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Supplementary Information

Three-Dimensionally Semi-Ordered Macroporous Air Electrodes for Metal-Oxygen Batteries

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Experimental Section

Materials

Silicon dioxide particles (SiO_2, Alfa Aesar, 1 μm), hydrofluoric acid (HF, 48%, Sigma-Aldrich), single walled carbon nanotubes (SWCNTs, CheapTubes), polyvinylidene fluoride (PVDF, average Mw ~530,000, Sigma Aldrich) and carbon paper (CP, FuelCellStore) were purchased. Polyethylene oxide (PEO, Sigma-Aldrich, MW 100,000) was purchased and pre-dried at 50 °C for 24 h under vacuum before use. Tetraethylene glycol dimethyl ether (G4, 99%, MilliporeSigma) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, Sigma Aldrich, 98% were dried with pre-activated molecular sieves (4Å, Sigma-Aldrich) for 7 days to remove residual water. Lithium trifluoromethanesulfonate (LiTf, 99.995%, MilliporeSigma) and lithium bis(trifuluoromethanesulfonyl)imide (LiTFSI, 99.95%, MilliporeSigma) were dried at 120 °C under vacuum for 3 days before use. Glass fiber (GF/B, Whatman) was used as the separator for lithium (Li)-oxygen (O_2) batteries (LOBs). CP with a carbon gas diffusion layer (Sigracet 39BC, SGL Carbon) (GDL) was used as air electrode without any additional catalysts and binders. The punched CP (1.27 cm in diameter) was dried in vacuum oven at 120 °C for 3 days. Li metal chips (1.56 cm in diameter and 200 μm

in thickness) were purchased from AOT Electronics Technology and used as received. Carbon paper (SG39BA, SGL Carbon) and carbon cloth (ELAT, Fuel Cell Store), potassium hydroxide (KOH, 99.95%, Sigma Aldrich), zinc (Zn) acetate (99.99%, Sigma Aldrich), three-dimensional (3D) nickel (Ni) foam (1.6mm thick, > 99.80%, MSE supplies), and Zn plate (1 mm thick, 99.99%, Sigma Aldrich) were purchased for Zn-O_2 battery (ZOB) tests.

Ruthenium-ruthenium oxide/single walled carbon nanotubes (Ru-RuO_2/SWCNTs) and three-dimensionally semi-ordered ruthenium-ruthenium oxide/single walled carbon nanotubes (3D-SOM Ru-RuO_2/SWCNTs) air (or oxygen) electrodes were prepared by modifying the experimental method of the previous paper.[1] 150 mg of SWCNTs (Tuball) and 200 mg of ruthenium (III) chloride hydrate ($RuCl_3 \cdot H_2O$, 99.98%, Sigma-Aldrich) were dissolved in deionized water (40 mL). After stirring for 48 h, the mixture was then transferred into a Teflon-lined stainless-steel autoclave, sealed, and maintained at 150 ℃ for 5 h. The resulting samples were collected, washed with deionized (DI) water, dried, and then thermally treated in a furnace under a mixture of argon (Ar) and hydrogen (H_2, 4%) at 400 ℃ for 2 h. After that, Ru-RuO_2/SWCNTs powders were obtained. The premixed slurry of Ru-RuO_2/SWCNTs and SiO_2 powder (4:3 by weight) and polyvinylidene fluoride (PVDF, average Mw ~530,000, Sigma Aldrich, 6.25 or 12.5 Wt. %) was prepared in N-methyl-2-pyrrolidone (NMP, 99.5%, Sigma Aldrich) and then deposited onto a CP, followed by slurry drying at 80 ℃ in a vacuum oven for 24 h. For 3D-SOM Ru-RuO_2/SWCNT electrode, SiO_2 particles were chemically etched by HF and were washed with DI-water and ethanol several times and then dried at 70 ℃ in vacuum oven for 2 days. After that, the electrode sheet of Ru-RuO_2/SWCNTs/PVDF/CP and 3D-SOM Ru-RuO_2/SWCNTs/PVDF/CP were punched into small electrode disks with a diameter of 1.27 cm and dried in a vacuum oven at 120 ℃ for 3 days. Mass loading of the air electrode was about 1.0 mg cm^{-2}. Li metal chips (1.56 cm in diameter and 250 μm in thickness) were used as the counter and reference electrodes.

PEO-based gel-like (PG) polymer coating on Li metal anodes

PG-coated Li metal anodes were prepared by applying the experimental method of the previous paper.[2] 1 M LiTf in G4 was prepared as the electrolyte in this study, where the molar ratio of LiTf to G4 was 1:4.1. To verify the effect of PG concentration, 5 wt.% of PG solution was prepared by dissolving PEO (MW 100,000) in the as-prepared 1 M LiTf or LiTFSI in G4 electrolyte by mechanical stirring at 70 °C for 5 hours in an argon (Ar)-filled glovebox where the moisture and oxygen contents were less than 0.1 ppm. Li metal chip was plated on a stainless steel (SS) coin-cell spacer by physical hand-rolling with a vial and a clean protective film. The Li/spacer was attached on the cross-shaped stir bar with a double-sided tape. The as-prepared PG solution (50 µl) was added onto the Li metal chip plated on SS coin-cell spacer by using a micro pipette and the magnetic hotplate stirrer preheated at 70 °C was turned on to perform spin coating. The spin coating was carried out on the magnetic hotplate stirrer at 1100 rpm and 70 °C for 3 minutes. After that, the PG-Li/spacers were cooled to room temperature in the glovebox for 30 minutes.

