Recycling Spent Zinc Ion Primary Batteries and Utilized as Superior Rechargeable Lithium-Ion Energy Storage

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1. Characterization

The structure and morphology of the synthesized ZMO@C sample were investigated using the following measurements: X-ray diffraction (XRD, D/max-2400, Rigaku, Ultima IV), Raman spectroscopy (Renishaw in Via RE04 Raman spectroscopy, with excitation laser wavelength of 532 nm), X-ray photoelectron spectra (XPS, Thermo Fisher electron spectrometer K-Alpha), N_2 adsorption-desorption isotherms (BEL-SORP-mini II (Microtac BEL, Inc., Tokyo, Japan, at 77 K to analyze the specific surface area and pore size distribution), scanning electron microscopy (SEM, Hitachi-S4800 at an accelerating voltage of 3 kV), and transmission electron microscopy (TEM, JEOL model JEM-22100F (Japan)).

2. Fabrication of supercapacitor and testing

The ZMO@C electrode was prepared utilizing a conventional slurry technique. The electrode mixture was developed by combining the ZMO@C (70 wt%), carbon black (20 wt%), and PVDF (10 wt%) with a sufficient quantity of NMP solution. The mixture was ground physically with a mortar and pestle until a homogenous paste was formed. The resulting mixture was coated onto a stainless steel (SS) current collector (1×1 cm^2) and allowed to dry overnight at 80 °C. The mass of the active material on the electrode was controlled between ~ 0.0035 and 0.004 g. The symmetric device (SDC) was assembled utilizing the stainless-steel split test cell (EQ-STC) from MTI Korea Limited. The SDC was fabricated by a pair of ZMO@C coated SS substrates as the positive and negative electrodes. A separator (Whatman filter paper) was positioned between the two parallelly assembled electrodes were arranged in a sandwich fusion. Additionally, several drops of a 1 M $LiClO_4$/acetonitrile (1 M LPC/ACN) electrolyte were added in between the electrodes.

3. Electrochemical measurements

To analyze the electrochemical properties of the ZMO@CC electrodes at room temperature, a VSP Biopotentiostat/galvanostat (BioLogic) electrochemical workstation (France) was used. Electrochemical studies, including electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD), and cyclic voltammetry (CV), were performed in a 1 M $LiClO_4$/acetonitrile (1 M LPC/ACN) electrolyte. The GCD was evaluated for various current densities 0.1, 0.2, 0.5, 0.7, 1, 2, 3, 4, and 5 A/g, and CV was examined for various scan speeds ranging from 5 to 100 mV/s for the symmetric supercapacitor (50 mV/s for three electrode configuration). EIS was assessed with a bias condition of 0 V and a sinus amplitude of 10 mV in the frequency range of 0.01 Hz to 100 kHz.

The specific capacitances (C_{sp}; F/g) were calculated from the CV curves according to the following equation (1),

$$C_{sp} = 2\left(\frac{\int idv}{m \times s \times \Delta V}\right) \quad (1)$$

where, m is the mass of active material on electrodes (g), s is the potential scan rate (mV/s), i is the voltammetric current (A), and ΔV is the potential window (V) of CV curve.

The specific capacitance (C_{sp}; F/g) value of the SDC was determined from the GCD curves using Equation. (2).

$$C_{sp} = 2\left(\frac{I\Delta t}{m\Delta V}\right) \quad (2)$$

Where I is the constant discharge current (A), Δt is the discharge time (s), m is the mass of active materials (g), and ΔV is the voltage window (V).

The real and imaginary components of the capacitance, combining to represent the SDC's capacitance in the low-frequency zone, are thoroughly described by Equations. (3), (4), and (5).

$$C = C^{'}(\omega) - jC"\ (\omega) \tag{3}$$

where the real and imaginary portions of capacitance can be expressed by C′ and C″, which are represented as,

$$C^{'} = \frac{Z"\ (\omega)}{\omega |Z\ (\omega)|^2} \tag{4}$$

$$C" = \frac{Z'\ (\omega)}{\omega |Z\ (\omega)|^2} \tag{5}$$

The specific Energy (E_{sp}) and specific power (P_{sp}) of SDC were calculated using Equations. (6) and (7),

$$E_{sp} = \frac{0.125 C_{sp} \times \Delta V^2}{3.6} \tag{6}$$

$$P_{sp} = \frac{E_{sp} \times 3600}{\Delta t} \tag{7}$$

Where, E_{sp} is the specific energy (Wh/kg), P_{sp} is the specific power (W/kg), ΔV is the GCD discharge time, C_{sp} is the specific capacitance (C_{sp}) of the SDC (g), and Δt is the discharge time (s).

