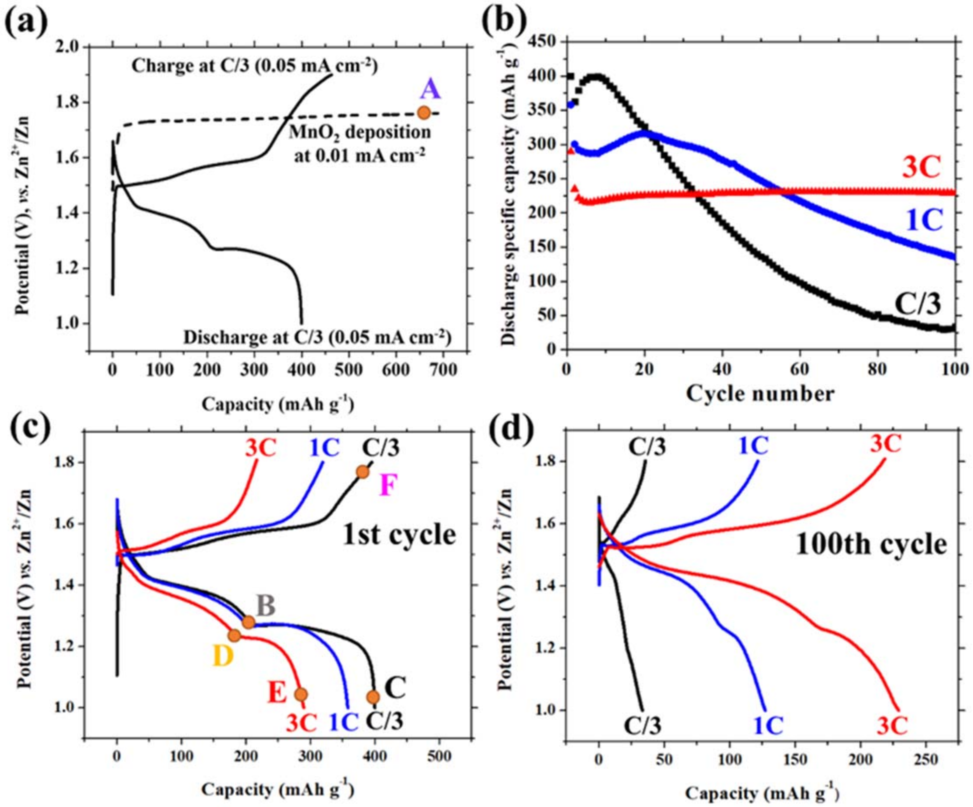
- Redox peaks observed for Zn^{2+}
- No redox for Li^+, Na^+, K^+

- H^+ conversion may not be the only reaction mechanisms for all Zn-MnO_2 systems.

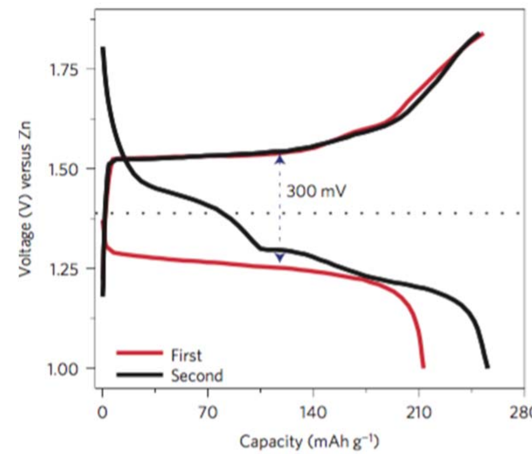
Proposed reaction mechanism in MnO_2

1. Angew. Chem. 2012, 124, 957 –959
2. Chem. Commun., 2015, 51, 9265--9268
3. Chem. Mater. 2015, 27, 3609−3620
4. Nat. Energy, 2016, 1, 16039

