

Electronic Supplementary Information

Anodic instability of carbon in non-alkaline Zn-air batteries

Roman R. Kapaev* and Malachi Noked*

Department of Chemistry and BINA – BIU Center for Nanotechnology and Advanced
Materials, Bar-Ilan University, Ramat-Gan 5290002, Israel

*E-mail: kapaevr@biu.ac.il (R.R.K.), malachi.noked@biu.ac.il (M.N.)

Experimental section

Materials: Zn foil (degreased, $\geq 99.95\%$, 80 μm thickness) was supplied by Grillo. $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (puriss., ACS reagent, $\geq 99.5\%$), $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (ACS reagent, $\geq 98\%$), ZnO (puriss., p.a., ACS reagent, $\geq 99.0\%$) and $^{13}\text{CH}_3^{13}\text{COOH}$ (99% at. ^{13}C) were supplied by Sigma Aldrich. $\text{Zn}(\text{OTf})_2$ (98%) was supplied by Acros Organics. Ketjenblack EC300J, Ketjenblack EC600JD and Sigracet 39BB carbon paper were supplied by Fuel Cell Store. Polytetrafluoroethylene preparation (60% dispersion in H_2O) was purchased from Sigma Aldrich. Deionized water (18.2 $\text{M}\Omega\text{ cm}$) was used for electrode and electrolyte preparation. Isopropanol (HPLC PLUS Gradient grade) was purchased from CARLO ERBA reagents. Whatman glass microfiber (GF/A grade) was used for separators.

Electrolyte preparation: To prepare 1M solutions of ZnSO_4 , $\text{Zn}(\text{OAc})_2$ and $\text{Zn}(\text{OTf})_2$, 2 mmol of respective salts ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Zn}(\text{OTf})_2$) were dissolved in water, and total volume of the solutions was adjusted to 2 ± 0.1 mL. Preparation of 2M and 3M solutions was similar: 4 or 6 mmol of the salts were dissolved in H_2O , the resulting volume of the solutions was adjusted to 2 ± 0.1 mL. To prepare 1M solution of ^{13}C -labeled zinc acetate, 2.0 mmol of ZnO (162.8 mg) were mixed with 4.0 mmol of $^{13}\text{CH}_3^{13}\text{COOH}$ (248.2 mg) and 1000 μL of H_2O . The mixture was heated to 50-60 $^\circ\text{C}$ in a closed vial for 2-3 min until complete dissolution of ZnO. After cooling down to room temperature, the total volume of the solution was adjusted to 2 ± 0.1 mL with water.

Positive electrode preparation: Ketjenblack EC300J (150 mg) was mixed with H_2O (300 μL) and polytetrafluoroethylene (15 mg, dispersed in H_2O) in an agate mortar, after which isopropanol (750 μL) was added, and the components were mixed once again. The resulting slurry was tape-cast onto the microporous side of carbon paper (Sigracet 39BB). The electrodes were dried at 100 $^\circ\text{C}$, then roll-pressed and cut into disks ($d = 11$ mm). For EC600JD, the procedures were similar but 600 μL of H_2O and 1500 μL of isopropanol were used per 150 mg

of carbon black. The loading of carbon blacks in the resulting electrodes was from 8.9 to 9.3 mg cm⁻².

Zn-air cell assembling and electrochemistry: Custom-made two-electrode cells with Swagelok valves, which accommodate ~16 mL of air (Fig. S6),¹ were used for electrochemical cycling. The cells were assembled in ambient air. Zinc foil ($d = 13$ mm disks) was used for negative electrodes, glass fiber ($d = 21$ mm disks) was used for separators, 120 μ L of electrolyte was added to each cell. Before cycling, the cells were kept at rest for 5 h. All electrochemistry was performed at room temperature using BioLogic VMP3.

OEMS measurements: Analysis of gas composition was carried out with HPR-20 eight-channel mass spectrometer (Hiden Analytical). SEM detector was used for signal acquisition. The cell outlets were connected to the OEMS capillaries in an air-tight way using Swagelok fittings with PTFE ferrules.