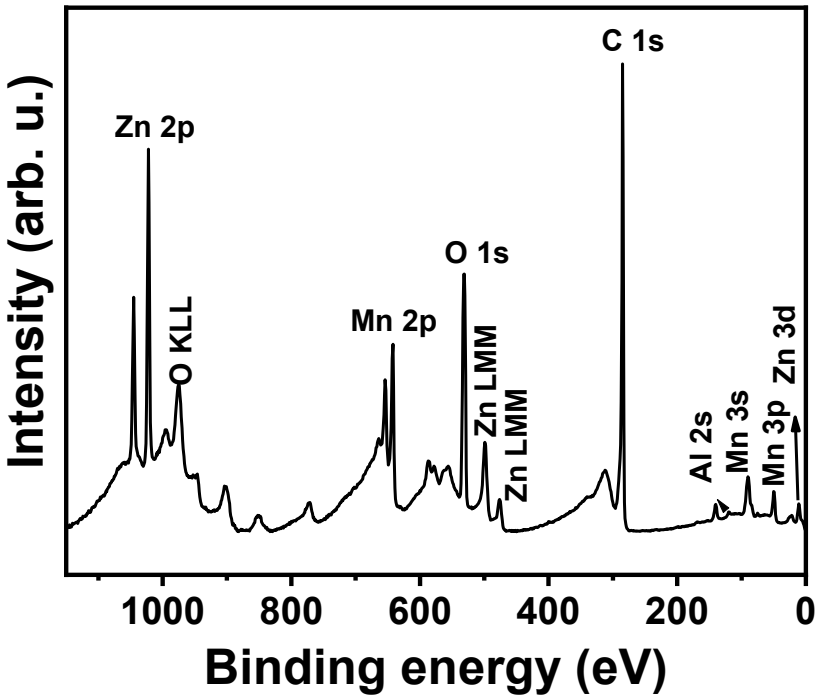

Figure. S1 XPS survey spectrum of ZMO@C composite

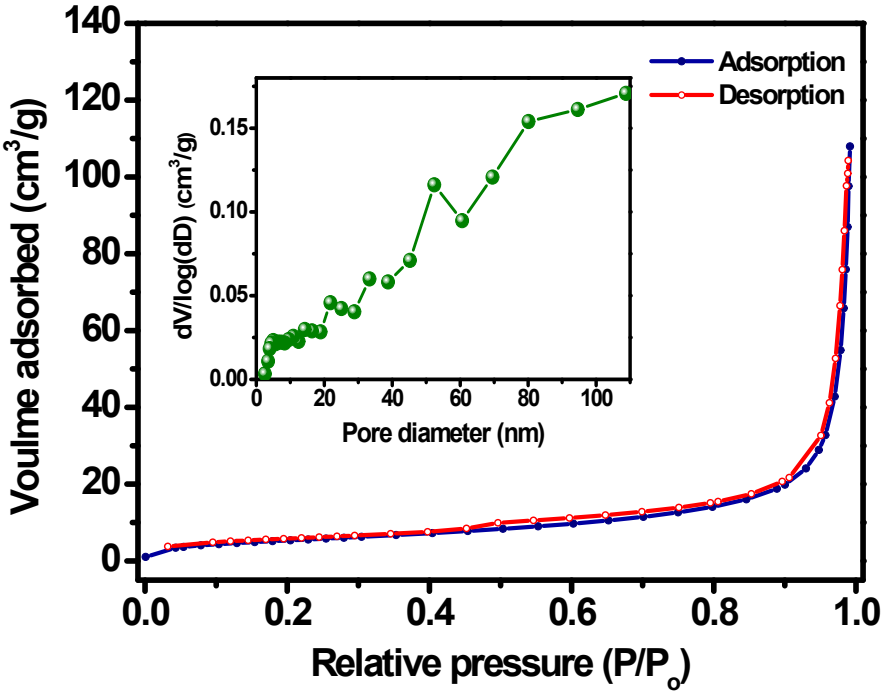

Figure. S2 Nitrogen adsorption-desorption isotherms, and inset BJH pore volume curve of ZMO@C composite

