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(54) Titre : BATTERIE ELECTROLYTIQUE POUR STOCKAGE D'ENERGIE A HAUTE TENSION ET ECHELONNABLE
(54) Title: ELECTROLYTIC BATTERY FOR HIGH-VOLTAGE AND SCALABLE ENERGY STORAGE

(57) Abrégé/Abstract:
A novel energy storage battery system is described that includes a highly reversible electrolytic Zn-MnO_2 system in which electrodeposition/electrolysis of Zn (anode side) and MnO_2 (cathode side) couple is employed with a theoretical voltage approximately 2 V and energy density of approximately 409 Wh kg^{-1} providing superior durability and excellent energy densities.

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(54) Title: ELECTROLYTIC BATTERY FOR HIGH-VOLTAGE AND SCALABLE ENERGY STORAGE

(57) Abstract: A novel energy storage battery system is described that includes a highly reversible electrolytic Zn-MnO_2 system in which electrodeposition/electrolysis of Zn (anode side) and MnO_2 (cathode side) couple is employed with a theoretical voltage approximately 2 V and energy density of approximately 409 Wh kg^{-1} providing superior durability and excellent energy densities.

ELECTROLYTIC BATTERY FOR HIGH-VOLTAGE AND SCALABLE ENERGY STORAGE

[001] FIELD OF THE INVENTION

[002] The field of the invention relates to rechargeable batteries and in particular rechargeable zinc-manganese dioxide (Zn-MnO_2) batteries that have increased output voltage and discharge capacity.

[003] BACKGROUND

[004] There is a great deal of attention and interest in battery technology and development, and in particular in the development of scalable energy storage solutions that are economical to produce whilst also providing high capacity storage and efficient, reliable discharge with light weight so as to be able to address energy demands in current applications such as electric vehicles and green energy storage solutions.

[005] Current battery types include lithium-ion battery, nickel batteries, and lead acid batteries, the latter of which has been around for quite some time.

[006] Lead-acid batteries, for example, are relatively cheap to produce and incorporate lead plates in an acidic solution, widely used for storage in back-up power supplies in hospitals as well as for computer related equipment.

[007] Lead acid batteries have significant drawbacks, not only in relation to their environmental impact using lead plates, which although may be recycled, are often discarded along with the highly corrosive sulphuric acid.

[008] Lithium-ion batteries are often seen as a preferable alternative in terms of their long life due to their high charge density. Lithium-ion batteries use organic solution as electrolyte and are rechargeable. Such batteries are commonly used in the field of portable electronics however they have a limited rechargeable battery life (the number of full charge–discharge cycles before significant capacity loss) and are vulnerable to exothermic degradation reactions. Lithium-ion batteries may also experience thermal runaway events which can lead to cell rupture and in extreme cases leakage of the contents, which may

present significant safety problems. Lithium-ion batteries are also relatively expensive with an approximate cost of US$300 per kWh (kilowatt hour). With lead acid batteries costing approximately US$48 per kWh, the lower cost is considered more commercially appealing, despite the drawbacks in limited storage and discharge capacity.

[009] SUMMARY OF THE INVENTION

[010] In one aspect of the invention, although this should not be seen as limiting in any way, there is a rechargeable electrolytic zinc-manganese dioxide battery, including an anode, a cathode-less substrate and aqueous electrolyte containing zinc and manganese ions, and an acid, the aqueous electrolyte having a pH value less than 2.5.

[011] In preference, the electrolyte includes sulphate ions.

[012] In preference, the acid is H_2SO_4.

[013] In preference, the anode is a zinc anode.

[014] In preference, the zinc anode is a zinc foam anode.

[015] In preference, the anode is made from at least one of carbon and/or pure zinc/zinc alloy.

[016] In preference, the zinc is fabricated onto graphite foam to form the zinc foam anode.

[017] In preference, the cathode-less substrate is selected from other suitable current collectors.

[018] In preference, the cathode-less substrate is carbon.

[019] In preference, the cathode-less substrate is carbon fibre cloth.

[020] In preference, MnO_2 is deposited onto the cathode-less substrate after charging.

[021] In preference, the pH of the electrolyte is controlled from 0 – 2.5.

[022] In preference, the pH of the electrolyte is less than 2.0.

[023] In preference, the pH of the electrolyte is 2.

[024] In preference, the pH of the electrolyte is less than 1.5.

[025] In preference, the electrolyte includes a soluble zinc salt and a soluble manganese salt.

[026] In preference, the rechargeable zinc-manganese dioxide battery of the present invention is charged at a constant voltage.

[027] In preference, the constant voltage is between approximately 2.00 V and 2.41 V.

[028] A further form of the invention resides in a method of recharging an electrolytic zinc-manganese dioxide battery, including an anode, a cathode-less substrate and aqueous electrolyte containing zinc and manganese ions, the aqueous electrolyte having a pH value less than 2.5, wherein the battery is recharged at a constant voltage between approximately 2.00 V and 2.41 V.

[029] BRIEF DESCRIPTION OF THE DRAWINGS

[030] By way of example, an embodiment of the invention is described with reference to the accompanying drawings, in which:

[031] Figure 1a is a schematic illustration and charge storage mechanism analysis of the battery in 1 M $ZnSO_4$ + 1 M $MnSO_4$ electrolyte (without H_2SO_4).

[032] Figure 1b is a schematic illustration of the charge storage mechanism of the electrolytic Zn-MnO_2 battery in 1 M $ZnSO_4$ + 1 M $MnSO_4$ + H_2SO_4 electrolyte.

[033] Figure 2a is a graph of the change of pH values at differing cycles of the present invention in electrolyte without H_2SO_4;

[034] Figure 2b is a graph of the pH values of the electrolytes with changes in molarity of H_2SO_4 (x M H_2SO_4);

[035] Figure 2c is a graph of the galvanostatic discharge curves in the electrolytes with x M H_2SO_4;

[036] Figure 2d is a graph of the electrochemical stability in electrolytes with 0.1 M H_2SO_4, shows the preferred deposition voltages on a graph potential vs current.

[037] Figure 2e is a graph of the galvanostatic discharge curves at different rates from 2 to 60 mA cm^{-2};

[038] Figure 2f is the rate capability at different rate from 2 to 60 mA cm^{-2}. Inset shows the digital photograph of the home-made electrolysis cell.

