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Supplementary Information

Metal-free Surface-microporous Graphene Electrocatalysts from CO_2 for Rechargeable All-Solid-State Zinc-Air Batteries

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Materials and Methods

Material synthesis *:* Surface-microporous conductive carbon (SMG) was successfully synthesized from the reactions between Na/K alloy and CO_2 gas as follows:

$4K_{(l)} + 3CO_{2(g)} = C(graphene)_{(s)} + 2K_2CO_{3(s)}$

$4Na_{(l)} + 3CO_{2(g)} = C(graphene)_{(s)} + 2Na_2CO_{3(s)}$

Briefly, 2 g of Na and 6 g of K were mixed in an Ar-filled glovebox at room temperature, resulting in a liquid alloy. Then, the Na/K liquid alloy was loaded into a ceramic tube batch reactor and then CO_2 was introduced into the reactor with an initial pressure of 50 psi at room temperature, followed by heating at 550 ^oC for 6 h. After cooling down to room temperature, the obtained material was purified with 36.5 wt.% HCl to remove carbonates and, then, completely washed with deionized water until Cl^- was not detectable. The as-prepared SMG sample was dried overnight at 80 ^oC.

The oxygen-free SMG was prepared via a vacuum heat process. Briefly, SMG was loaded into a quartz boat and, then, placed into the central area of a quartz tube reactor. After the reactor was vacuumed (below 10 Pa) for more than 5 h, the SMG sample was heated to remove oxygen groups at 800 ^oC for 1 h. The obtained oxygen-free SMG was denoted as SMG-800.

Reduced graphene oxide (GO) was synthesized as follows: The aqueous GO solution was prepared using the modified Hummer method. [1,2] To reduce the GO, 450 mg of $NaHSO_3$ was added into 75 mL of the GO solution (2 mg mL^{-1}), and then the mixture was sealed in a cylindrical vessel and hydrothermally processed at 180 ^oC for 3 h. The obtained reduced-GO (rGO) powder was washed with deionized water and dried overnight at 80 ^oC.

Materials characterization: The morphology was observed by field emission scanning electron microscope (FESEM, ZEISS SUPRA 55VP), coupled with BRUKER X Flash Detector 5010. The microstructures and surface compositions were evaluated by the high-resolution transmission electron microscopy (HRTEM), energy-dispersive X-ray spectrometry (EDS), and selected-area electron diffraction (SAED) using a FEI Tecnai G2 F20, equipped with a field emission gun, operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was carried out using a Thermo ESCALAB 250Xi spectrometer with a monochromatic Al Kα radiation source, and the C 1s peak (284.8 eV) was used as a reference. The instrument of ThermoFisher Flash Smart was exploited for element analysis. Raman spectra were recorded with a Renishaw inVia Raman microscope, equipped with a 532 nm laser. X-ray diffraction (XRD) patterns were obtained using the SHIMADZU XDS-6100 powder X-ray diffractometer with Cu Kα (λ=1.5406 Å) radiations. Surface areas were determined by nitrogen adsorption/desorption at liquid-nitrogen temperature (77 K) with the Brunauer-Emmett-Teller (BET) model. Resistances were measured by a four-point probe system (ST2722-SZ, Suzhou Jingge, Electronic Co.). The affinity of as-prepared SMG towards the water was evaluated by measuring water contact angle (SL200KB).

Fabrication and evaluation of solid-state zinc-air batteries: A solid-state ZAB was fabricated by placing the polyvinyl alcohol (PVA) gelled electrolyte membrane between a polished zinc foil (0.15~0.25 mm) and the air electrode. The air electrode was composed of the catalytic layer and the current collector, with an effective area of 1.76 cm^2, to allow O_2 from ambient air to reach the catalyst. To obtain the catalytic layer, 0.15 g of catalyst (SMG, SMG-800, rGO, 5% Pt/C, or 20% Pt/C) was ball-milled in isopropyl alcohol for 2 h and then mixed with 230 uL of polytetrafluoroethylene (PTFE, 60 wt.%) to obtain a homogenously mixed paste. After rolling into a 0.2 mm slice, the catalytic layer was pressed on Ni foam under the uniaxial pressure of 10 MPa, leading to the catalyst mass loading of approximately 5 mg cm^{-2}. The as-prepared electrode was vacuum dried at 180 ^{o}C for 8 h. The PVA gel electrolyte was prepared by dissolving 5 g of PVA powder in 50 mL of deionized water with stirring at 95 °C for 2 h. Then, 5 mL of 18 M KOH solution was added into the above mixture and stirred for another 20 min. Then, the solution was poured on a glass plate to form a thin membrane, which was subsequently frozen at -25 °C for 3 h and stored at 5 °C.

Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were carried out with the METROHM Autolab PGSTAT302N electrochemical workstation. EIS data was conducted in the frequency range of 100 kHz to 0.05 Hz, with a potential amplitude of 5 mV. LSV was obtained at a scan rate of 1.0 mA/s, with a cut-off voltage of 0.5 V and 2.5 V (*vs.* Zn/Zn^{2+}) during discharge and charge, respectively. The cycle voltammetry (CV) tests for ZABs were conducted in the potential range of 0-2 V (*vs.* Zn/Zn^{2+}) using a sweep rate from 5 to 100 mV s^{-1}. The galvanostatic discharge and charge/discharge data were collected with LAND CT2001A battery test unit.

Electrochemical measurements: All electrochemical measurements were performed by using a METROHM Autolab PGSTAT302N electrochemical workstation at room temperature. The ORR electrocatalytic activity was measured by a rotating disk electrode (RDE Pt-GC, 00654867) technique. The disk diameter was 5.00 mm. A Pt wire and Ag/AgCl electrode served as counter and reference electrode, respectively. The glassy carbon electrode was polished and cleaned prior to use. The catalyst (4 mg) was dispersed in water and ethanol mixed solvent (1 mL, v/v = 4:1) with Nafion solution (80 µL, 5 wt.%, Sigma-Aldrich). Then, the mixture was ultrasonicated for over 1 h to generate a homogeneous ink. Next, 10 µL of dispersion was transferred and uniformly loaded onto the glassy carbon disk. Finally, the as-prepared catalyst film was dried at room temperature over 6 h. Then, 0.1 M KOH solution was used as the electrolyte at room temperature, which was purged with a high-purity O_2 flow for at least 30 min prior to the measurements and continuously flowed O_2 above the liquid level during measurements. The linear scan voltammograms (LSV) were obtained at a scan rate of 50 mV/s in the voltage range of 0.2 to -0.8 V (*vs.* Ag/AgCl) and 0.2 to 1.2 V (*vs.* Ag/AgCl) at a rotating speed of 1600 rpm, respectively. The potential was converted to the reversible hydrogen electrode (RHE) potential by using the given equation: [3]

$$E_{RHE} = E_{Ag/AgCl} + 0.059\,pH + 0.209$$

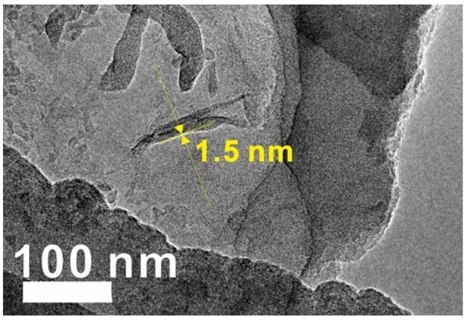

Fig. S1 TEM image of SMG with the thickness evaluated.

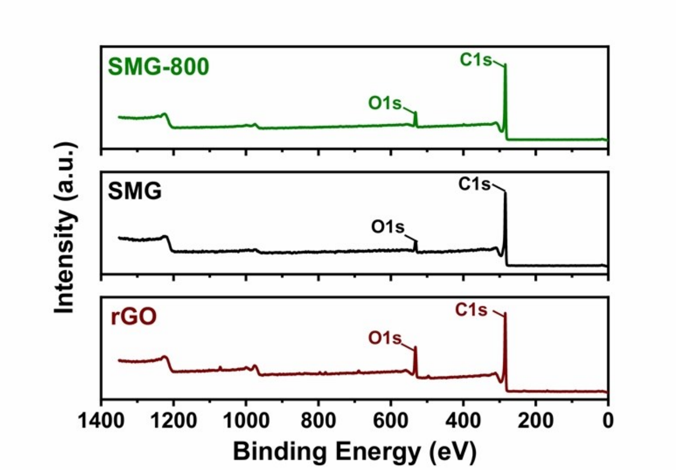

Fig. S2 Wide-range XPS spectra of SMG, SMG-800 and rGO.

Table S1. The composition and structure parameters of SMG, SMG-800 and rGO.