Cell Assembly and Pretreatment process

The Li-O_2 cells were electrochemically pretreated by pre-charging the Li||CP cells under O_2 gas in cell containers to generate an in-situ formed solid electrolyte interphase (SEI) layer on Li metal anodes with PG layer. The cells were then assembled using the Ru-RuO_2/SWCNTs and 3D-SOM-Ru-RuO_2/SWCNTs as air electrodes, GF/B as separator with electrolyte solutions (200 µL 1 M LiTf or LiTFSI in G4) and PG5Li-O_2 (PEO based gel-like film on Li anode using 5 wt.% of PG solution) in an Ar-filled glovebox (water and oxygen contents < 0.1 ppm). For the open system, the positive cans of the coin cells were opened with mesh disc (Ø1 mm holes). For PG coated Li anodes, pure O_2 gas (99.99%) was injected into the Teflon cell containers for the pretreatment. The pretreatment to the LOB cells was conducted by charging the cells from open-circuit voltage (OCV) to 5 V versus Li/Li^+ under O_2 gas at 0.2 mA cm^{-2} and then holding the cells at 5 V for 1 h. Electrolytes with 1 M LiTf or LiTFSI in G4 electrolyte and 0.1 M TEMPO (redox mediator) were prepared by mechanically stirring for 5 h. For the LOB cells with TEMPO, the pretreatment was carried out by charging the cells from OCV to 5 V and discharging to 3 V under O_2 gas at 0.2 mA cm^{-}

^{2} and then holding the cells at 5 V for 1 h. After the pretreatment, the Li-O_2 cells were filled with an O_2 gas and stabilized for 3 h before LOB operation. The Zinc-O_2 cells were tested under O_2 gas in cell containers as well. The cells were assembled using the SWCNTs, Ru-RuO_2/SWCNTs, and 3D-SOM Ru-RuO_2/SWCNTs as air electrodes (Figure S5), GF/B as separator with electrolyte solutions (200 µL 9 M KOH with 0.2M Zinc acetate). The same positive cans of the coin cells were used. The Zn-O_2 cells were filled with an O_2 gas.

Electrochemical Tests

All in-situ pre-charging and LOB cycling tests were carried out using an Arbin battery tester. For cycling tests of LOB cells, controlled current density (0.2 mA cm^{-2}) and capacity (1.0 mAh cm^{-2}) were used in the voltage window of 2.0-4.5 V. For ZOB cycling tests, cells were cycled within a voltage window of 0.6-2.0 V under a constant current density (1 mA cm^{-2}, 30 min charge / 30 min discharge (t_{limit}=30min)). Ex-situ electrochemical impedance spectroscopy (EIS) analysis was carried out under identical experimental conditions at OCV over a frequency range from 100 kHz to 1 mHz with a signal amplitude 10 mV using a BioLogic Science Instruments (VMP-300).

Characterizations

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX, Aztec) maps and line profiles were collected on FEI Helios FE-SEM with an accelerating voltage of 10 kV. For the cross-sectional images of the air electrodes, samples were prepared by cutting from bottom to the top of Li metal with a blazer. The specific surface areas of the air electrodes were calculated using N_2 adsorption isotherms at 77 K with a Quadrasorb EVO/SI automatic gas sorption system (Quantachrome Instruments). The samples were degassed under vacuum at 100 °C for 4 h before the adsorption measurements. Barrett-Joyner-Halenda (BJH) method was employed to determine pore size distribution and specific pore volume. Qualitative analysis of samples was carried out by Fourier-transform infrared spectroscopy (FT-IR) attenuated total reflection (ATR) mode. X-ray diffraction analysis (XRD, Rigaku Miniflex II) was carried

out to determine the crystallographic structures of the samples. For postmortem analyses, tested coin cells were disassembled inside the glovebox to harvest the air electrodes. These electrodes were thoroughly rinsed to remove residual electrolytes and vacuum dried before further characterizations. For the cross sectional SEM images, samples were prepared by cutting from bottom to the top of the electrodes with a blazer. Thermogravimetric Analysis (TGA, Netzsch F3 Jupiter) was employed for quantifying Ru amount in the air electrodes. The as-prepared Ru-RuO_2/SWCNTs and the 3D-SOM Ru-RuO_2/SWCNTs electrodes and discharged electrodes were removed from the LOB cells and dried in Ar-filled glovebox with moisture and oxygen concentration less than 10 ppm for 24h. The samples were mounted in an Ar-filled glovebox and then transferred to an XPS analysis chamber using an *in-vacuo* transfer mechanism. XPS analysis was performed using a Kratos Axis Ultra DLD spectrometer, which consists of an Al Kα monochromatic X-ray source (1486.6 eV) and a high-resolution spherical mirror analyzer. The X-ray source was operated at 150 W power and the emitted photoelectrons were collected at the analyzer entrance slit normal to the sample surface. The high-resolution spectra were collected at a pass energy of 40 eV with a step size of 0.1 eV. The XPS measurement was conducted without applying a charge neutralizer to avoid the decomposition of surface components. XPS data were analyzed using CasaXPS software. All the XPS peaks were charged referenced to the C 1s signal of graphitic carbon (C sp2) at 284.5 eV.

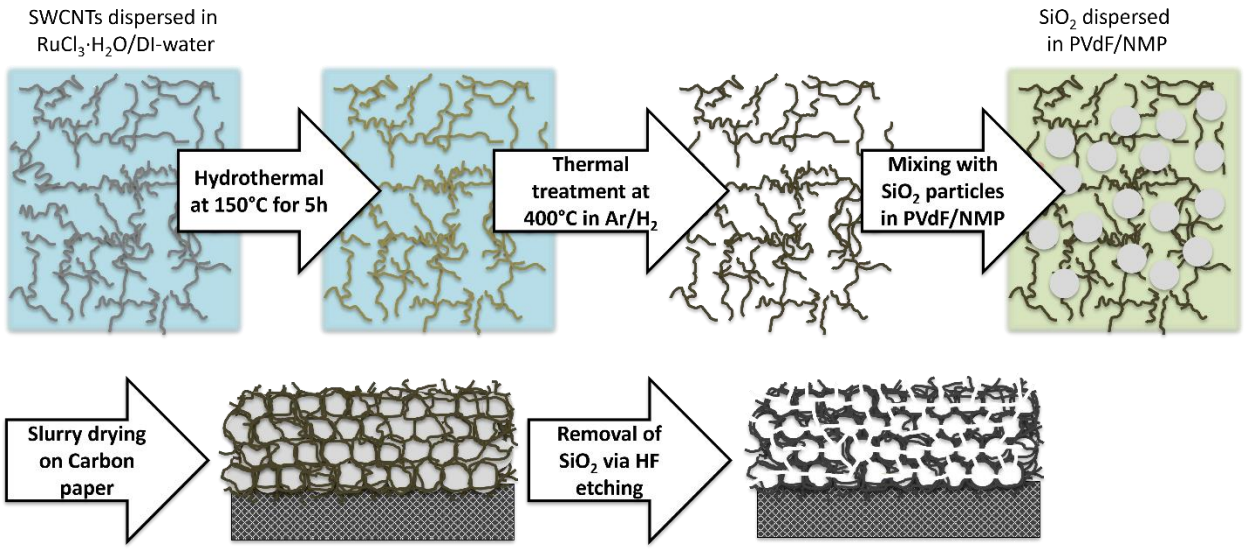


Figure S1. Preparation process of 3D-SOM Ru-RuO_2/SWCNTs air electrode for LOBs and ZOBs.