Electrochemical Performance of in-situ Deposited Zn/MnO_2

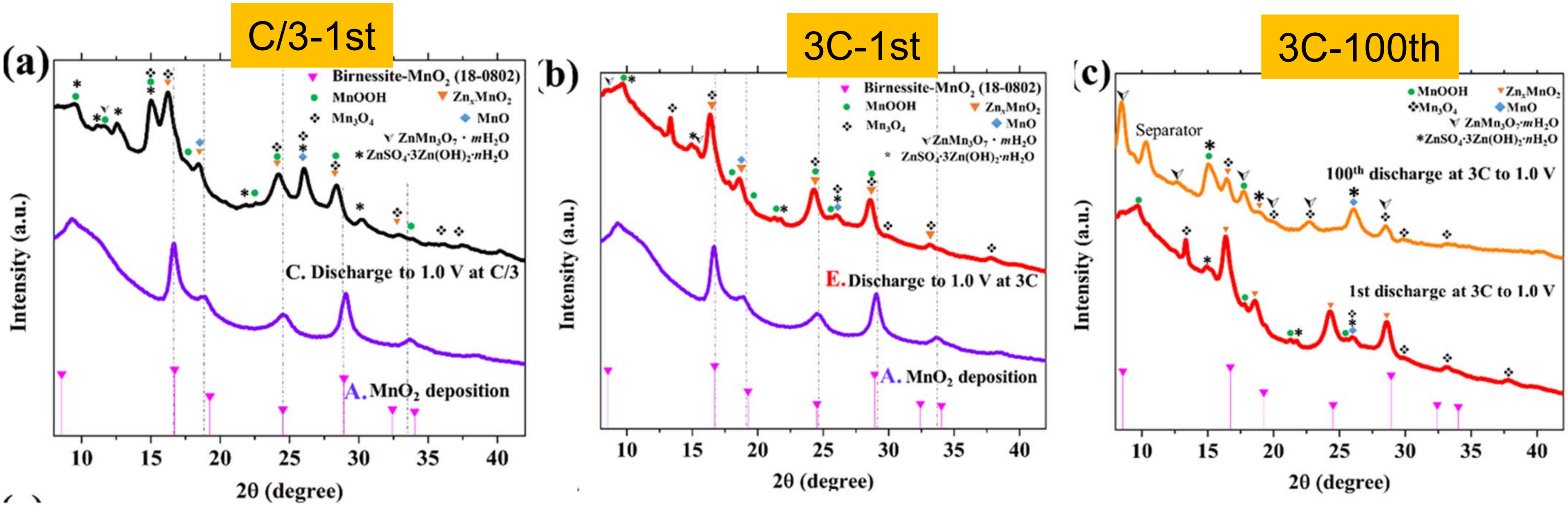


Two-plateaus



a) 1st deposition at 1.73 V, discharge at **1.40/1.26 V**, charge at **1.51/1.58 V**,
b) The capacity retention largely improved at 3C
c) 1.40 V: kinetic-favored reaction
   1.26 V: kinetic-limited reaction
d) Large contribution of 1.26 V to the capacity leading to poor capacity retention at C/3