Specimen	Content of O (wt%)	I_D/I_G	BET Surface Area (m^2/g)	Pore Area (m^2/g)	Pore Diameter (nm)
rGO	18.59	0.94	456.1	140.5	2.4
SMG	4.37	1.07	1104.1	809.9	2.6
SMG-800	0.88	0.98	1059.6	789.5	2.7

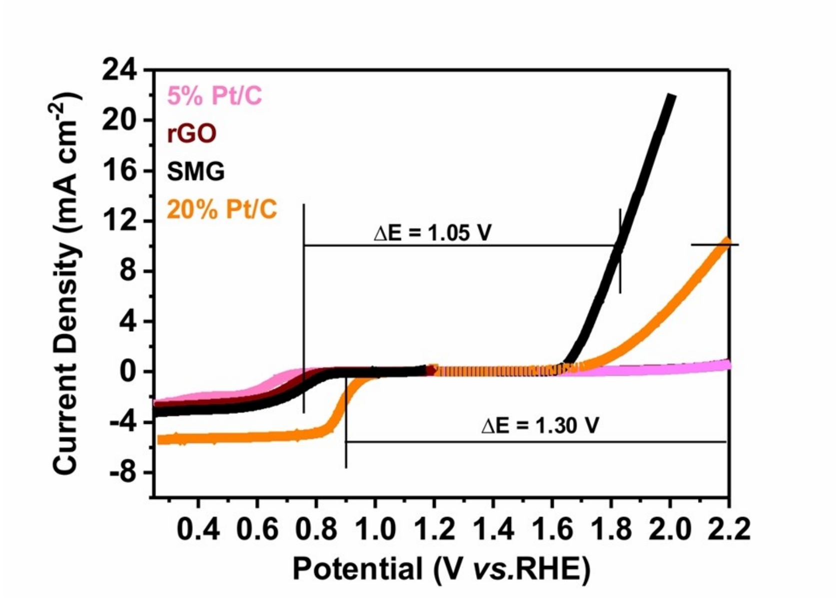

Fig. S3 LSV curves of ORR activity and OER activity for SMG, rGO, 5% Pt/C and 20% Pt/C (measured at a rotation speed of 1600 rmp with rotating disk electrode (RDE)).

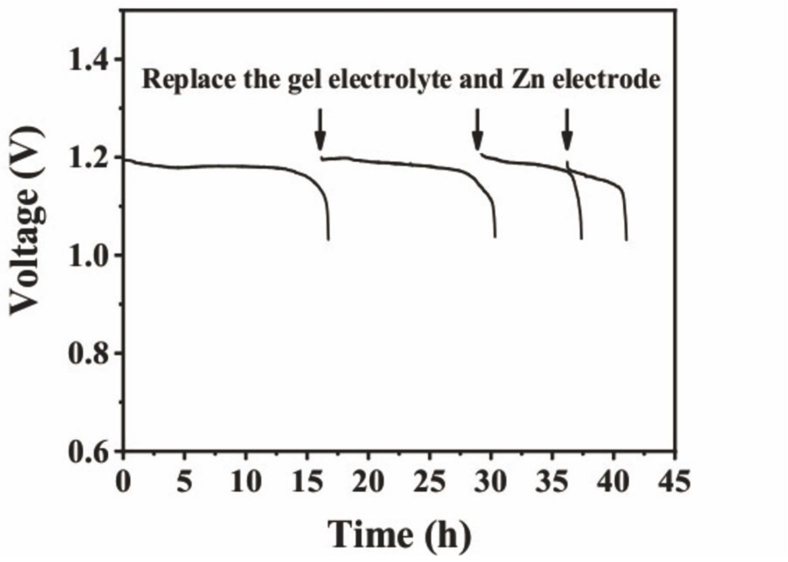

Fig. S4 The discharge curve of SMG-ZAB in air atmosphere at a current density of 2 mA cm^{-2}.

Table S2. The EIS fitting parameters from the proposed equivalent circuit of Figure 4d.

Specimen	L/nH	R_s/Ω	R_{int}/Ω	R_{ct}/Ω	Q_{int}/ (Y_o/mΩ^{-1}s^n[n])	Q_{dl}/ (Y_o/mΩ^{-1}s^n[n])	Q/ (Y_o/mΩ^{-1}s^n[n])
SMG	184	0.21	3.47	27.9	0.59 [0.91]	3.81 [0.74]	142 [0.77]
SMG-800	242	0.21	13.40	110	10.7 [0.58]	110 [1.10]	43.7 [0.58]
rGO	231	0.24	4.51	24.3	0.8 [0.83]	4.2 [0.78]	491 [0.66]
5% Pt/C	242	0.46	297.00	220	4.8 [0.60]	9.85 [0.59]	56.3 [1.02]
20% Pt/C	188	0.17	1.49	18.4	1.0 [0.89]	4.55 [0.74]	60.6 [0.76]

Table S3. The EIS fitting parameters from the proposed equivalent circuit of Figure 5d.