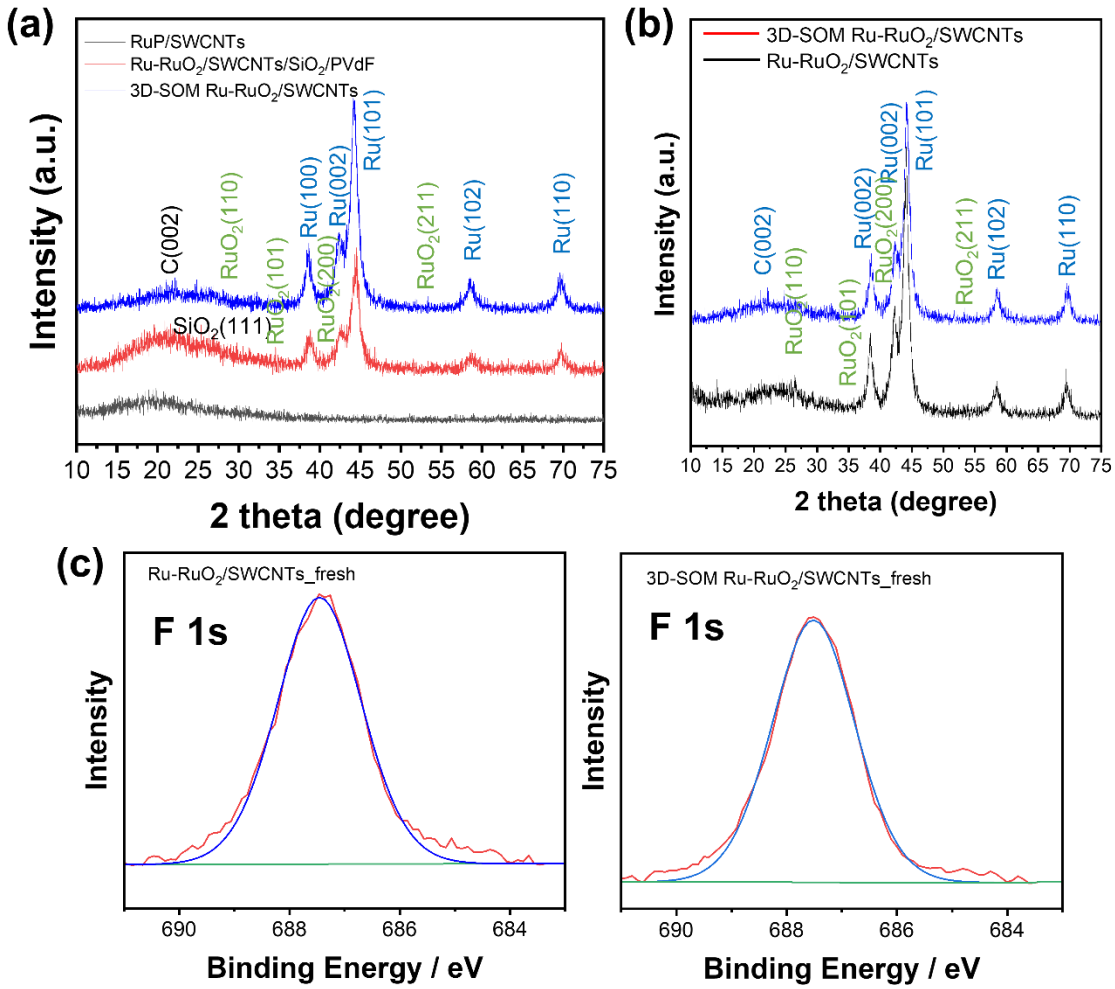


Figure S2. XRD patterns of the (a, grey) ruthenium precursor/SWCNTs prepared by hydrothermal process, (a, red) after mixing with SiO_2 as a hard template and PVdF binder and (a and b, blue) 3D-SOM Ru-RuO_2/SWCNTs after HF etching process, and (b, black) Ru-RuO_2/SWCNTs without a 3D-SOM structure. (c) XPS spectra of the F 1s from the as-prepared Ru-RuO_2/SWCNTs and 3D-SOM Ru-RuO_2/SWCNTs electrodes.

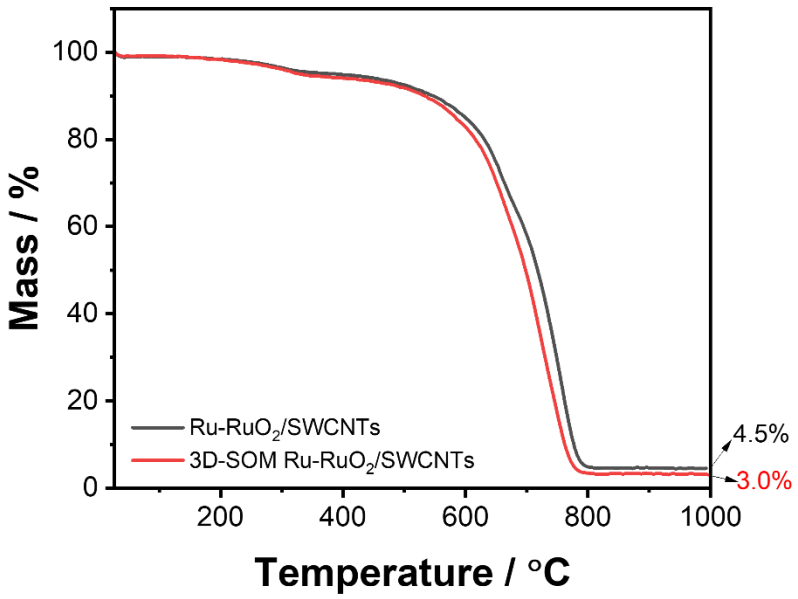


Figure S3. TGA curves of (black) Ru-RuO_2/SWCNTs and (red) 3D-SOM Ru-RuO_2/SWCNTs electrodes in air atmosphere at a heating rate of 10 °C min^{-1}.