Redox Reaction Mechanism in Zn/MnO_2

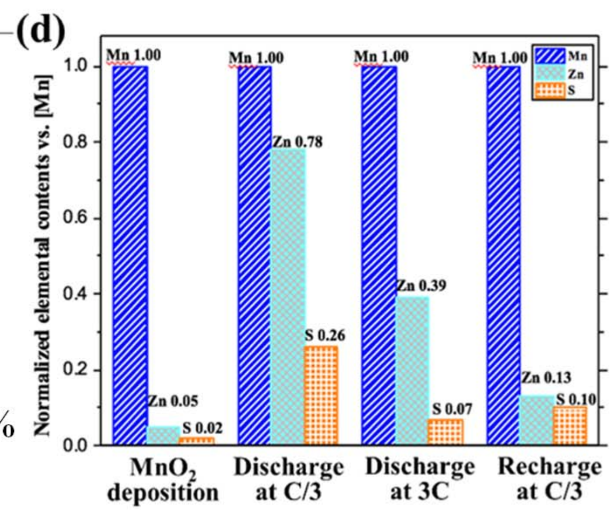


C/3

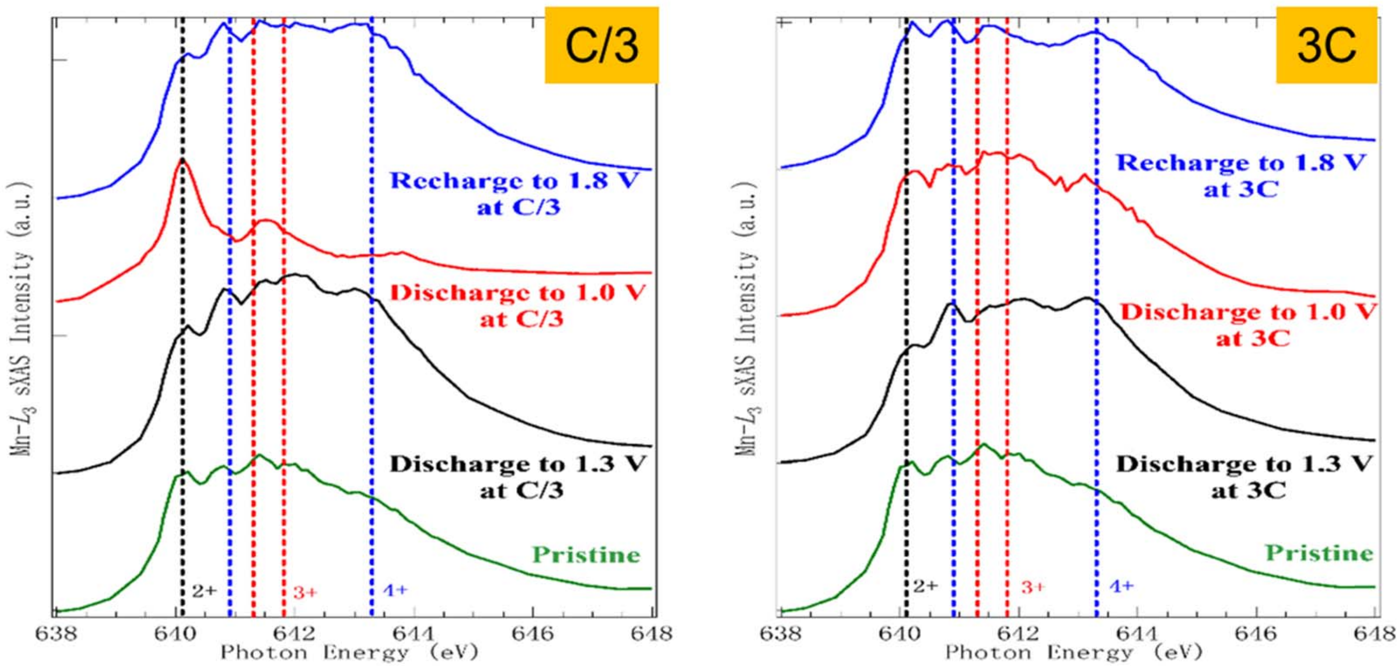
- MnO_2 peak shift by Zn^{2+}/H^+ insertion, appearance of MnOOH
- Appearance of Mn_3O_4, MnO, and $ZnSO_4{\cdot}3Zn(OH)_2{\cdot}nH_2O$

3C

- Similar Zn^{2+} insertion + MnOOH
- suppressed Mn_3O_4, MnO, and $ZnSO_4{\cdot}3Zn(OH)_2{\cdot}nH_2O$
- After 100 cycles, appearance of $ZnMn_3O_7{\cdot}mH_2O$
- 11% Zn from Zn_xMnO_2 or $ZnMn_3O_7{\cdot}mH_2O$, while all the rest 28% Zn from $ZnSO_4{\cdot}3Zn(OH)_2{\cdot}nH_2O$