Cycle no.	L/nH	R_s/Ω	R_{int}/Ω	R_{ct}/Ω	Q_{int}/ (Y_o/mΩ^{-1}s^n[n])	Q_{dl}/ (Y_o/mΩ^{-1}s^n[n])	Q/ (Y_o/mΩ^{-1}s^n[n])
1st cycle	184	0.21	3.47	27.9	0.59 [0.91]	3.81 [0.74]	142 [0.77]
22nd cycle	226	0.24	2.78	24.4	0.53 [0.89]	8.54 [0.66]	324 [0.63]
43rd cycle	204	0.28	2.55	23.7	0.77 [0.87]	11.4 [0.59]	364 [0.51]
116th cycle	183	0.32	—	9.7	—	4.06 [0.63]	272 [0.49]
179th cycle	86.4	0.78	11.6	12.4	14.2 [0.79]	41.8 [0.30]	553 [1.02]

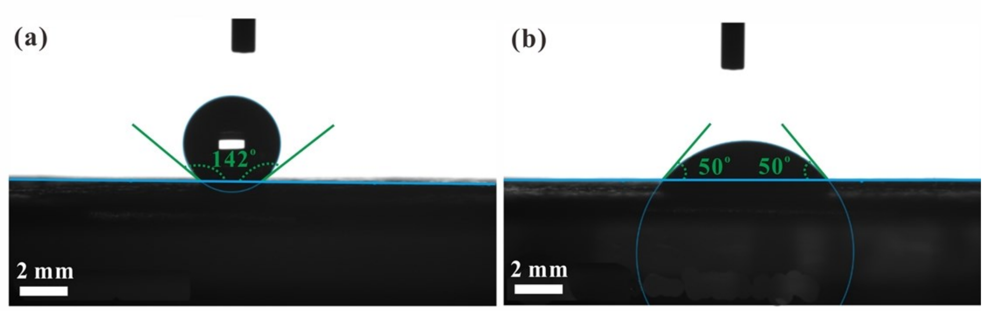

Fig. S5 Water contact angle on SMG cathode surface (a) before and (b) after pulse cycles.

Table S4. Performance comparison of the solid-state SMG-ZAB with reported solid-state ZABs

Catalyst	Electrolyte	OCV	Current density	Recharge ability	Discharge-charge voltage and their voltage gap	Ref.
Co_4N/CNW/CC	PVA gel	1.35 V	0.5mA/cm^2	20 min/cycle for 36 cycle; 12h	1.20 V - 2.00 V (gap=0.8V)	[1]
			5 mA/cm^2	20 min/cycle for 24 cycle; 8h	0.75 V - 2.25 V (gap=1.5V)	
NCNF-1000 fibers	PVA gel	_ _	2 mA/cm^2	10 min/cycle for 36 cycle; 6 h	1.0 V - 1.78 V (gap=0.78V)	[2]
N-CNTs–HGF	PEO-PVA gel	_ _	2 mA/cm^2	10 min/cycle for 78 cycle, 13 h	1.0 V - 2.0 V (gap=1.0V)	[3]
Co/N/O tri-doped graphene	PVA gel KOH $ZnCl_2$	1.44 V	1 mA/cm^2	60 min/cycle, for 18 cycle, 18 h	1.19 V - 1.89 V (gap=0.7V)	[4]
o-CC-H_2	PVA gel KOH $ZnCl_2$	1.26 V	1 mA/cm^2	2 min/cycle for 40 cycles	1.04 V - 2.01 V (gap=0.97V)	[5]
Co-doped np-graphene	PVA gel	1.35 V	2 mA/cm^2	10 min/cycle for 258 cycles; 43 h	1.20 V - 1.97 V (gap=0.77V)	[6]
SMG	PVA gel	1.37 V	2 mA/cm^2	10 min/cycle for 180 cycles; 30h	1.25 V - 1.50 V (gap=0.25V)	This work