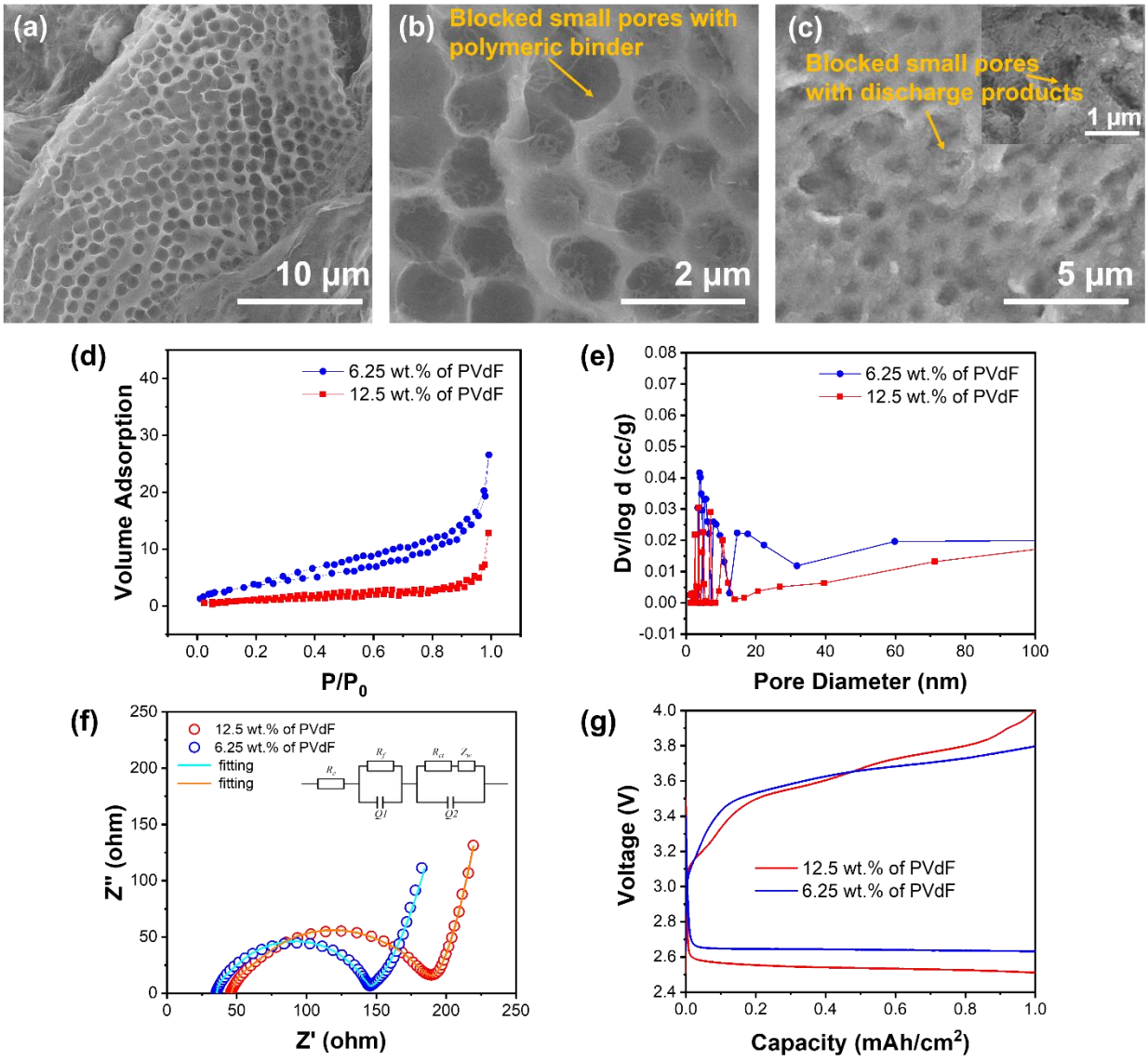


Figure S4. SEM images for the macroporous Ru-RuO_2/SWCNTs prepared with higher amount (12.5 wt.%) of PVdF binder (a and b) before and (c) after discharge to 2.0V at a current density of 0.2 mA cm^{-2} under a capacity-limited protocol of 1.0 mAh cm^{-2}. (d) the N_2 adsorption/desorption isotherm comparison of two Ru-RuO/SWCNTs electrodes made with 6.25 and 12.5 wt.% of PVdF binder, and their (e) BJH pore size distributions (adsorption). (f) Nyquist plots with fitted results and (g) 1st charge-discharge voltage profiles of LOB cells with the (blue) 3D-SOM Ru-RuO_2/SWCNTs electrode and (red) macro porous Ru-RuO_2/SWCNTs electrode prepared with 6.25 wt.% and 12.5 wt.% of PVdF binder.

	Ru-RuO_2/SWCNTs	3D-SOM Ru-RuO_2/SWCNTs	
PVdF binder (wt.%)	6.25	6.25	12.5
Surface area (m^2/g)	24.4	13.9	6.3
Pore volume (cc/g)	0.06	0.04	0.018

Table S1. The weight ratios of PVdF binder, BET surface areas, and pore volumes of Ru-RuO_2/SWCNTs and 3D-SOM Ru-RuO_2/SWCNTs.

