Supporting Information

Mussel-inspired one-pot synthesis of transition metal and nitrogen co-doped carbon (M/N-C) as efficient oxygen catalyst for Zn-air batteries

Bing Li,‡[a] Ye Chen, ‡[b] Xiaoming Ge,[a] Jianwei Chai,[a] Xiao Zhang,[b] T. S. Andy Hor,[a,c] Guojun Du,[a] Zhaolin Liu,*[a] Hua Zhang*[b] and Yun Zong*[a]

[a] *Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore.*
E-mail: zl-liu@imre.a-star.edu.sg; y-zong@imre.a-star.edu.sg

[b] *Center for Programmable Materials, School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Republic of Singapore.*
E-mail: hzhang@ntu.edu.sg

[c] *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore*

Supporting Information

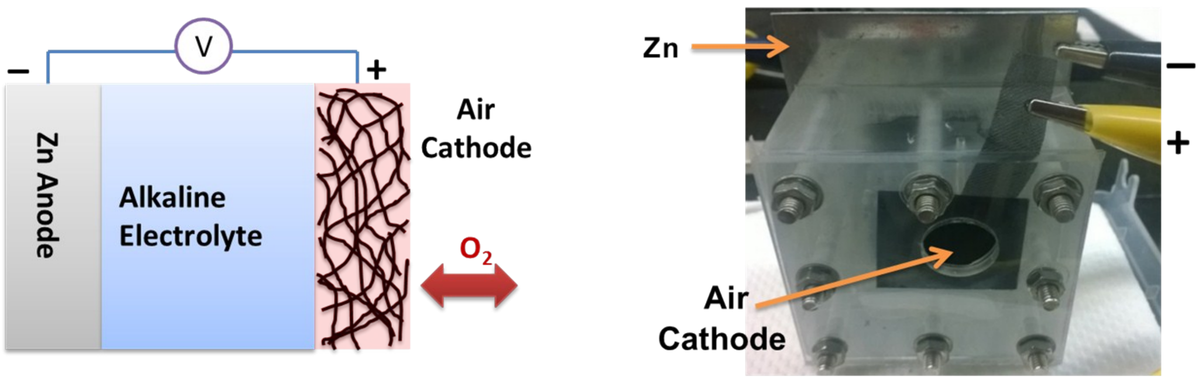


Fig. S1 Schematic depiction of the structure of ZnAB (left) and a photograph of home-built ZnAB employed in this study (right).

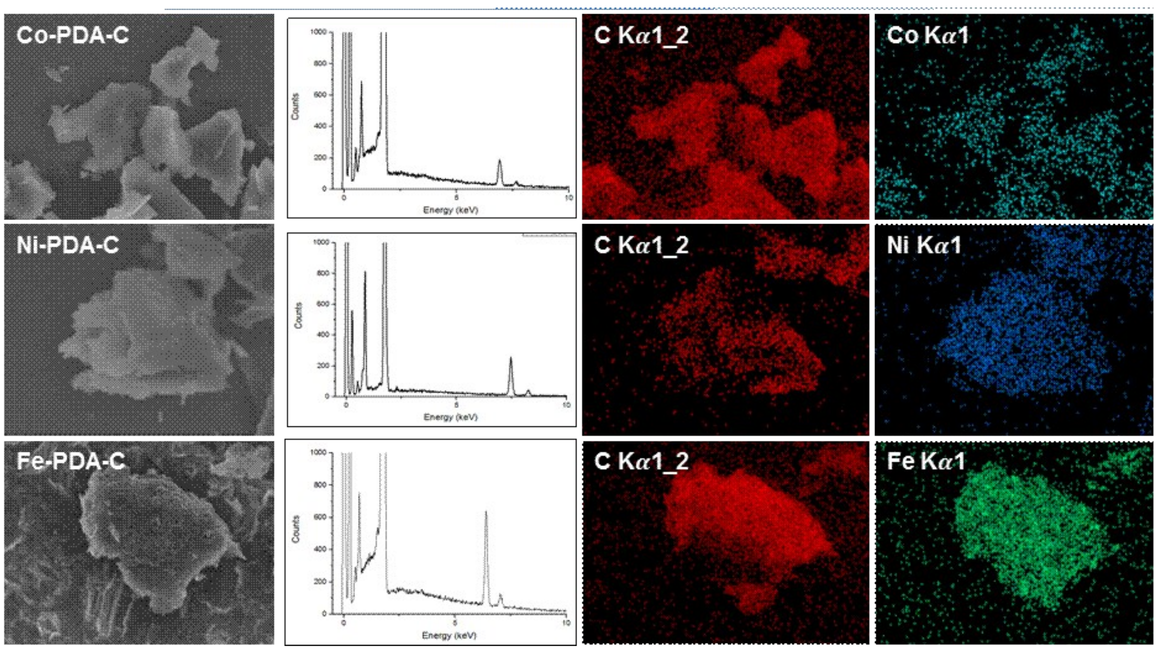
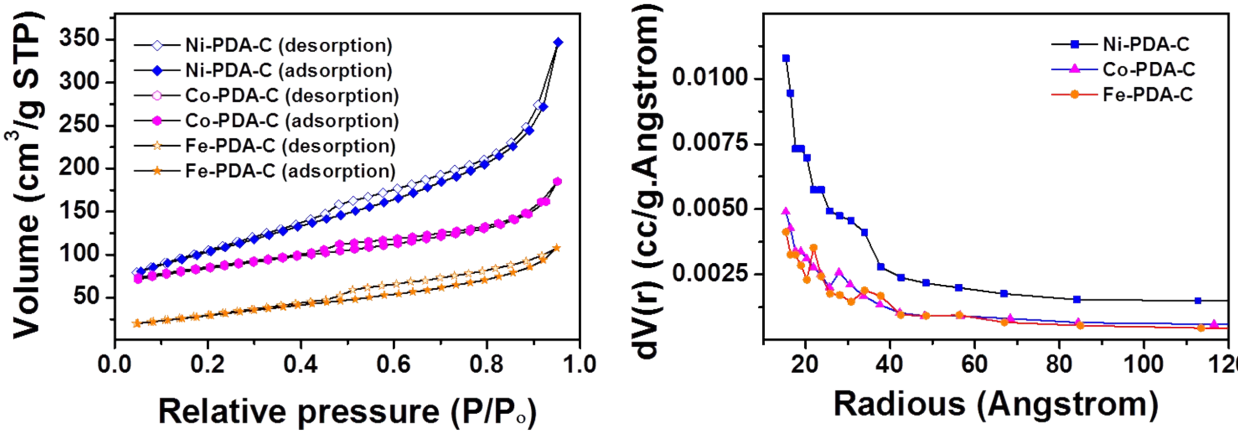