[039] Figure 2g is a graph of the galvanostatic discharge curves for the first 50 cycles of the battery of the present invention with 0.1 M H_2SO_4;

[040] Figure 2h is cycling stability test at 30 mA cm^{-2};

[041] Figure 3 is a plot of various Zn-based batteries and their capacity vs voltage vs energy density.

[042] RESULTS

[043] Charge storage mechanism in electrolytic zinc-manganese dioxide battery.

[044] With reference to figure 1, the present invention is schematically illustrated as a result of chronoamperometric electrodeposition.

[045] The cell of the present invention as shown in figure 1 is includes a Zn foam anode, glass fiber separator, cathode-less carbon fiber cloth, and $ZnSO_4$ + $MnSO_4$ aqueous electrolyte for figure 1a and $ZnSO_4$ + $MnSO_4$ + H_2SO_4 aqueous electrolyte for figure 1b. Advantageously, $ZnSO_4$ and $MnSO_4$ are low cost, highly stable and soluble in water. Three-dimensional (3D) light-weight Zn foam is applied as a protype to replace a

conventional compact Zn foil anode, in consideration of suppressing Zn dendrite, and improving Zn utilization and corresponding overall energy/power density.

[046] In the initial chronoamperometry charge process at 2.2 V as shown in Figure 1, the Zn^{2+} and Mn^{2+} ions from the electrolyte solution are reduced to Zn on the anode and oxidized to form solid MnO_2 onto carbon fiber. This synthetic approach provides uniform and robust contact with substrates without use of binder or conductive additives. Multi redox reactions occurs in $ZnSO_4$ + $MnSO_4$ aqueous electrolyte (without H_2SO_4) during the galvanostatic discharge process (see figure 1a). Referring to figure 2c, a discharge curve shows three main discharge regions, D1 (2.0–1.7 V), D2 (1.7–1.4 V), and D3 (1.4–0.8 V). The average discharge voltage plateau is only ~ 1.4 V in the electrolyte without H_2SO_4.

[047] Monitoring the pH values of the electrolyte in the above MnO_2 battery without H_2SO_4 are shown in figure 2a, and the pH values decrease as the increase of cycling number, i.e., from 4.60 at its original state to 2.32 after 10 cycles, and then stabilize at 2.30 after 20 cycles. Addition of H_2SO_4 simulates the effect of the increase in acidity in the electrolyte (see pH changes in figure 2b), in which a series of concentrations of H_2SO_4 was added into 1 M $ZnSO_4$ and 1 M $MnSO_4$ electrolyte directly (noted as x M H_2SO_4). The pH value drops dramatically from 4.60 without H_2SO_4 to 1.47 with 0.05 M H_2SO_4, and then decreases gradually to 0.67 and 0.31 with 0.30 and 0.60 M H_2SO_4 respectively. The corresponding galvanostatic discharge curves in figure 2c shows an intrinsic change in the capacity percentage of the high-voltage region D1, from ~26% without H_2SO_4 to ~67% with only 0.05 M H_2SO_4 and ~100% with 0.10 M or higher concentration. Moreover, the discharge plateau keeps rising (see figure 2c and Table 1), benefiting from the higher electrolyte conductivity, increased protons concentration, and decreased electrochemical polarization at high acidity

Electrolytic Zn- MnO_2 battery	without H_2SO_4	0.05 M H_2SO_4	0.10 M H_2SO_4	0.15 M H_2SO_4	0.30 M H_2SO_4
Capacity (mAh cm^{-2})	1.92	1.94	1.97	1.94	1.89
Coulombic efficiency	96.0%	97.0%	98.5%	97.0%	94.5%

High voltage percentage (>1.7 V)	26.0%	67.0%	98.5%	98.9%	99.4%
Average plateau (V)	1.44	1.79	1.95	1.97	1.99

Table 1 The discharge capacity, Coulombic efficiency, and average discharge plateau of the electrolytic Zn-MnO_2 battery in 1 M ZnSO4, 1 M MnSO4, and x M H2SO4 electrolyte.

[048] Electrochemical stability tests of the Zn foam anode were performed and the electrolyte with 0.10 M H_2SO_4 shows superior stability and reversibility than ones with 0.15 and 0.30 M H_2SO_4 during Zn plating/stripping even at a high current of 20 mA cm^{-2}. As shown in figure 2d, the electrolyte with 0.10 M H_2SO_4 exhibits a wide electrochemical window and the parasitical H_2 (zinc anode) and O_2 (MnO_2 cathode) evolution reactions are significantly suppressed up to –1.06 V and 1.35 V vs. Ag/AgCl, respectively. The results indicate that a minimum deposition voltage of approximately 2.00 V is required for the simultaneous deposition of Zn and MnO_2. A maximum working voltage window of approximately 2.41 V was obtained within the H_2 and O_2 evolution potentials.

[049] High-rate capability has been regarded as an important indicator for large scale application of batteries, such as fast-charging for electric vehicles and cell phones, and regenerative braking. The designed electrolytic Zn-MnO_2 battery of the present invention was then galvanostatically discharged at different current densities from 2 to 60 mA cm^{-2} as shown in figures 2e and 2f. The discharge curves in the electrolyte with 0.10 M H_2SO_4 showed a typical battery behaviour with flat discharge plateaus of 1.95 V at 2 mA cm^{-2} and 1.55 V even at 60 mA cm^{-2} (in 100 s).

[050] The discharge plateau and the acidity of the electrolyte are also proved stable along with the cycles (figure 2g). The discharge capacities retain higher than 1.96 mAh cm^{-2} at 4C (8 mA cm^{-2}) and 1.67 mAh cm^{-2} at 30C (60 mA cm^{-2}). The electrolytic Zn-MnO_2 battery of the present invention shows excellent cycling sustainability even at high rates. Around 92% of the maximum discharge capacity is maintained after 1800 cycles at 30 mA cm^{-2} (figure 2h). This rate stability can be ascribed to the synergetic effects of the favourable and solo electrolysis reaction, higher electrolyte conductivity, smaller ohm and charge transfer resistances, and faster ion diffusion.