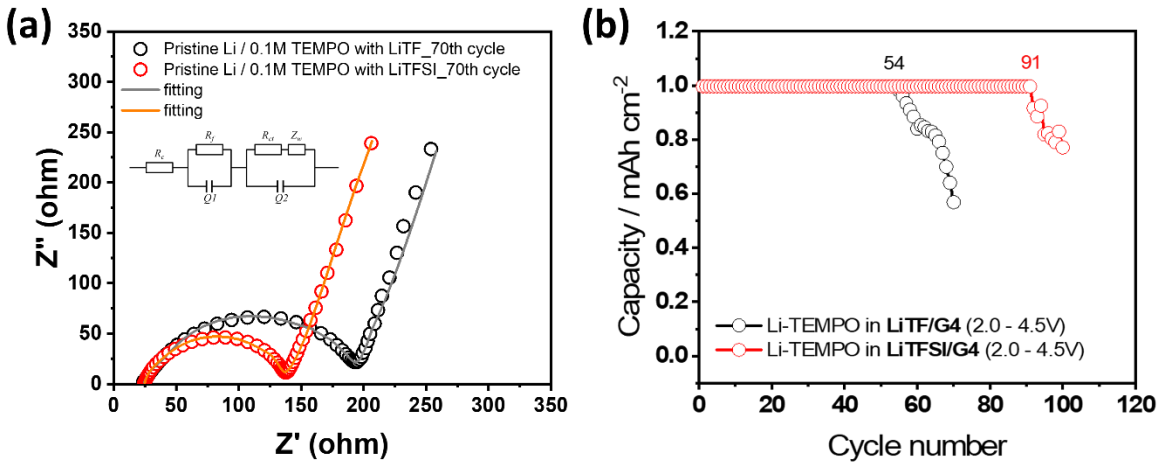


Figure S5. (a) Nyquist plots of the LOB cells with (black) LiTf and (red) LiTFSI based G4 electrolytes with fitted results and equivalent circuit and (b) their cycle performances at a current density of 0.2 mA cm^{-2} under a capacity limited protocol of 1.0 mAh cm^{-2} in the cut-off voltage range of 2.0 – 4.5 V.

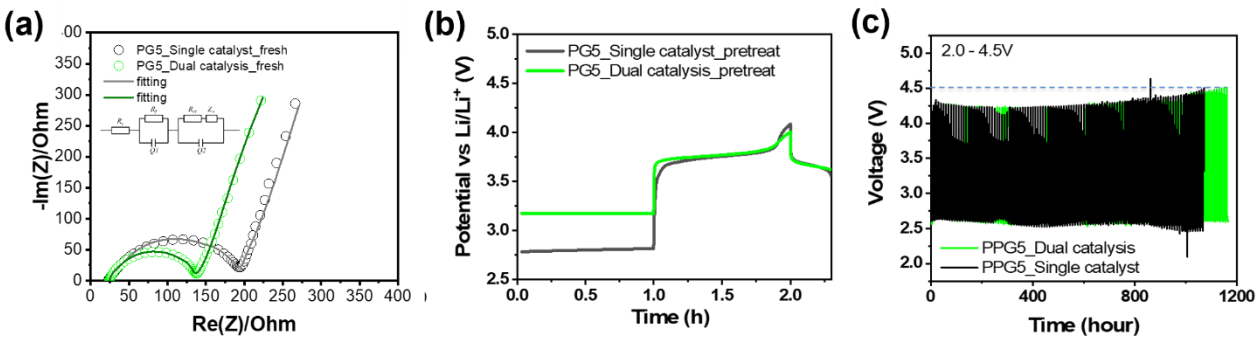


Figure S6. (a) Nyquist plots with fitted results and equivalent circuit, (b) voltage profiles of pre-charging to 5 V for the LOB cells with (black) single catalyst (TEMPO) and (green) dual catalysis (TEMPO/Ru formed on the air electrode) and their (c) cycle life of LOB cells at a current density of 0.2 mA cm^{-2} under a capacity limited protocol of 1.0 mAh cm^{-2} in the cut-off voltage range of 2.0 – 4.5 V.

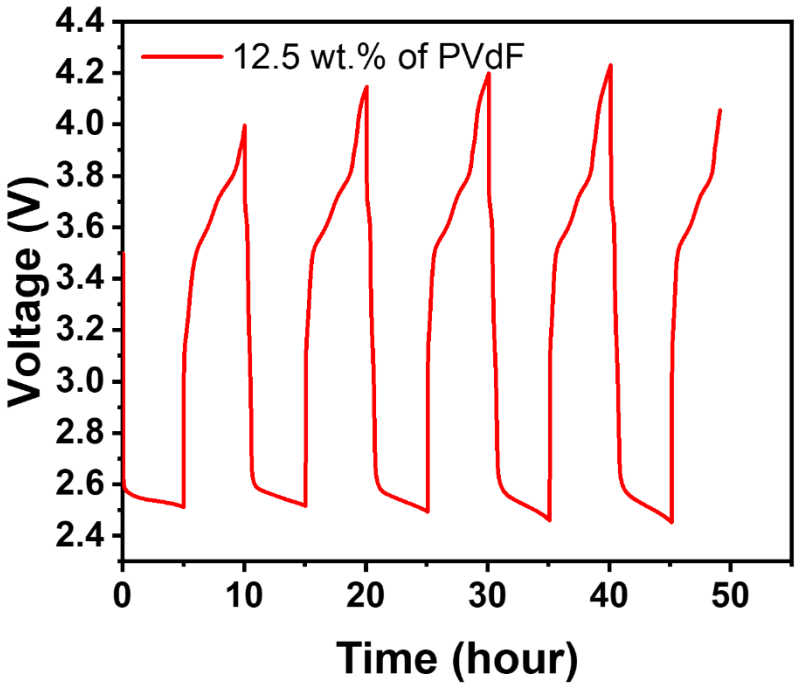
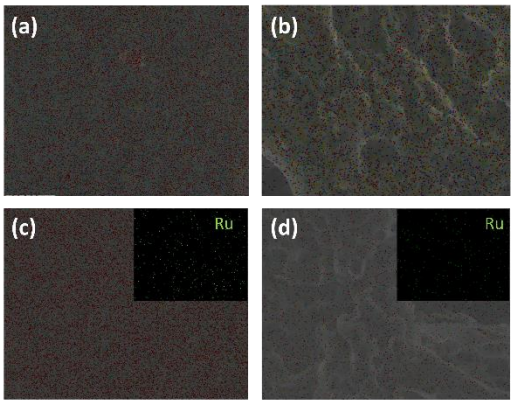


Figure S7. Voltage profile of LOBs with the macro porous Ru/SWCNTs air electrode prepared with higher amount (12.5 wt.%) of PVdF binder cycled within the cut-off voltage range of 2.0 – 4.5 V at a current density of 0.2 mA cm^{-2} under a capacity-limited protocol of 1.0 mAh cm^{-2}.