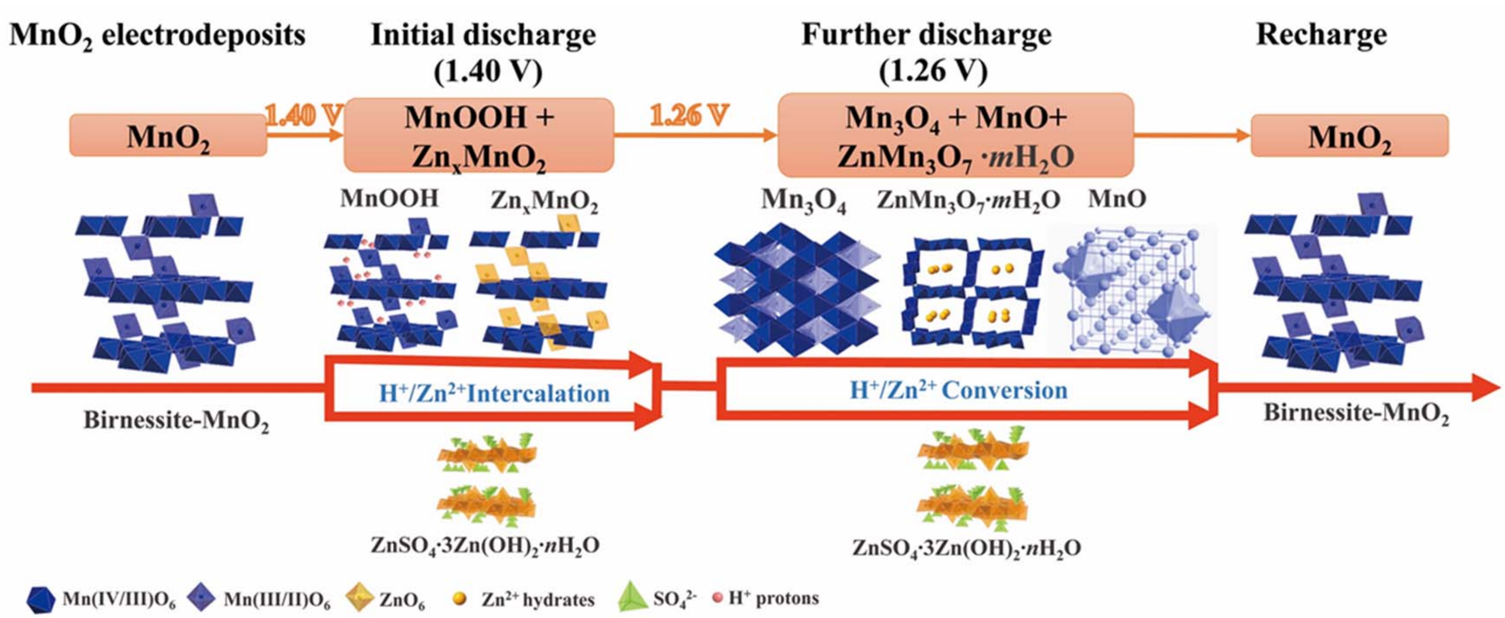


Redox Reaction Mechanism in Zn/MnO_2



1) Pristine MnO_2 electrode contains Mn^{4+}, Mn^{3+}, and Mn^2 → [$Mn^{4+}/^{3+}O_6$] and [$Mn^{3+}/^{2+}O_6$]
2) MnO_2 discharged to 1.3 V retain the $Mn^{4+/3+/2+}$ mixture
(the current density has a minor effect on the H^+/Zn^{2+} intercalation reactions at ~ 1.40 V)
3) MnO_2 fully discharged to 1V : Mn^{2+} peak was enhanced at C/3, while Mn^{3+} and Mn^{2+} increase moderately at 3C.
   - Complete reduction of $Mn^{4+/}Mn^{3+}$ to Mn^{2+} at C/3
   - The kinetics-limited conversion reaction at 1.26V was largely suppressed at high rate.
   - Hence a slight Mn valence change

Redox Reaction Mechanism Summary



DFT Calculation:

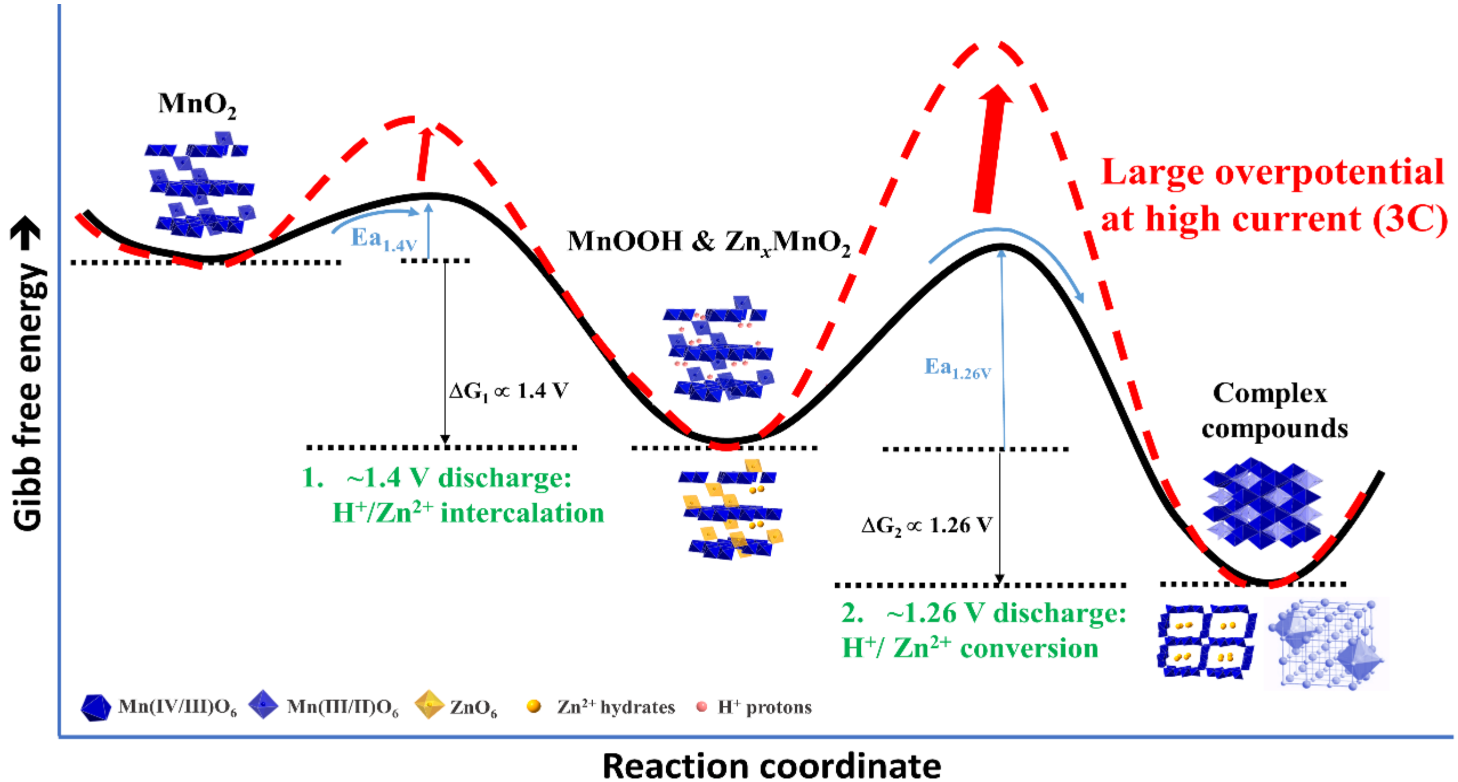
i. initial H^+/Zn^{2+} intercalation reactions (E=1.39 V, ΔG=-92.067 eV)

$$84MnO_2 + 33Zn + 10ZnSO_4 + 100H_2O \xrightarrow{H^+/Zn^{2+}\ intercalation} 60MnOOH + 24Zn_{0.125}MnO_2 + 10[ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O]$$

ii. further H^+/Zn^{2+} conversion reactions (E=1.26 V, ΔG=-10.075 eV)

$$8Zn_{0.125}MnO_2 + 16MnOOH + 4Zn + ZnSO_4 + 3H_2O \xrightarrow{H^+/Zn^{2+}\ conversion} 5Mn_3O_4 + 3MnO + 2[ZnMn_3O_7 \cdot 2H_2O] + ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$$