[051] The gravimetric capacities of electrolytic Zn-MnO_2 batteries are shown in figure 3, which were calculated based on the deposited mass of MnO_2 after 10 cycles on carbon fiber cathode. The electrolytic $ZnMnO_2$ batteries of the present invention stand out in both the gravimetric capacities and the discharge plateaus. The gravimetric capacities of the MnO_2 ZIBs with 0 and 0.05 M H_2SO_4 are much lower than that of the electrolytic Zn-MnO_2 batteries (0.01-0.5 M) due to the presentence of both one- and two- electron reactions. The electrolytic Zn-MnO_2 battery of the present invention with 0.10 M H_2SO_4 exhibits the best gravimetric capacities as a result of high CE. As can be seen in figure 3, at 0 M H_2SO_4 the energy density of the battery of the present invention is approximately 500 Wh kg^{-1}. The energy density increases significantly at both 0.05 M and 0.1 M H_2SO_4.The electrolytic Zn-MnO_2 battery demonstrates unprecedented energy densities of ~1100 Wh kg^{-1} based on the active material mass of cathode, and ~409 Wh kg^{-1} when taking mass of Zn anode into consideration. These values correspond to at least 300 % increase in the energy density compared with reported ZIBs.

[052] The electrolytic Zn-MnO_2 battery of the present shows charging/discharging at an areal capacity up to 10 mAh cm^{-2} with 96.0% CE and improvements such as increasing the thickness or surface area of the substrates can be used to further enhance the areal and volumetric behaviours. In further embodiments magnetic stirring or flowing design of the cell could be included. An electrolytic Zn-MnO_2 battery stack of the present invention with three cells in series connection was able to charge a cellphone (5 V, 5 W), after charging for only 60 s at 6.6 V with open-circuit potential of 6.24 V. The output voltage, energy efficiency, and cost of the electrolyte outperform conventional aqueous flow battery systems, such as Zn-Fe, Zn-Br_2, Zn-Ce, Zn-air, and all vanadium flow batteries. The electrolytic Zn-MnO_2 battery of the present invention exhibits excellent charge storage properties and high energy/power density which can meet the rapid power change from the grid.

[053] The Zn-MnO_2 battery of the present invention uses low-cost electrolytic electrochemistry, and demonstrated outstanding properties, such as unprecedented voltage and capacity, as well as energy density compared with rechargeable known Zn-based batteries. The superior plateau performance is believed a result of both the improved proton reactivity and the cation vacancy activated MnO_2 in acidic electrolyte.

[054] METHODS

[055] Materials. All reagents and materials in this work are all commercially available and used without further purification. Zinc sulfate monohydrate ($ZnSO_4 \cdot H_2O$, ≥99.0%), manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$, ≥99.0%), sulfuric acid (H_2SO_4, 95.0–98.0%), sodium sulfate (Na_2SO_4, ≥99.0%), and boric acid (H_3BO_3, ≥99.5%) were purchased from Sigma-Aldrich.

[056] Electrodeposition/electrolysis Zn-MnO_2 cell design. The Zn-MnO_2 aqueous batteries were assembled in the home-made electrolysis cell (see inset in figure 2f) using carbon fiber cloth as the cathode-less current collector and the Zn foam as the anode. 1 M $ZnSO_4$, 1 M $MnSO_4$ and x M H_2SO_4 solution was used as the electrolyte for electrolytic batteries. The carbon fiber cloth was treated hydrophilic by air plasma for 5 min before acting as a current collector. Zn foam anode was fabricated onto graphite foam via electrodeposition method with a solution with 2 g $ZnSO_4 \cdot H_2O$, 3 g Na_2SO_4, and 0.5 g H_3BO_3 dissolved in 20 mL DI water, and a constant current of 10 mA cm^{-2} for 60 mins. The areal mass loading of the Zn foam was 3.6 mg cm^{-2} . The cathode and anode were sandwiched by glass fiber paper separator and assembled in a typical coin-cell stack. Ti/Cu foil was used as current collector for the electrodes, which was separated and not directly contacted with the electrolyte to avoid any side reactions.

[057] MEASUREMENTS

[058] The chronoamperometry charge, galvanostatic discharge, cycling, and electrochemical impedance spectroscopy (EIS) measurements were recorded using LAND battery cycler (CT2001A), and IM6e potentiostat (Zahner Elektrik Co., Germany) at room temperature. The cell was charged at 2.2 V (vs. Zn/Zn^{2+}) to 2 mAh cm^{-2} with a constant-voltage technique to form uniform and mesoporous MnO_2 fluff. Then galvanostatic discharge at different current densities from 2−60 mA cm^{-2} was applied with a cut off voltage of 0.8 V vs. Zn/Zn^{2+} . The electrolytic Zn-MnO_2 single cell was performed in a two-electrode set-up, where Zn foam was applied as the anode and carbon fiber cloth for the cathode-less substrate.

[059] The electrochemical stability and reversibility of electrolytes were tested in symmetrical Zn foam/Zn foil set-up in electrolyte with 0.10, 0.15 and 0.30 M H_2SO_4 . The OER and HER tests were carried out in a three-electrode set-up with deposited MnO_2 as positive electrode, Ag/AgCl as the reference electrode, and Zn foam as the negative electrode. Liner sweep voltammetry was tested at 1 mV s^{-1} . The recorded areal capacities and current densities were calculated based on the geometric area of the deposited MnO_2 . The reported gravimetric capacity was determined according to the mass of deposited MnO_2 active material. The energy and power densities were normalized to the total mass from both anode and cathode active materials.

Claims

1. A rechargeable electrolytic zinc-manganese dioxide battery, including an anode, a cathode-less substrate and aqueous electrolyte containing zinc and manganese ions, and an acid, the aqueous electrolyte having a pH value less than 2.5, wherein the rechargeable zinc-manganese dioxide battery is charged at a constant voltage, and wherein the constant voltage is between approximately 2.00 V and 2.41 V.

2. The rechargeable electrolytic zinc-manganese dioxide battery of claim 1, wherein the electrolyte includes sulphate ions.

3. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the acid is H_2SO_4.

4. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the anode is a zinc anode.

5. The rechargeable electrolytic zinc-manganese dioxide battery of claim 4, wherein the zinc anode is a zinc foam anode.

6. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims 1-3 or 5, wherein the anode is made from at least one of carbon and/or pure zinc/zinc alloy.