	EDX results for discharged to 2.0V			
	a	b	c	d
	Ru-RuO_2 /SWCNTs	3D-SOM Ru-RuO_2/SWCNTs	Ru-RuO_2 /SWCNTs	3D-SOM Ru-RuO_2/SWCNTs
	Surfaces		Cross-section (area-scan)	
	wt. %			
Carbon	45.5	54.3	50.1	45.1
Sulfur	3.4	4.0	4.0	5.3
Florine	17.7	23.7	23.2	15.1
Oxygen	33.5	18.1	22.3	33.9
Ruthenium	0.0	0.0	0.5	0.6

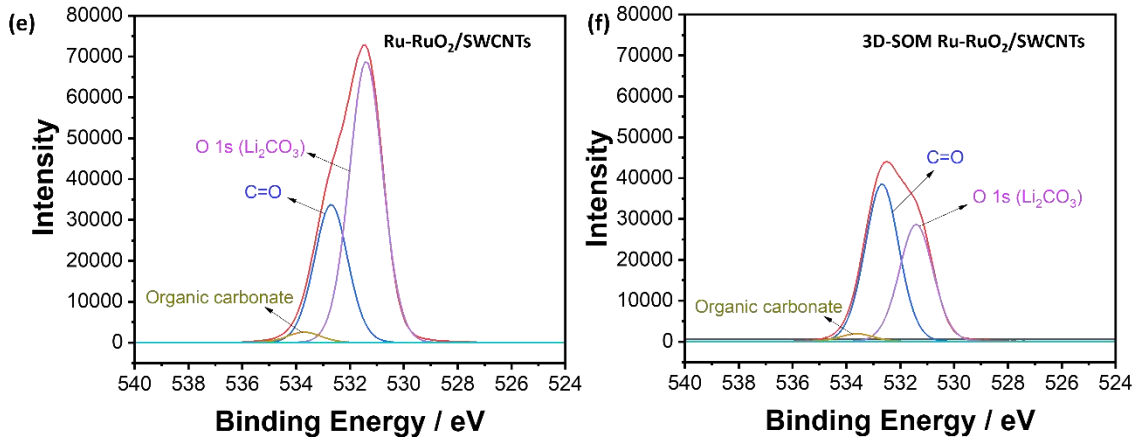


Figure S8. (a - d) EDX maps for all elements on SEM images with an (inset) EDX map of ruthenium scanned on the same area from the (a and b) surfaces and (c and d) cross-sections of (a and c) Ru-RuO_2/SWCNTs and (b and d) 3D-SOM Ru-RuO_2/SWCNTs electrodes after 1st discharges to 2.0 V at 0.2 mA cm^{-2} in LOB cell with 1 M LiTFSI/G4 including 0.1 M TEMPO as a redox mediator and corresponding element quantities summarized in the table, and their (e and f) XPS spectra of the O 1s from the electrode surfaces.

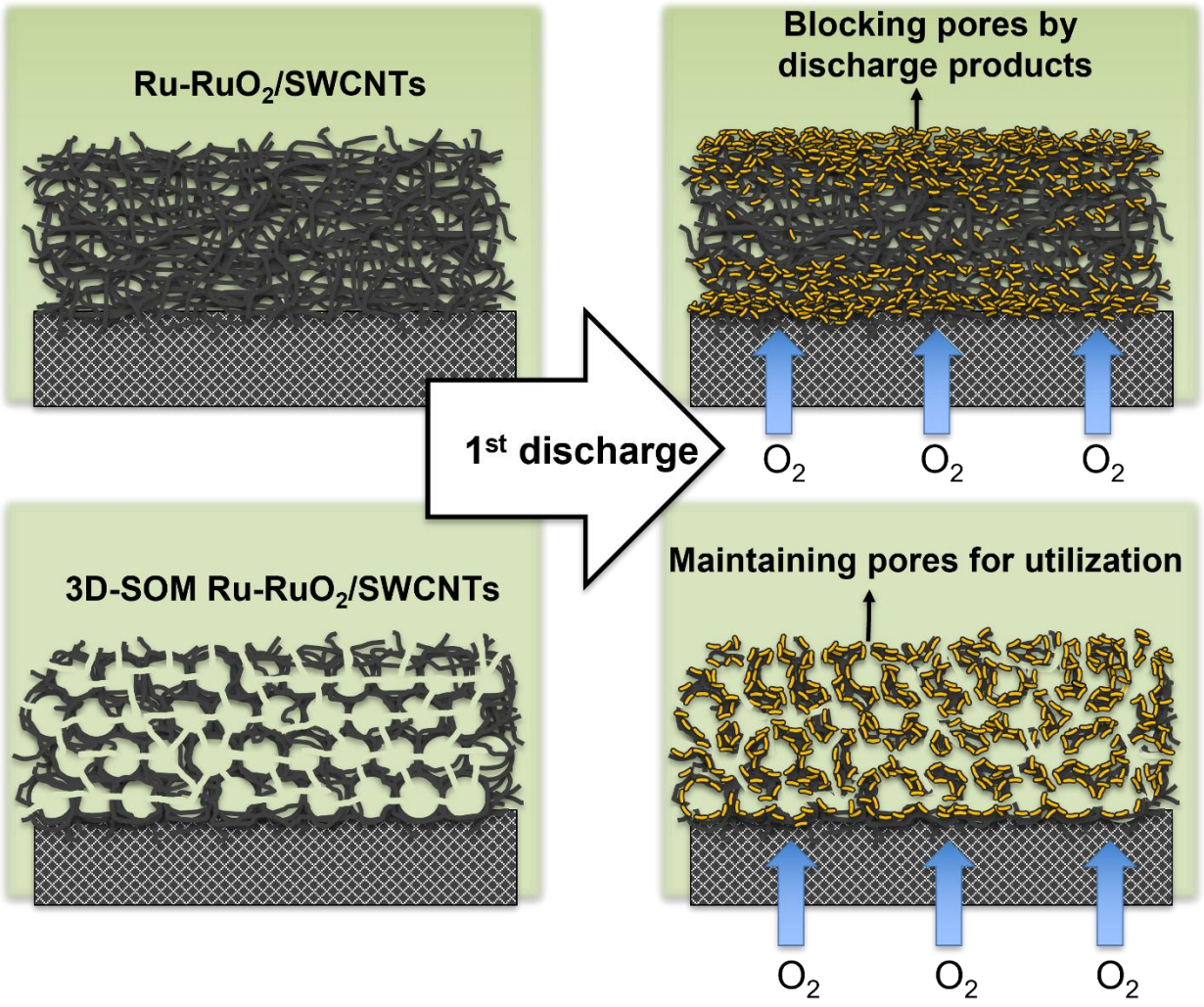
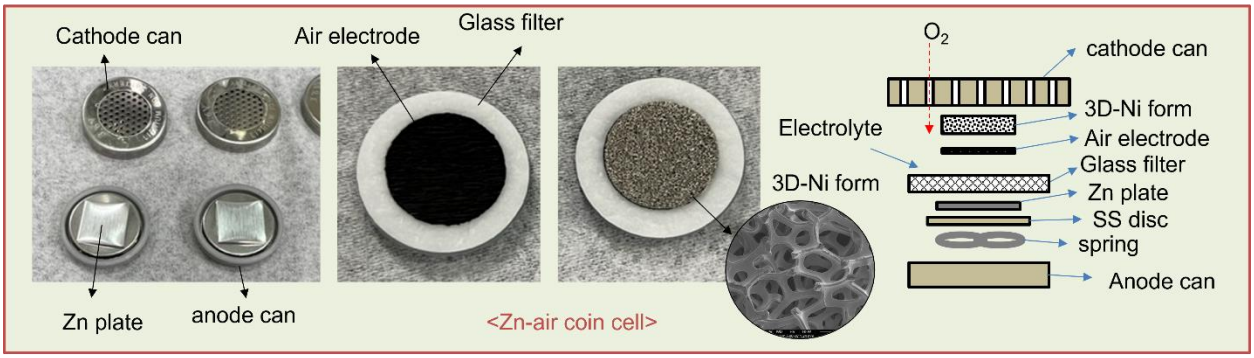