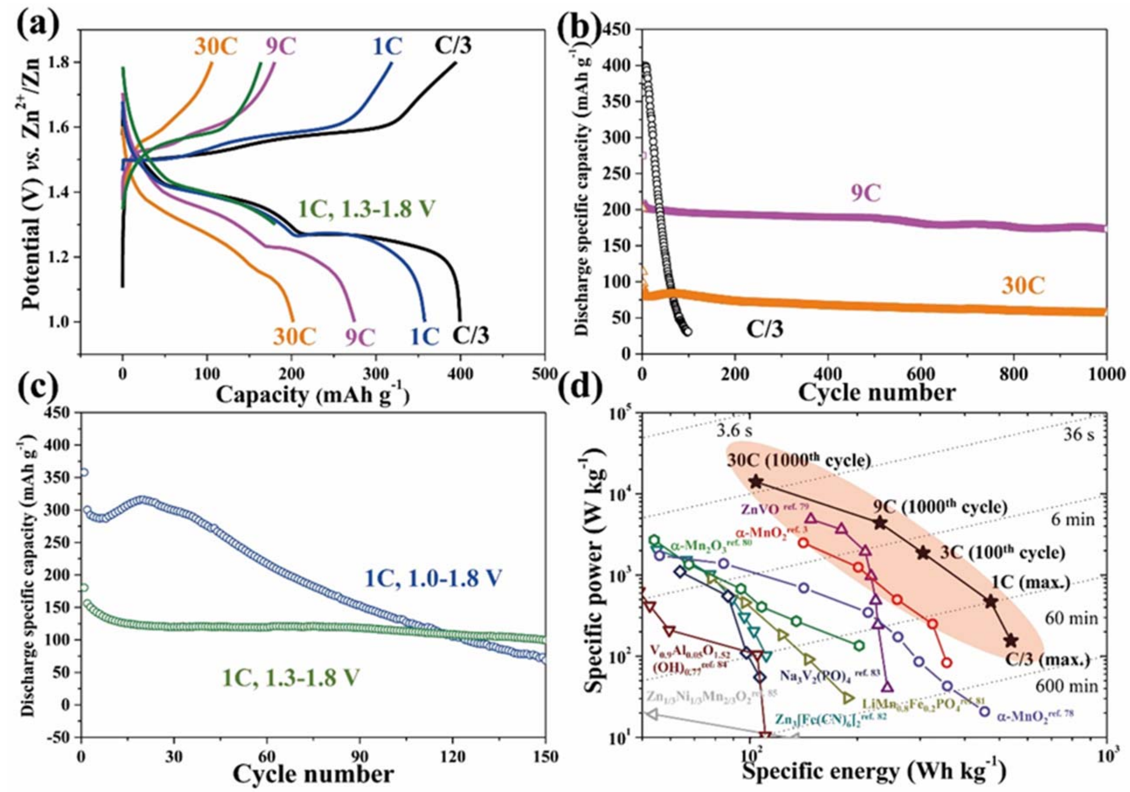
Kinetic Behavior of Zn/MnO_2



1) Small $k^\circ_{1.26V}$ → high $E_{a,1.26V}$ & large $\eta_{1.26V}$ → small achieved capacity of reactions at 1.26 V

2) High current (3C): suppressed conversion reactions at 1.26 V, causing a capacity reduction but improving capacity retention

Optimizing Power Capability and Cycling Stability of Zn/MnO_2



- Increasing C-rate or narrowing the voltage range (1.3-1.8 V) to restrain the irreversible conversion at 1.26 V
- 175 mAh g^{-1} at 9C, 75 mAh g^{-1} at 30C after 1000 cycles
- 1C, 1.3-1.8 V: a negligible capacity fading after 150 cycles
- Our cells display competitive electrochemical performances for stationery grid storage

Nature Energy, 2016, 16039. *Chemical Physics Letters*, 2016, **650**, 64-68. *Electrochimica Acta*, 2015, **182**, 971-978. *Journal of Materials Chemistry A*, 2017, **5**, 8367-8375 *Electrochimica Acta*, 2017, **229**, 422-428. *Nano Energy*, 2016, **25**, 211-217 *Advanced Energy Materials*, 2015, **5**. *Electrochemistry Communications*, 2016, **69**, 6-10 *Nature Energy*, 2016, **1**, 16119.