7. The rechargeable electrolytic zinc-manganese dioxide battery of claim 5, wherein the zinc is fabricated onto graphite foam to form the zinc foam anode.

8. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the cathode-less substrate is selected from other suitable current collectors.

9. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the cathode-less substrate is carbon.

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10. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the cathode-less substrate is carbon fibre cloth.

11. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein MnO_2 is deposited onto the cathode-less substrate after charging.

12. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the pH of the electrolyte is controlled from 0 – 2.5.

13. The rechargeable electrolytic zinc-manganese dioxide battery of claim 12, wherein the pH of the electrolyte is less than 2.0.

14. The rechargeable electrolytic zinc-manganese dioxide battery of claim 12, wherein, the pH of the electrolyte is 2.

15. The rechargeable electrolytic zinc-manganese dioxide battery of claim 13, wherein the pH of the electrolyte is less than 1.5.

16. The rechargeable electrolytic zinc-manganese dioxide battery of any one of the above claims, wherein the electrolyte includes a soluble zinc salt and a soluble manganese salt.

Date reçue / Date received 2021-11-03

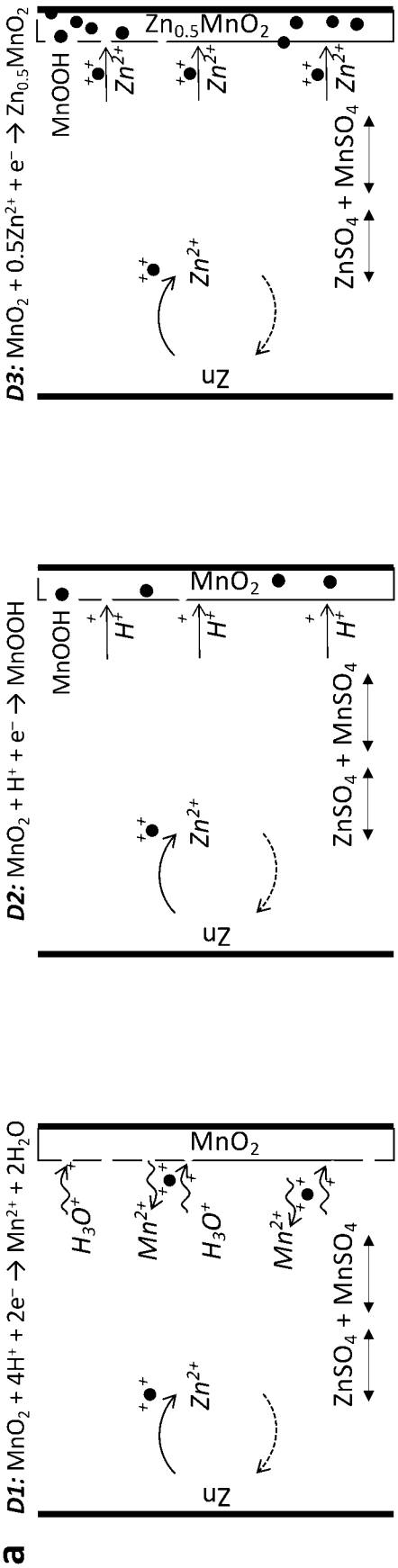
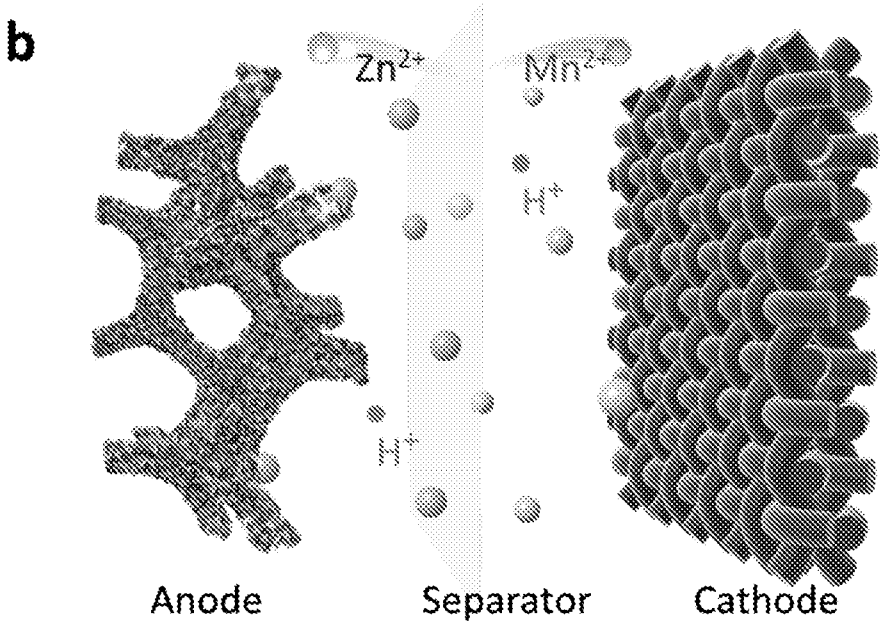

a
D1: MnO2 + 4H+ + 2e− → Mn2+ + 2H2O
MnO2
H3O+
Mn2+
H3O+
Mn2+
Zn2+
ZnSO4 + MnSO4
uZ
D2: MnO2 + H+ + e− → MnOOH
MnO2
MnOOH
H+
H+
H+
Zn2+
ZnSO4 + MnSO4
uZ
D3: MnO2 + 0.5Zn2+ + e− → Zn0.5MnO2
Zn0.5MnO2
MnOOH
Zn2+
Zn2+
Zn2+
Zn2+
ZnSO4 + MnSO4
uZ

Figure 1a



Anode: $Zn^{2+} + 2e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn$ $E^0 = -0.763$ V *vs.* SHE

Cathode: $Mn^{2+} + 2H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} MnO_2 + 4H^+ + 2e^-$ $E^0 = 1.228$ V *vs.* SHE

Overall: $Zn^{2+} + Mn^{2+} + 2H_2O \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn + MnO_2 + 4H^+$ $E = 1.991$ V *vs.* Zn/Zn^{2+}