Figure S9. Effect of 3D-SOM structure of Ru-RuO_2/SWCNTs air electrode on the formation of discharge products after electrochemical discharging to 2 V in LOB cell.



<Air container for Zn-air cell>

Figure S10. Illustration of a coin cell configuration with cell components and Teflon air container used for aqueous Zinc-oxygen battery cycling test.

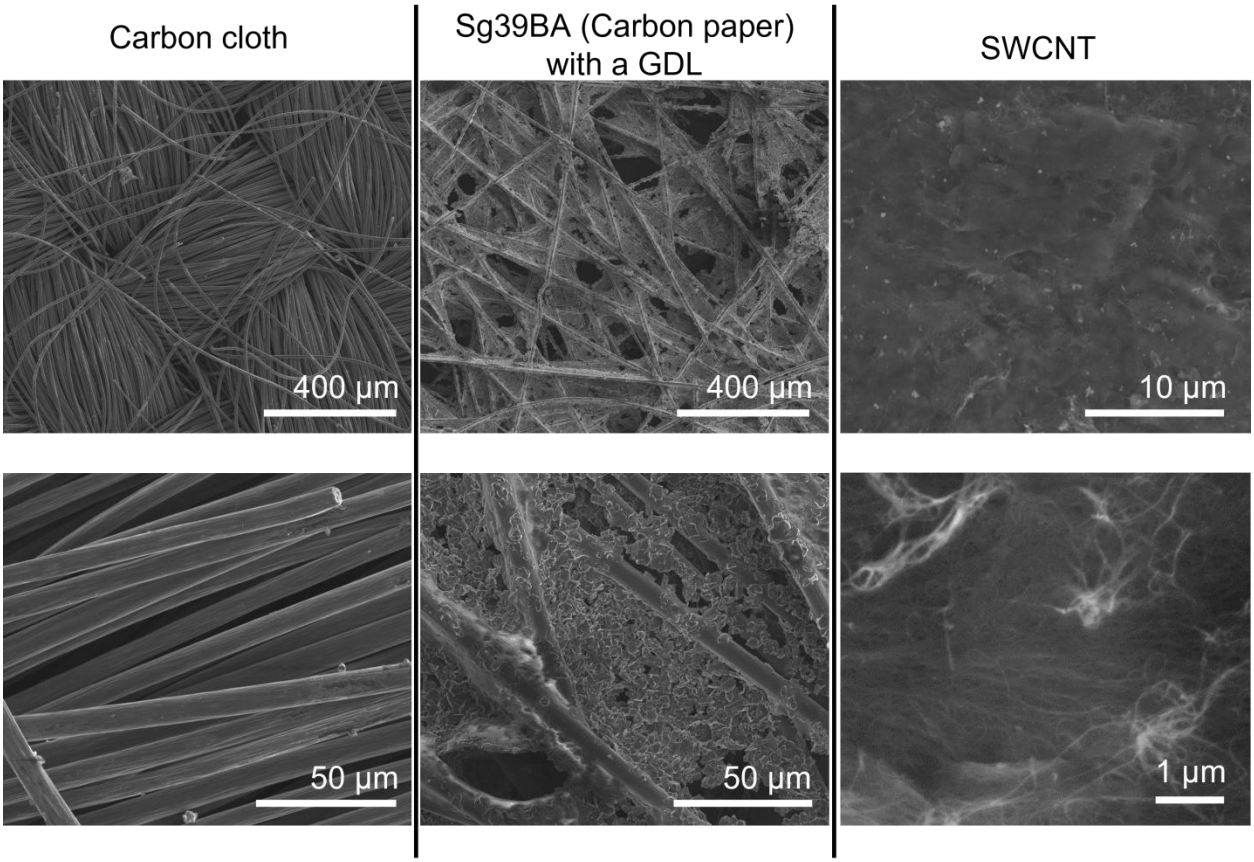


Figure S11. SEM images for the top views of three different materials for the air electrodes in aqueous ZOB cells; carbon cloth, carbon paper, and SWCNT.