Characterization: Raman spectroscopy measurements were performed with Horiba LabRAM Soleil Raman microscope; the laser excitation wavelength was 532 nm, the laser power was 0.79 mW, the grating was 1800 lines mm⁻¹ for monitoring carbon D/G band ratio and 600 lines mm⁻¹ for other measurements. X-ray diffraction patterns were measured with Bruker D8 diffractometer using CuK α radiation. X-ray photoelectron spectra were measured with a PHI 5600 Multi-Technique System that has an Al K α monochromatic source (1486.6 eV); peaks were calibrated by setting the binding energy of the major C1s peak to 285.0 eV; two measurements were made for each sample to check reproducibility; peak deconvolution was carried out with Thermo Scientific Avantage software. Scanning electron microscopy studies were performed using an FEI Magellan 400L high-resolution scanning electron microscope.

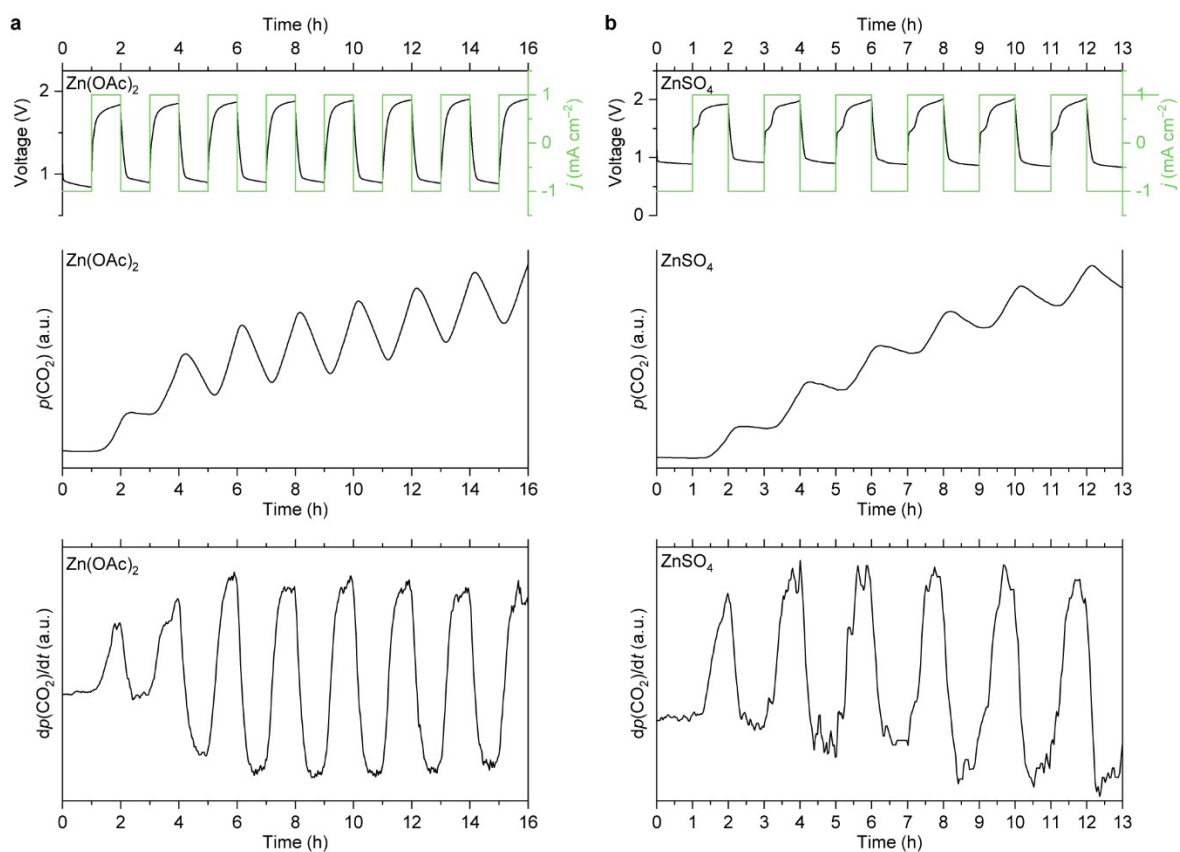


Fig. S1. Cell voltage and current density vs. time, evolution of CO_2 partial pressure and its derivative during a prolonged OEMS measurements with 1M Zn(OAc)_2 (a) and 1M ZnSO_4 (b).