Figure 1b

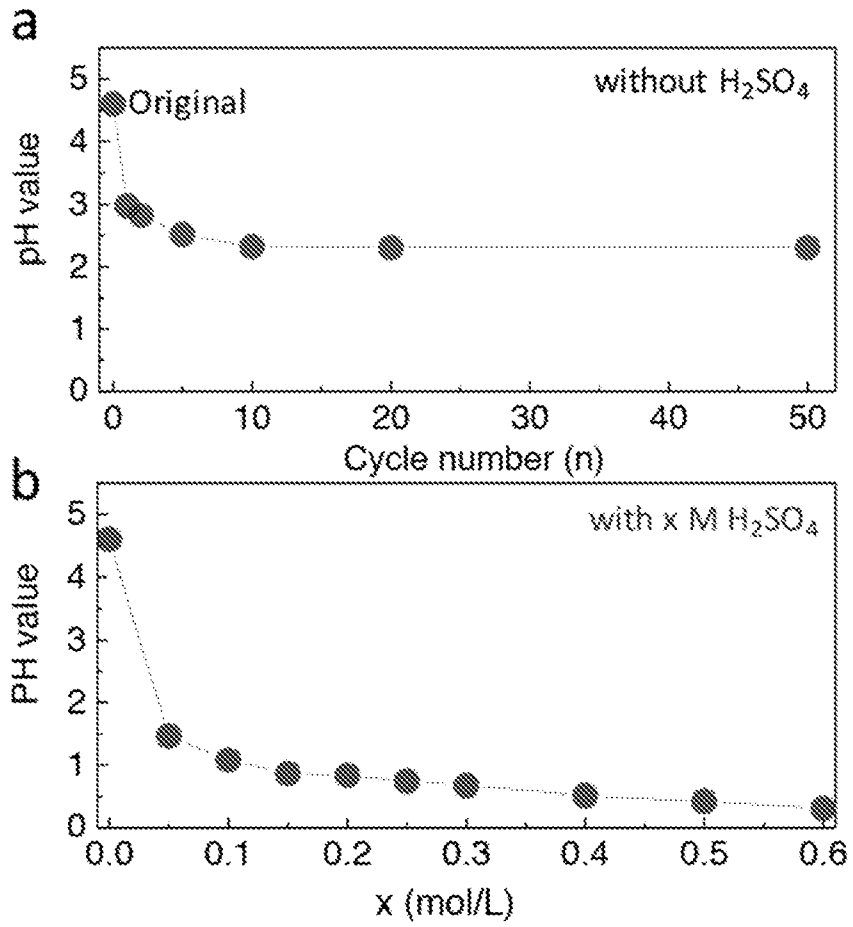

a
Original
without H_2SO_4
pH value
Cycle number (n)
b
with x M H_2SO_4
PH value
x (mol/L)

Figure 2

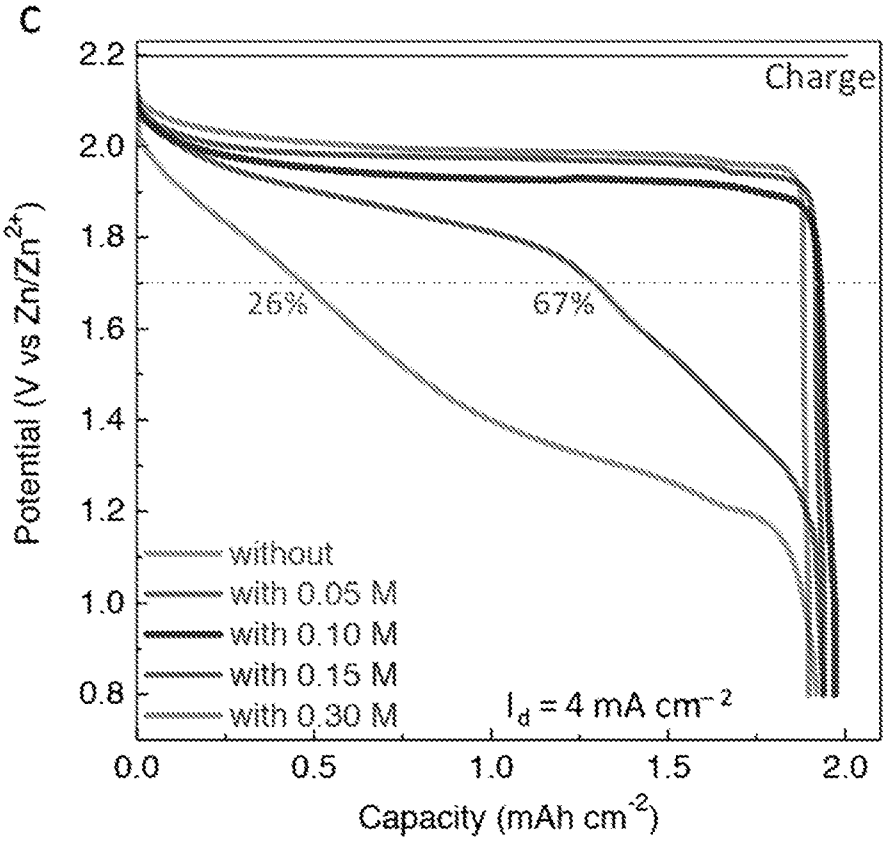

c
Charge
Potential (V vs Zn/Zn2+)
Capacity (mAh cm-2)
26%
67%
without
with 0.05 M
with 0.10 M
with 0.15 M
with 0.30 M
Id = 4 mA cm-2
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.0
0.5
1.0
1.5
2.0