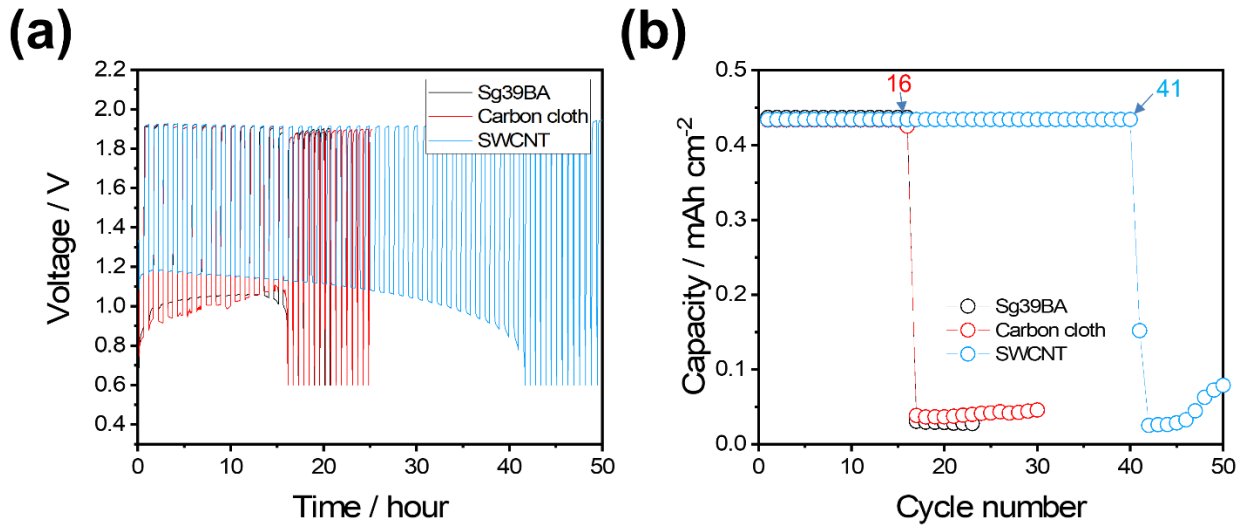


Figure S12. (a) Voltage profiles of the aqueous ZOBs with Sg39BA (carbon paper, black), Carbon cloth (red) and SWCNT (blue) air electrodes within the cut-off voltage range of 0.6 – 2.0 V at a current density of 1 mA cm^{-2} being 30min charge and discharge (t_{limit}=30min) limits and corresponding (b) cycle life of ZOB cells.

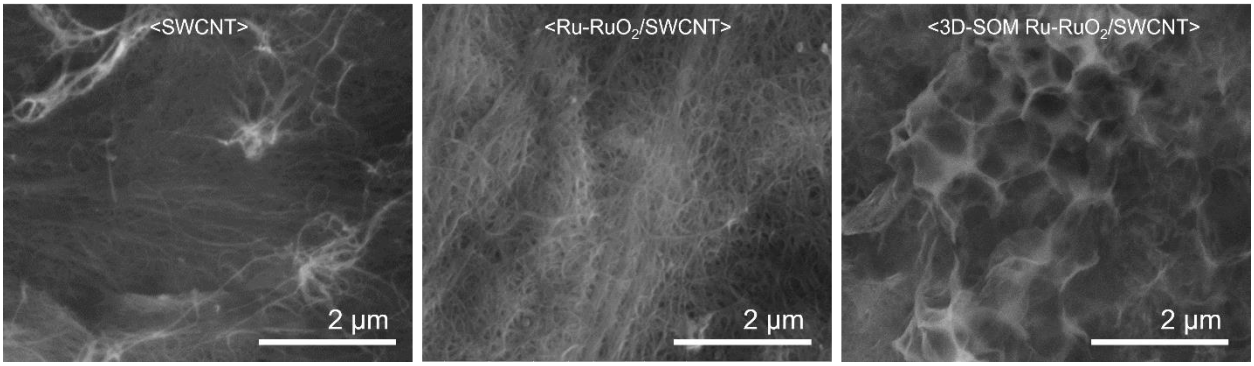


Figure S13. SEM images of (a) SWCNTs, (b) with the decorated ruthenium (Ru-RuO_2) catalyst, and (c) 3D-SOM Ru-RuO_2/SWCNTs air electrodes for the aqueous ZOBs.

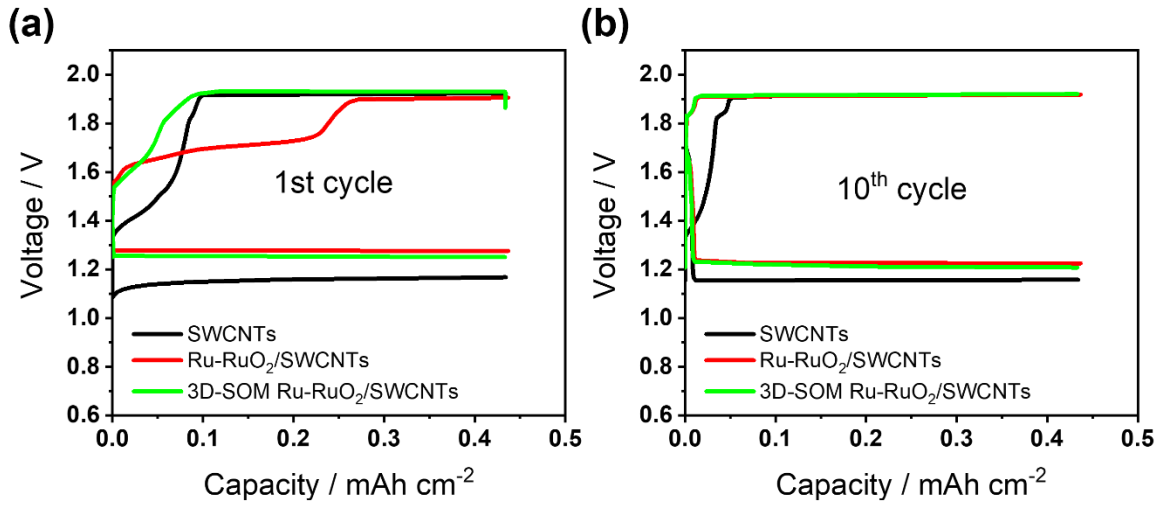


Figure S14. Representative voltage profiles of the aqueous ZOBs with SWCNTs (black), Ru-RuO_2/SWCNTs (red) and 3D-SOM Ru-RuO_2/SWCNTs (green) air electrodes of (a) 1st and (b) 10th cycles within the cut-off voltage range of 0.6 – 2.0 V at a current density of 1 mA cm^{-2} being 30 min charge and discharge (t_{limit}=30min) limits.