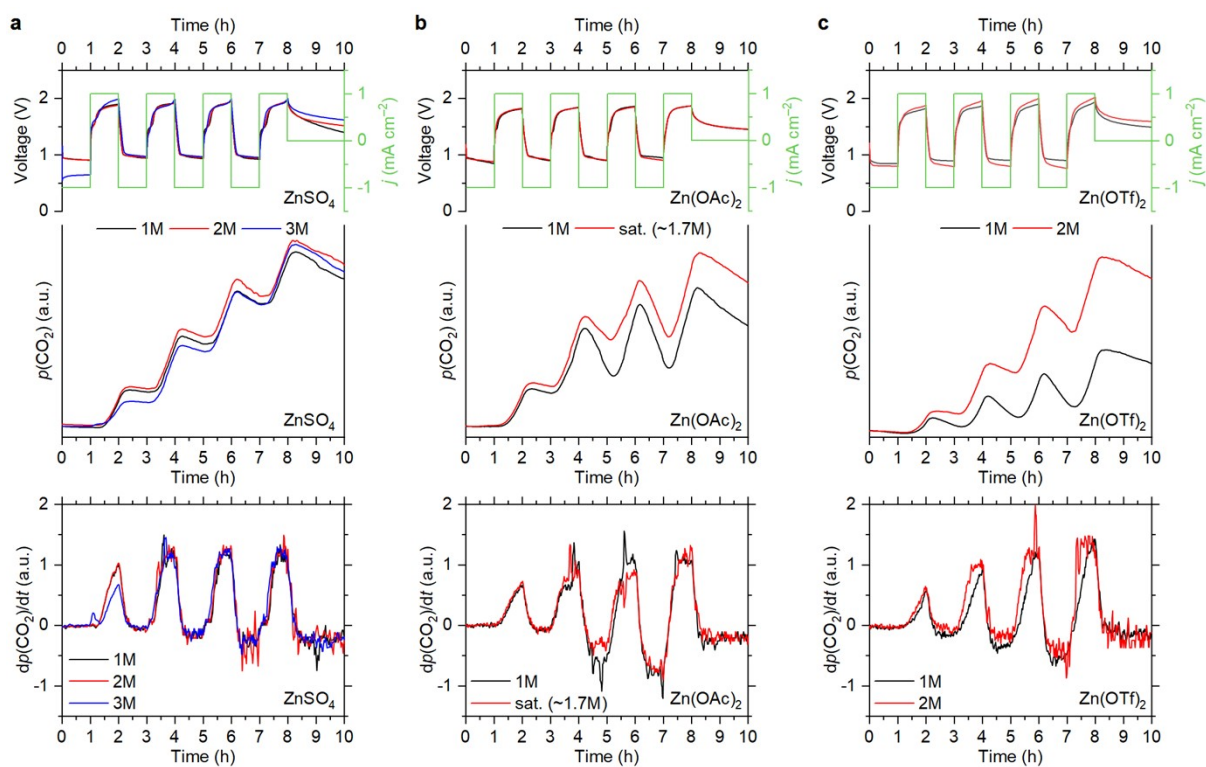


Fig. S2. Cell voltage and current density vs. time, evolution of CO₂ partial pressure and its derivative during the OEMS measurements with ZnSO₄ (a), Zn(OAc)₂ (b) and Zn(OTf)₂ (c) solutions as electrolytes.