Figure 2c

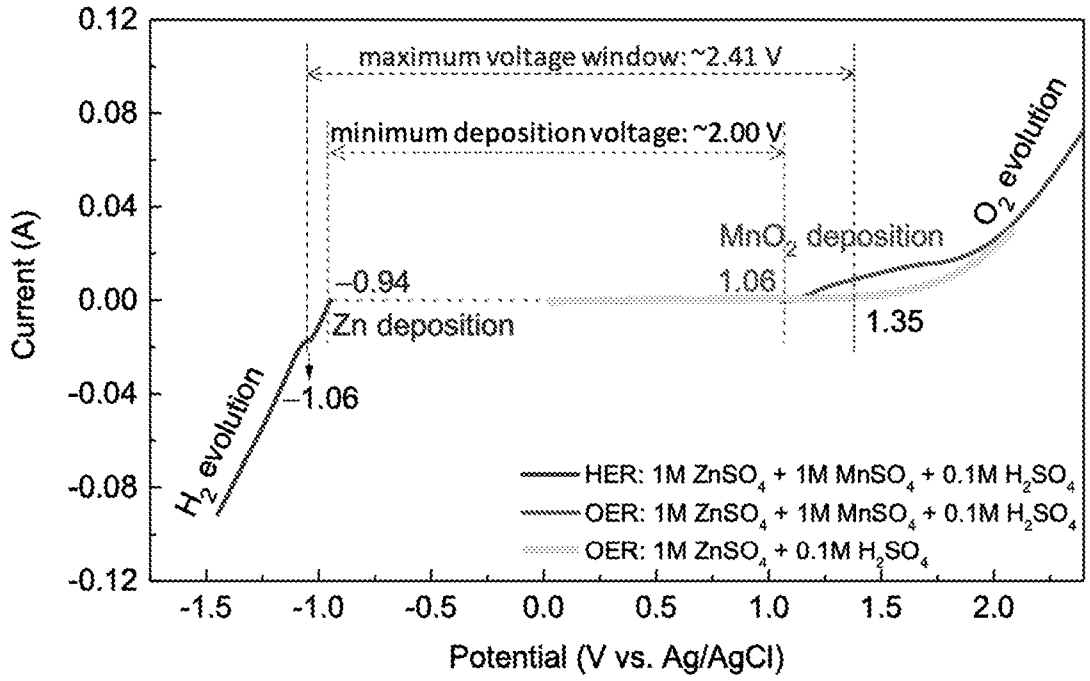

maximum voltage window: ~2.41 V
minimum deposition voltage: ~2.00 V
MnO2 deposition
O2 evolution
-0.94
1.06
Zn deposition
1.35
-1.06
H2 evolution
HER: 1M ZnSO4 + 1M MnSO4 + 0.1M H2SO4
OER: 1M ZnSO4 + 1M MnSO4 + 0.1M H2SO4
OER: 1M ZnSO4 + 0.1M H2SO4
Current (A)
Potential (V vs. Ag/AgCl)
0.12
0.08
0.04
0.00
-0.04
-0.08
-0.12
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

Figure 2d

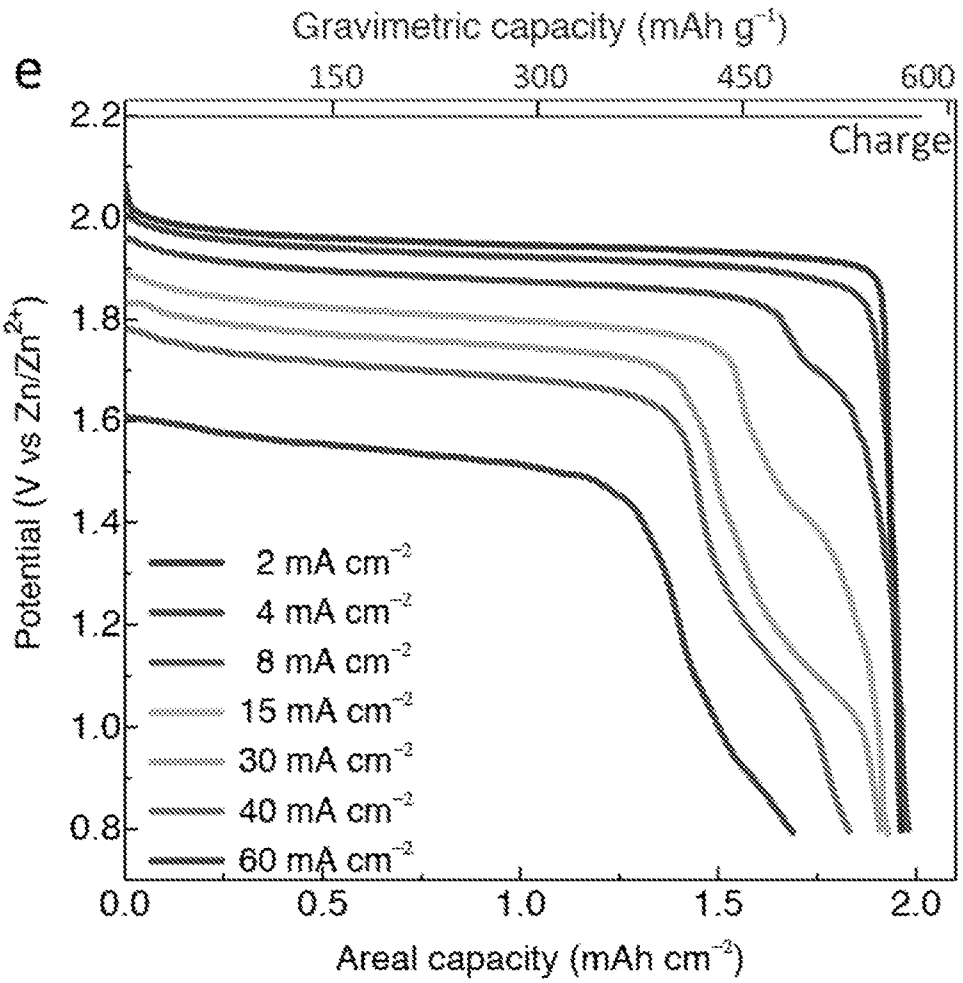

e
Gravimetric capacity (mAh g^{-1})
150
300
450
600
Charge
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
Potential (V vs Zn/Zn^{2+})
2 mA cm^{-2}
4 mA cm^{-2}
8 mA cm^{-2}
15 mA cm^{-2}
30 mA cm^{-2}
40 mA cm^{-2}
60 mA cm^{-2}
0.0
0.5
1.0
1.5
2.0
Areal capacity (mAh cm^{-2})