Summary

- Unravel concomitant intercalation and conversion reactions of H^+/Zn^{2+} occurring at 1.40 V and 1.26 V in the Zn/MnO_2 system
- Attribute the rapid capacity fading to the rate-limiting conversion reactions at 1.26 V
- Establish high performance of Zn/MnO_2 cells, delivering high energy and power density of 231 Wh kg^{-1} and 4 kW kg^{-1} at 9C (3.096 A g^{-1}) with negligible capacity fading after 1000 cycles

Thank you!

Contributors

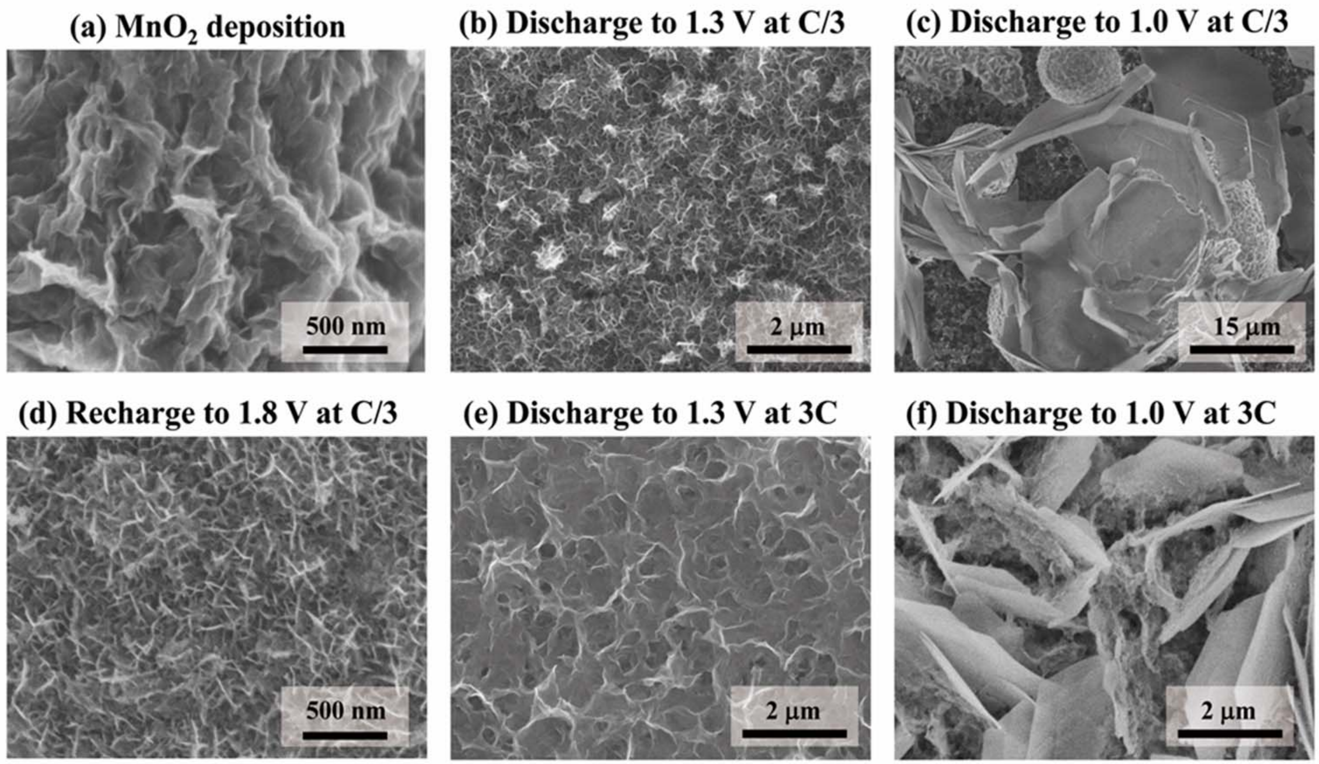
1. April Li & Shanyu Wang (UW)
2. James Salvador (GM)
3. Jinpeng Wu & Wanli Yang (LBNL)
4. Jiong Yang and Wenqing Zhang (Shanghai Univ.)
5. Huilin Pan and Jun Liu (PNNL)

Reactions Examined by DFT

Table S1.