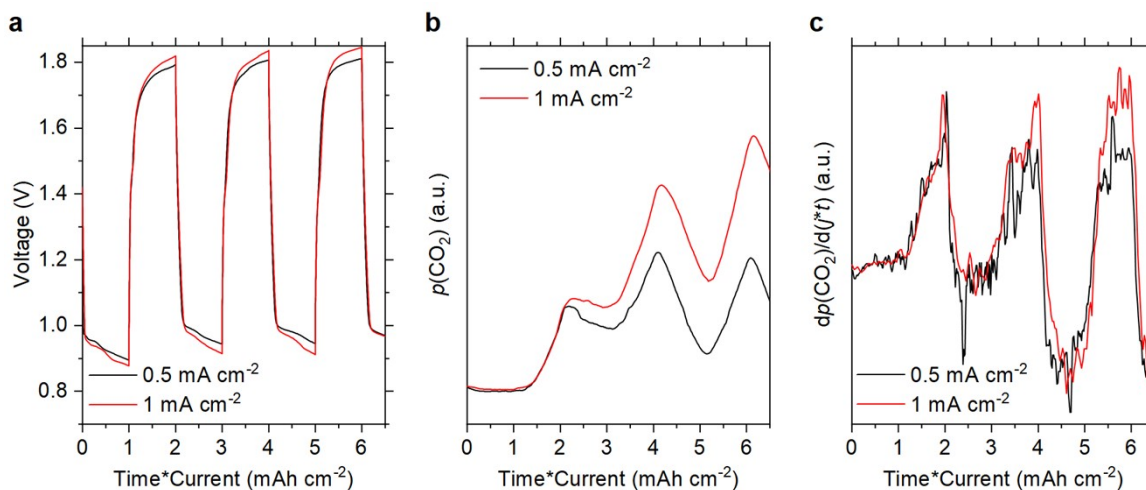
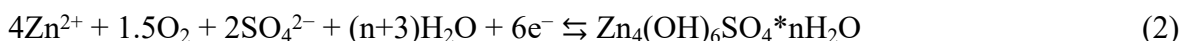


Fig. S3. Cell voltage and current density vs. cumulative capacity (a), evolution of CO₂ partial pressure (b) and its derivative (c) during the OEMS measurements with different applied current rates. The electrolyte was 1M Zn(OAc)₂, the active material was EC300J.

Section S1. Charge-discharge mechanisms

As reported in our previous study¹ and other reports,^{2, 3} Zn(OAc)₂- and ZnSO₄-based electrolytes enable four-electron oxygen reduction according to the following equations:



As seen in Fig. S4, trends of oxygen partial pressure during OEMS measurements are similar for the acetate-, sulfate- and triflate-based electrolytes. This indicates that the four-electron oxygen reduction mechanism is also relevant for the triflate-based electrolyte.

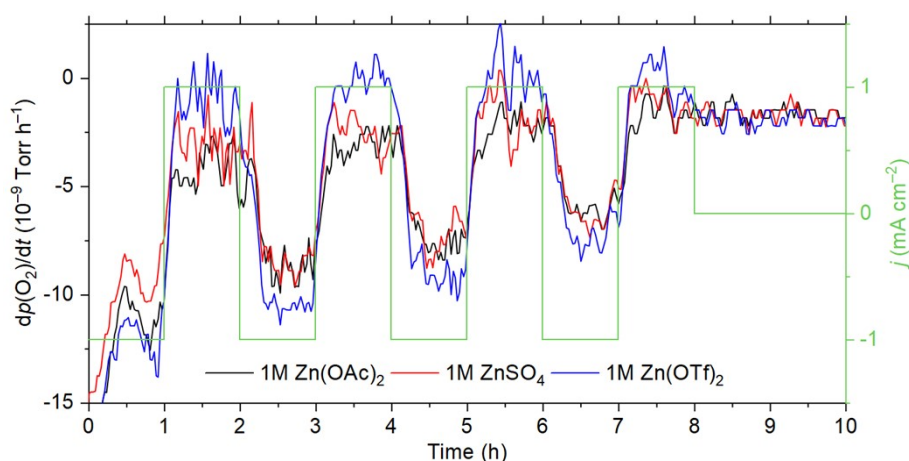


Fig. S4. Derivatives of O₂ partial pressure measured during cycling with various electrolytes. Ketjenblack EC300J was used as a cathode material.