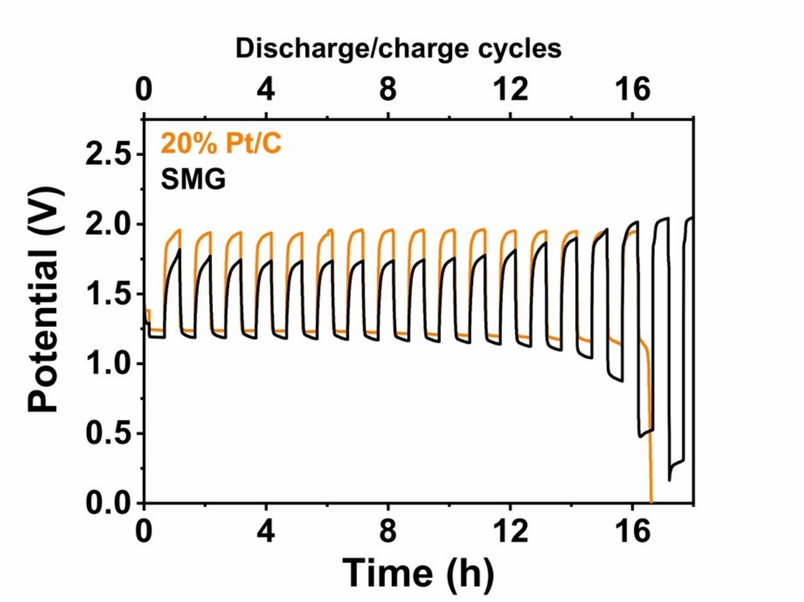

Fig. S6 The galvanostatic discharge/charge profiles at 2 mA cm^{-2} with a 1 h cycle period.

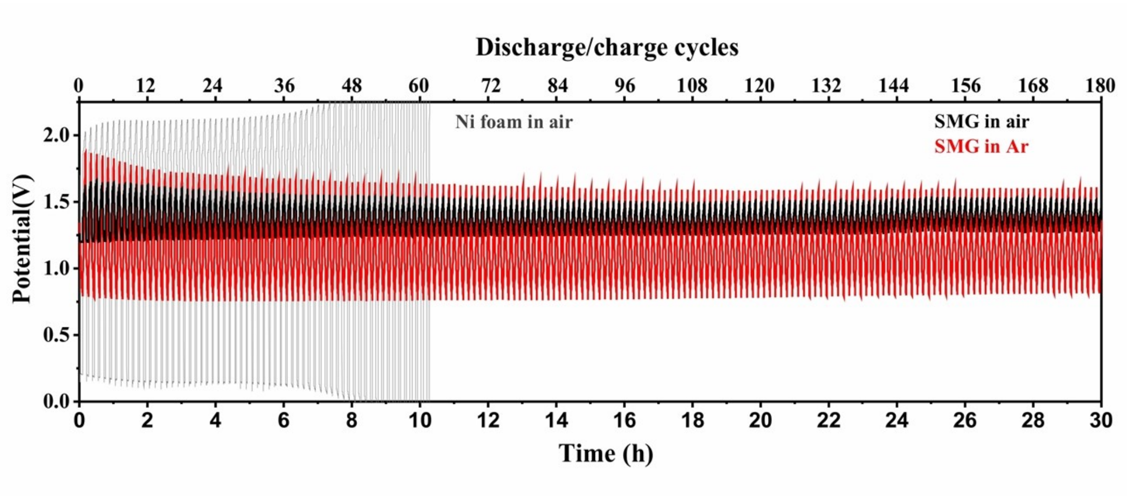

Fig. S7 Charge/discharge profiles at the current density of 2 mA cm^{-2} for SMG-based ZABs in air (black) and Ar atmosphere (red), and Ni foam-based ZAB (grey) as a reference (Note: 10 min for each charge-discharge cycle).