EQUATIONS		ΔG(eV)	Voltage(V)
1)	$2MnO_2 + Zn + 2H_2O \rightarrow 2MnOOH + Zn(OH)_2$	-2.868	1.43
2)	$8MnO_2 + Zn \rightarrow 8Zn_{0.125}MnO_2$	-2.009	1.01
3)	$28MnO_2 + 11Zn + 20H_2O \rightarrow$ $20MnOOH + 8Zn_{0.125}MnO_2 + 10Zn(OH)_2$	-30.689	1.39
4)	$6MnOOH + Zn \rightarrow 2Mn_3O_4 + Zn(OH)_2 + 2H_2O$	-2.127	1.06
5)	$2MnOOH + Zn \rightarrow 2MnO + Zn(OH)_2$	-1.463	0.73
6)	$24Zn_{0.125}MnO_2 + 13Zn + 16H_2O \rightarrow 8Mn_3O_4 + 16Zn(OH)_2$	-36.885	1.42
7)	$24Zn_{0.125}MnO_2 + 21Zn + 8ZnSO_4 + 56H_2O \rightarrow 24MnO + 8[ZnSO_4 \bullet 3Zn(OH)_2 \bullet 4H_2O]$	-45.948	1.09
8)	$8Zn_{0.125}MnO_2 + Zn + 4H_2O \rightarrow 2[ZnMn_3O_7 \bullet 2H_2O] + 2MnO$	-4.026???	2.013???
9)	$8Zn_{0.125}MnO_2 + 16MnOOH + 4Zn \rightarrow$ $5Mn_3O_4 + 3MnO + 2[ZnMn_3O_7 \bullet 2H_2O] + 3Zn(OH)_2 + H_2O$	-10.075	1.26
10)	$48Zn_{0.125}MnO_2 + 74MnOOH + 41Zn + 10H_2O \rightarrow$ $38Mn_3O_4 + 8MnO + 47Zn(OH)_2$	-103.02	1.26

Redox Reaction Mechanism in Zn/MnO_2



Ex-situ SEM:

1) δ-MnO_2 deposits: hydrangea-shape cluster, reverted after recharged to 1.8 V
2) Discharge to 1.3V (C/3 & 3C): well retained MnO_2 cluster
3) Discharge to 1.0 V (C/3): large flakes of $ZnSO_4 \cdot 3Zn(OH)_2 \cdot nH_2O$ blocking the ion diffusion and disrupting the cathode structure
4) Discharge to 1.0 V (3C): Intergrowth between MnO_2 nanosheets and $ZnSO_4 \cdot 3Zn(OH)_2 \cdot nH_2O$ flakes

Performance, Life, Cost Metrics For PHEV

- ❑Cost
- ❑Cycle life
- ❑Reliability
- ❑Energy/Power
- ❑Safety

USABC Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		High Power/Energy	High Energy/Power
Reference Equivalent Electric Range	miles	10	40
Peak Pulse Discharge Power (10 sec)	kW	45	38
Peak Regen Pulse Power (10 sec)	kW	30	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	11.6
Available Energy for CS (Charge Sustaining) Mode	kWh	0.5	0.3
Minimum Round-trip Energy Efficiency (USABC HEV Cycle)	%	90	90
Cold cranking power at -30°C, 2 sec - 3 Pulses	kW	7	7
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17	5,000 / 58
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000	300,000
Calendar Life, 40°C	year	15	15
Maximum System Weight	kg	60	120
Maximum System Volume	Liter	40	80
Maximum Operating Voltage	Vdc	400	400
Minimum Operating Voltage	Vdc	>0.55 x Vmax	>0.55 x Vmax
Maximum Self-discharge	Wh/day	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature Range	°C	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66
Maximum System Production Price @ 100k units/yr	$	$1,700	$3,400

P/E, 1/hr	13	3.3
P/E, 1/hr, EFlex/Volt:		~8

More battery requirements:
www.uscar.org