Raman spectrum of the cathode that was discharged with 1M Zn(OTf)₂ electrolyte contains peaks that correspond to triflate anions (Fig. S5a).⁴ No peak of O–O stretching vibration^{2, 5} (840 cm⁻¹) is observed, so there is no evidence of two-electron oxygen reduction. Peaks of ZnO₂ are also not seen in the X-ray diffraction pattern (Fig. S5b).^{2, 5} The XRD signals could not be assigned to a known phase, but the pattern looks similar to zinc hydroxyacetate Zn₅(OH)₈(OAc)₂·2H₂O. The data suggest that formation of zinc hydroxytriflate hydrate⁶ occurs upon discharge.

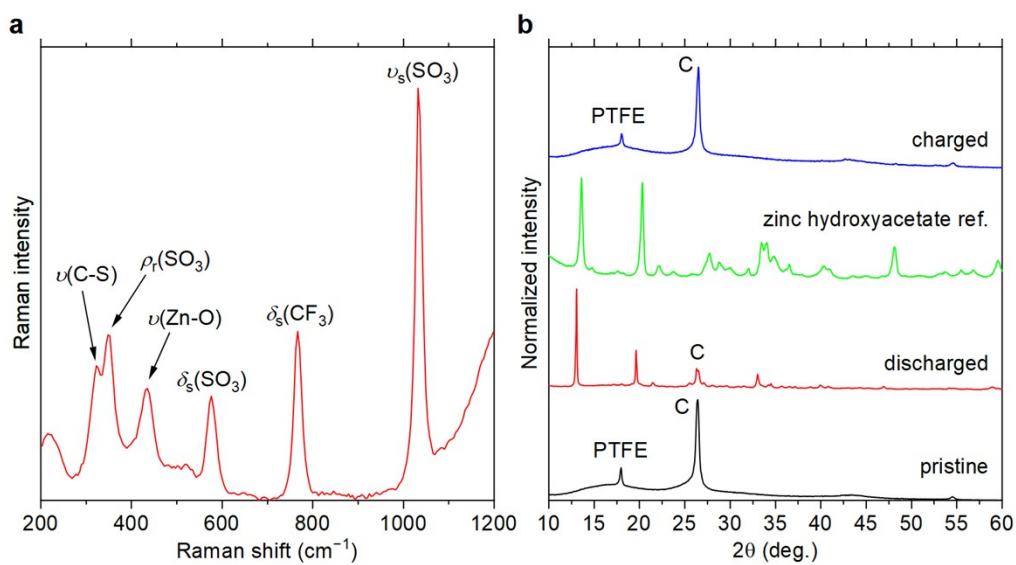


Fig. S5. Characterization of cathodes from Zn-air cells with 1M Zn(OTf)₂ electrolyte: (a) Raman spectrum of the discharged cathode with peaks assigned according to ref.⁴; (b) XRD patterns of pristine, discharged and charged electrodes compared to XRD pattern of zinc hydroxyacetate from ref.¹.