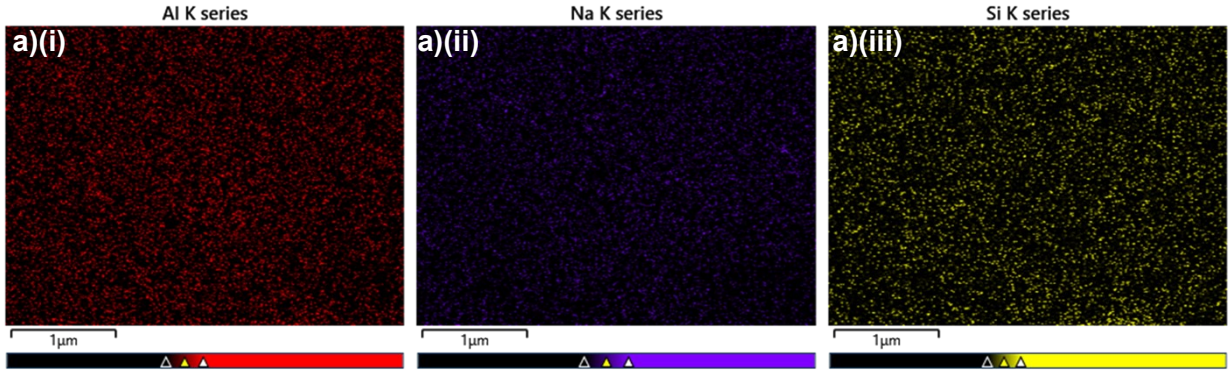

Figure. S3 FE-SEM (a)(i-iii) elemental mapping images of ZMO@C composite

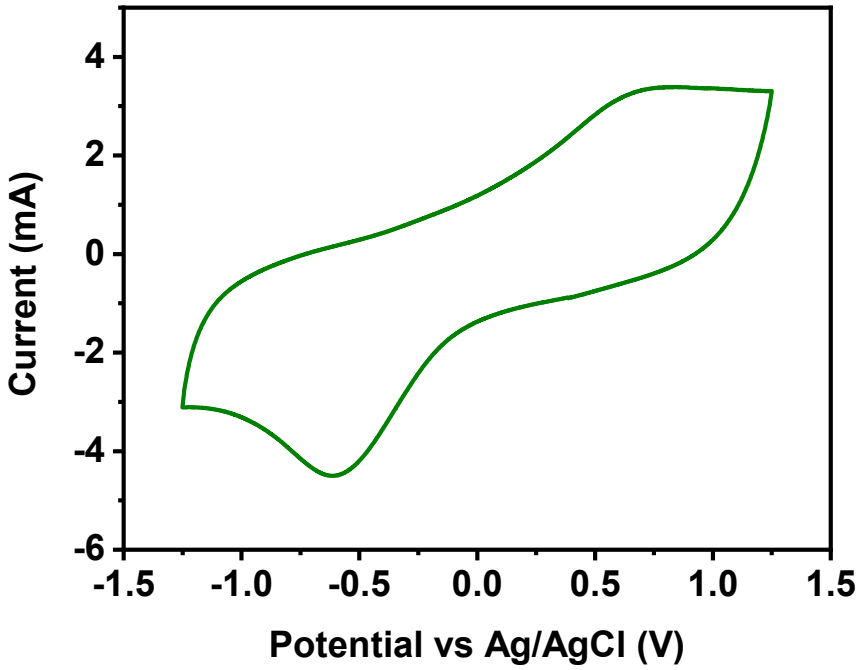

Figure. S4 CV measurements using a three-electrode cell tested in 1 M LCP/ACN electrolyte at the scan rate of 25 mV/s in the potential window between -1.25 to 1.25 V

Table S1. Elements weight and atomic percentages from the SEM EDS spectra of ZMO@C composite.

Element	Wt%	Atomic %
C	42.06	55.89
O	38.08	37.99
Na	0.49	0.34
Al	0.82	0.49
Si	0.11	0.06
Mn	15.84	4.60
Zn	2.60	0.63
Total:	100.00	100.00

Table S2. Coulombic efficiency of SDCs at various specific currents.

Specific current ($A\ g^{-1}$)	Charging time (s)	Discharging time (s)	Columbic efficiency (%)
0.1	461	523	113
0.2	197	199	101
0.5	62	63	101
0.7	36	37	102
1	23	23	100
2	9	9	100
3	5	5	100
4	4	3.9	97
5	2	1.9	95

Table S3. EIS fitted parameters of before cycling test of SDC cell, after cycling test of SDC cell, serially connected two SDC cells, and parallelly connected two SDC cells

Parameters	before cycling test of SDC cell	after cycling test of SDC cell	serially connected two SDC cells	parallelly connected two SDC cells
R_s (Ω cm^2)	2.8	2.8	6.5	1.6
R_{sl} (Ω cm^2)	16	17.6	193	147
C_{sl} (mF/cm^2)	0.61	0.027	0.43	0.50
Rct (Ω cm^2)	43.1	58.53	101	22.8
C_p (mF/cm^2)	0.04	0.039	0.02	0.041
C_{dl} (mF/cm^2)	0.69	0.66	0.77	0.86
W_R (Ω cm^2)	0.46	38	200	68.1