Figure 2e

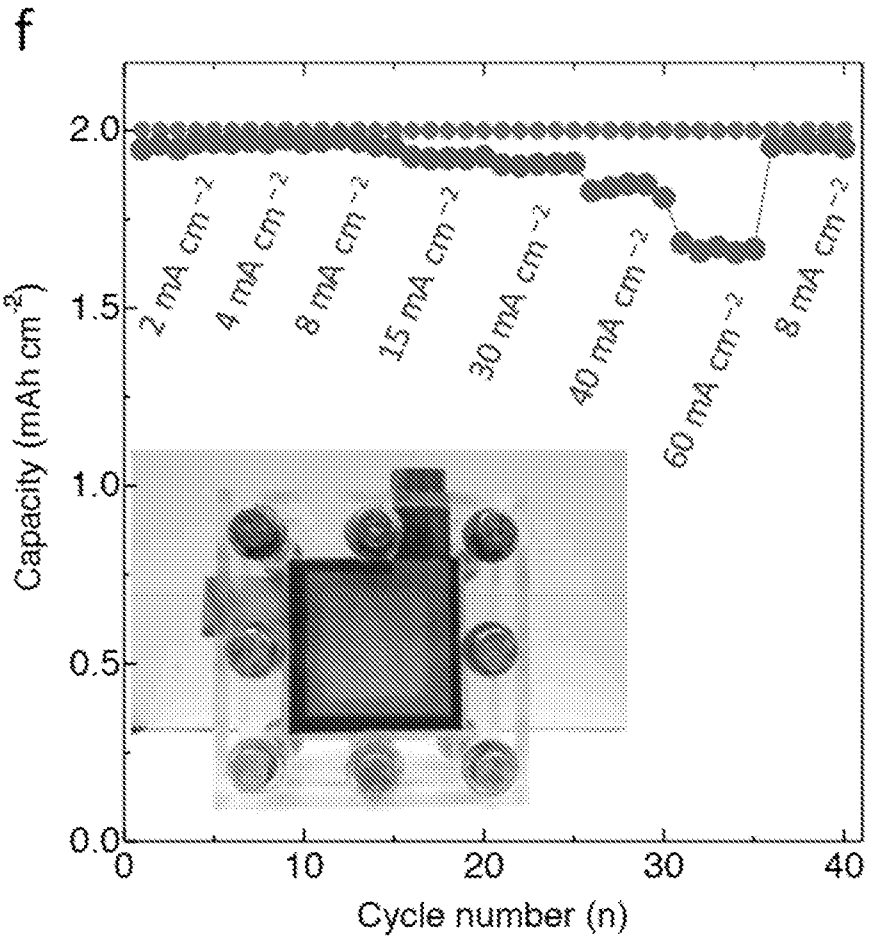

f
Capacity (mAh cm^{-2})
Cycle number (n)
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
2 mA cm^{-2}
4 mA cm^{-2}
8 mA cm^{-2}
15 mA cm^{-2}
30 mA cm^{-2}
40 mA cm^{-2}
60 mA cm^{-2}
8 mA cm^{-2}

Figure 2f

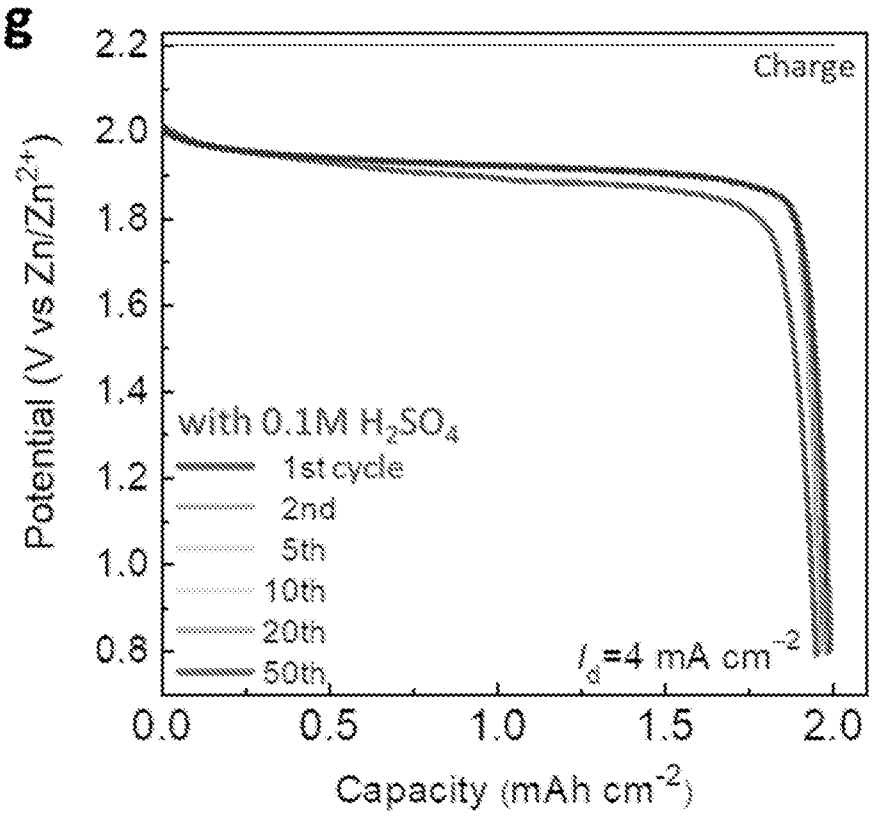

g
Potential (V vs Zn/Zn2+)
Capacity (mAh cm-2)
Charge
with 0.1M H2SO4
1st cycle
2nd
5th
10th
20th
50th
I=4 mA cm-2
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.0
0.5
1.0
1.5
2.0