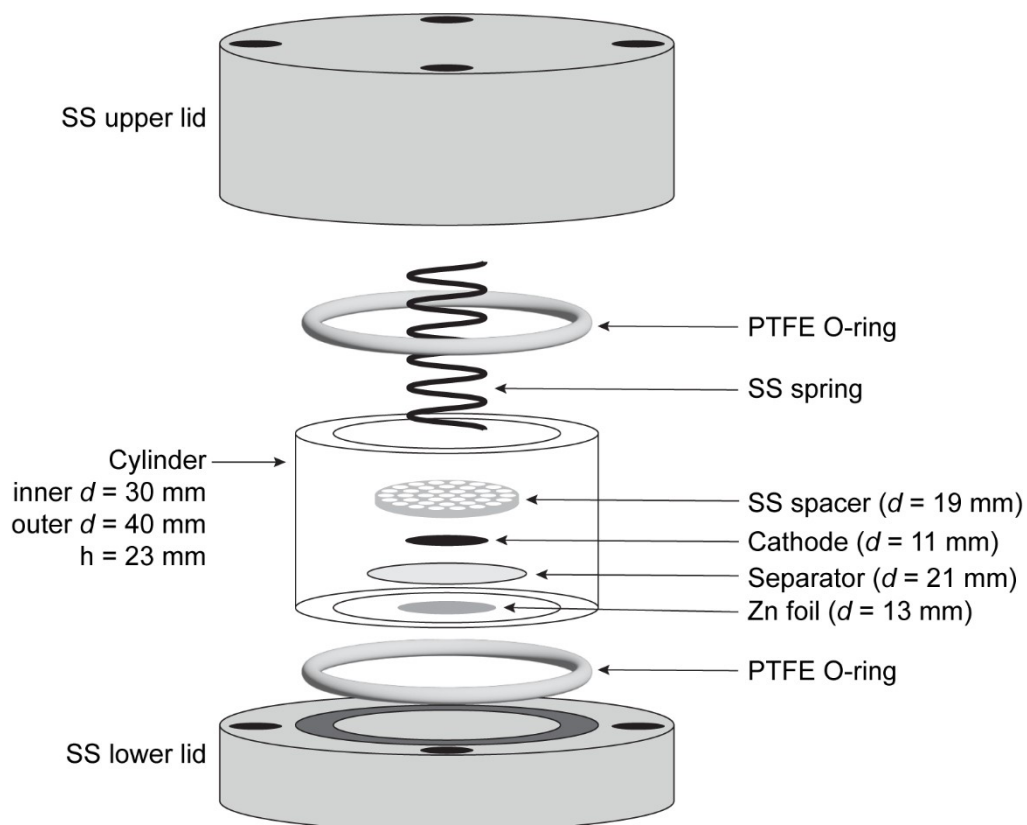


Fig. S6. Scheme of the cell used for electrochemical tests. Screws and valves of the upper lid are not shown for clarity. Photos of the cell in assembled and disassembled states are available in ref.¹ SS = stainless steel, PTFE = poly(tetrafluoroethylene).

References

- (1) Kapaev, R. R.; Ohayon, A.; Sonoo, M.; Tzadikov, J.; Shalom, M.; Noked, M., Structure-performance relations for carbons in Zn-air battery cathodes with non-alkaline electrolytes. *Electrochim. Acta* **2023**, *456*, 142462.
- (2) Sun, W.; Wang, F.; Zhang, B.; Zhang, M. Y.; Kupers, V.; Ji, X.; Theile, C.; Bieker, P.; Xu, K.; Wang, C. S.; Winter, M., A rechargeable zinc-air battery based on zinc peroxide chemistry. *Science* **2021**, *371* (6524), 46-51.
- (3) Sun, W.; Küpers, V.; Wang, F.; Bieker, P.; Winter, M., A Non-Alkaline Electrolyte for Electrically Rechargeable Zinc-Air Batteries with Long-Term Operation Stability in Ambient Air. *Angew. Chem. Int. Ed.* **2022**, *61* (38), e202207353.
- (4) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S., Raman and infrared spectra and normal coordinates of the trifluoromethanesulfonate and trichloromethanesulfonate anions. *Spectrochimica Acta Part A: Molecular Spectroscopy* **1969**, *25* (9), 1515-1526.
- (5) Giannakoudakis, D. A.; Florent, M.; Wallace, R.; Secor, J.; Karwacki, C.; Bandosz, T. J., Zinc peroxide nanoparticles: Surface, chemical and optical properties and the effect of thermal treatment on the detoxification of mustard gas. *Applied Catalysis B: Environmental* **2018**, *226*, 429-440.
- (6) Jo, J. H.; Aniskevich, Y.; Kim, J.; Choi, J. U.; Kim, H. J.; Jung, Y. H.; Ahn, D.; Jeon, T.-Y.; Lee, K.-S.; Song, S. H.; Kim, H.; Ragoisha, G.; Mazanik, A.; Streltsov, E.; Myung, S.-T., New Insight on Open-Structured Sodium Vanadium Oxide as High-Capacity and Long Life Cathode for Zn-Ion Storage: Structure, Electrochemistry, and First-Principles Calculation. *Adv. Energy Mater.* **2020**, *10* (40), 2001595.