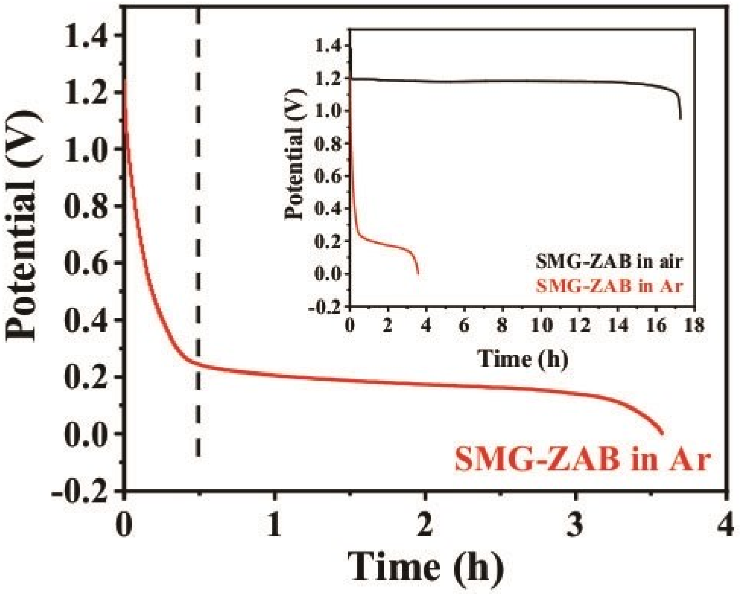

Fig. S8 The discharge curve of SMG-ZAB in Ar atmosphere at a current density of 2 mA cm^{-2}, and comparison with that in air atmosphere (insert)

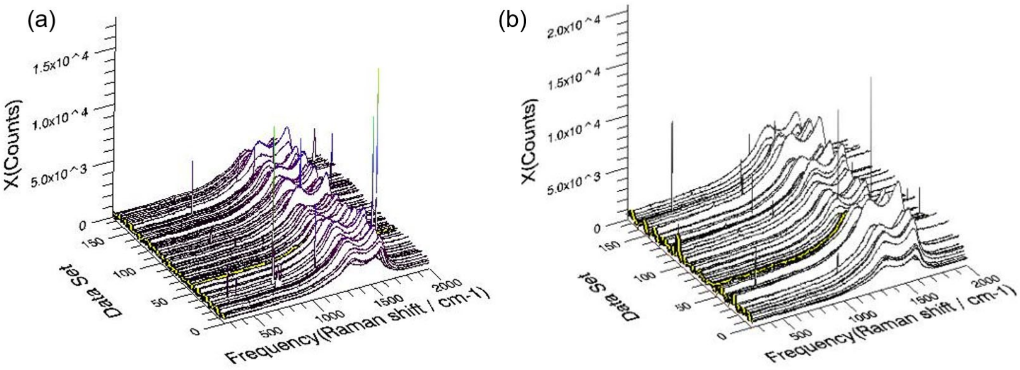

Fig. S9. Confocal Raman imaging mapping of SMG cathode (a) before and (b) after pulse cycles

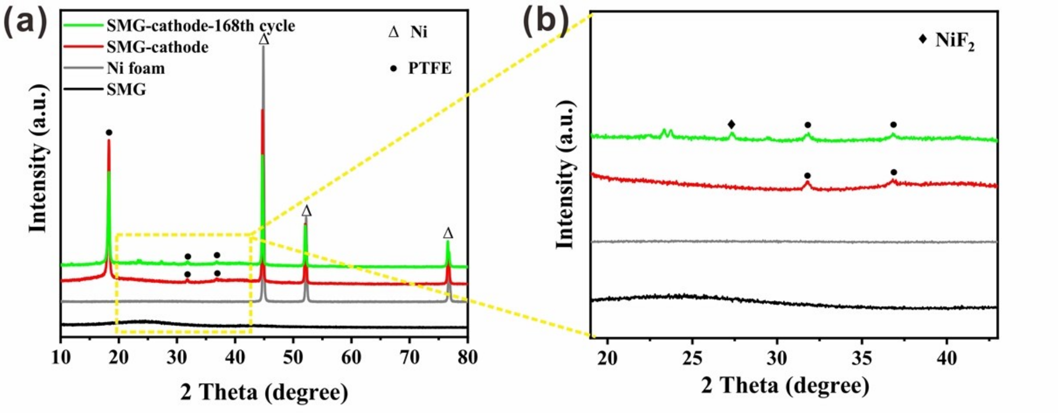

Fig. S10 (a, b) XRD patterns of SMG, Ni foam, SMG-cathode and SMG-cathode after 168 pulse cycles.

Note: XRD patterns of SMG cathodes exhibit diffraction peaks at $2\vartheta = 44.7^{\circ}$, 52.1° and 76.6°, corresponding to (111), (200) and (220) planes of nickel [JCPDS card no. 04-0850], respectively. Peaks at $2\vartheta = 18.3^{\circ}$, 31.8° and 36.9° are associated with PTFE [JCPDS card no. 45-1595]. It is worth noting that ZnO peaks have not been observed in electrochemically-cycled SMG cathode. However, the impurity peaks occuured at $2\vartheta = 23.2^{\circ}$ and 23.8°, corresponding to the organic material from the degrdation of PTFE, and one at $2\vartheta = 27.3^{\circ}$ can be assigned to nickel fluoride [JCPDS card no. 24-0792].

References

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