Figure 2g

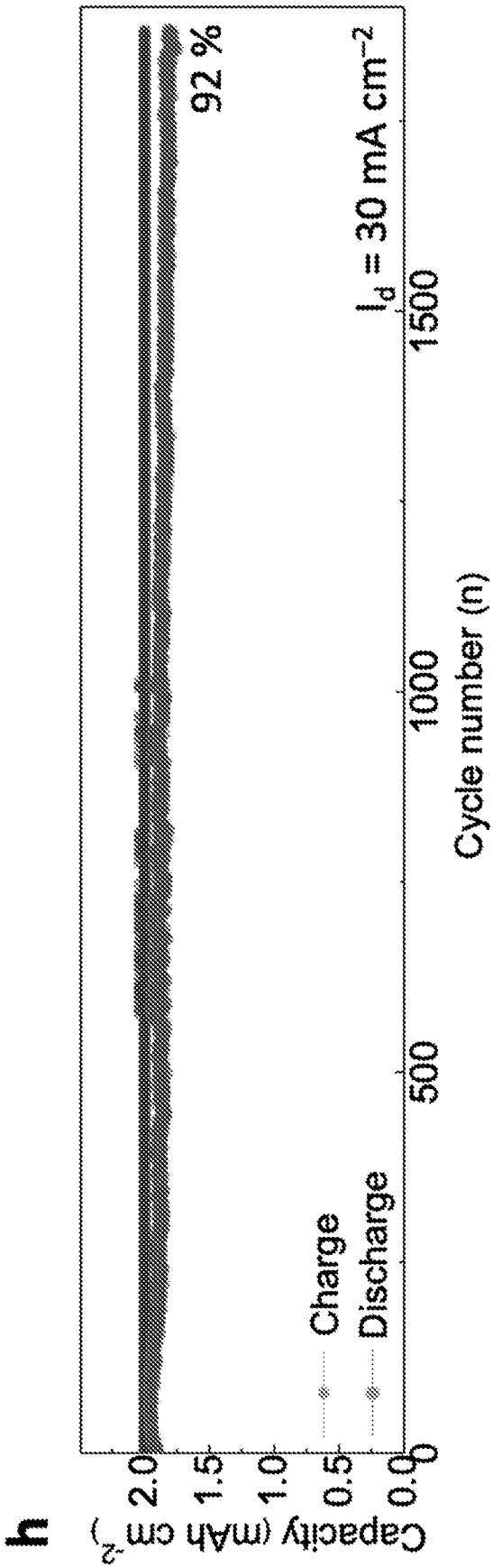

h
Capacity (mAh cm-2)
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
Cycle number (n)
Charge
Discharge
92 %
Id = 30 mA cm-2

Figure 2h

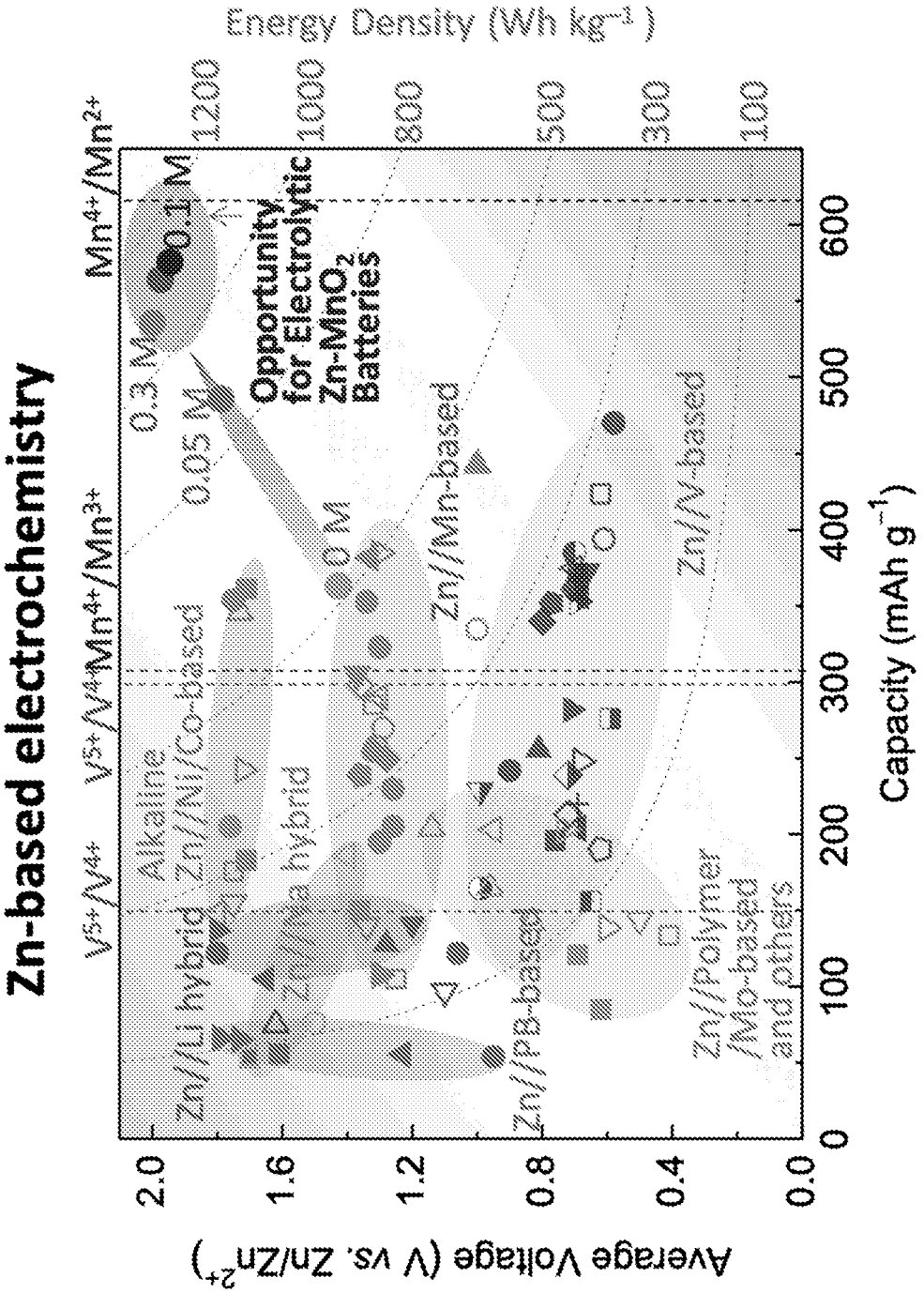

Zn-based electrochemistry
Energy Density (Wh kg^{-1})
1200
1000
800
500
300
100
V^{5+}/V^{4+}
$V^{5+}/V^{4+}Mn^{4+}/Mn^{3+}$
Mn^{4+}/Mn^{2+}
Alkaline
Zn//Li hybrid
Zn//Ni/Co-based
Zn//Na hybrid
Zn//K hybrid
Zn//Mn-based
Zn//Pb-based
Zn//Polymer /Mo-based and others
Zn//V-based
0.1 M
0.3 M
0.05 M
0 M
Opportunity for Electrolytic Zn-MnO_2 Batteries
Capacity (mAh g^{-1})
0
100
200
300
400
500
600
Average Voltage (V vs. Zn/Zn^{2+})
2.0
1.6
1.2
0.8
0.4
0.0

Figure 3