Fig. S2 A) EDX spectra of the Co-PDA-C, Ni-PDA-C and Fe-PDA-C, and the corresponding elemental mappings for C and the respective metals.



Sample	S_{BET}(m^2/g)	V_{total} (cc/g)	Pore vol % (<2 nm)
Ni- PDA-C	368.4	0.425	12.1
Co-PDA-C	276.1	0.176	13.2
Fe- PDA-C	113.3	0.138	13.9

Fig. S3 Nitrogen adsorption/desorption isotherms and pore size distribution for Co-PDA-C, Ni-PDA-C and Fe-PDA-C, respectively. The major information for BET surface area (S_{BET}), total pore volume (V_{total}) and pore vol % (<2nm) are summarized in the table accordingly.

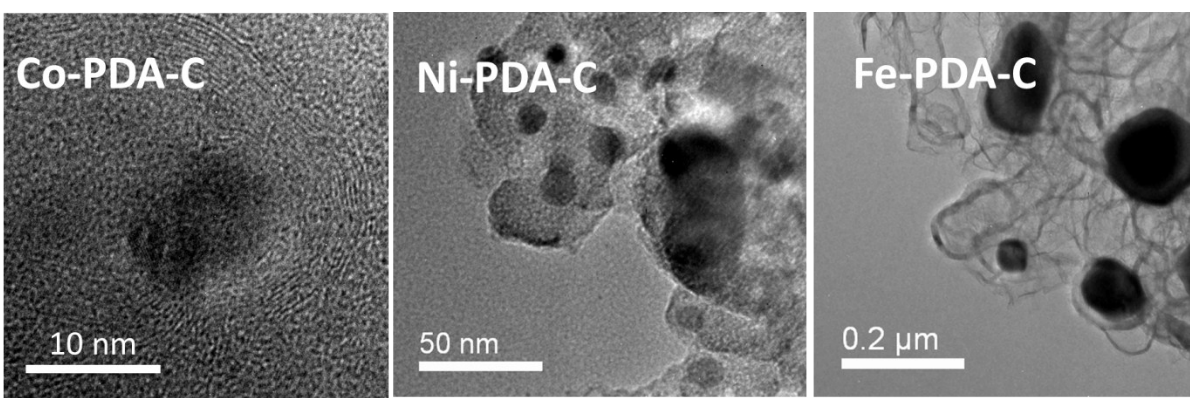


Fig. S4 High magnification TEM images of Co-PDA-C, Ni-PDA-C and Fe-PDA-C, respectively, showing carbon layers covered nature of the metal nanoparticles.

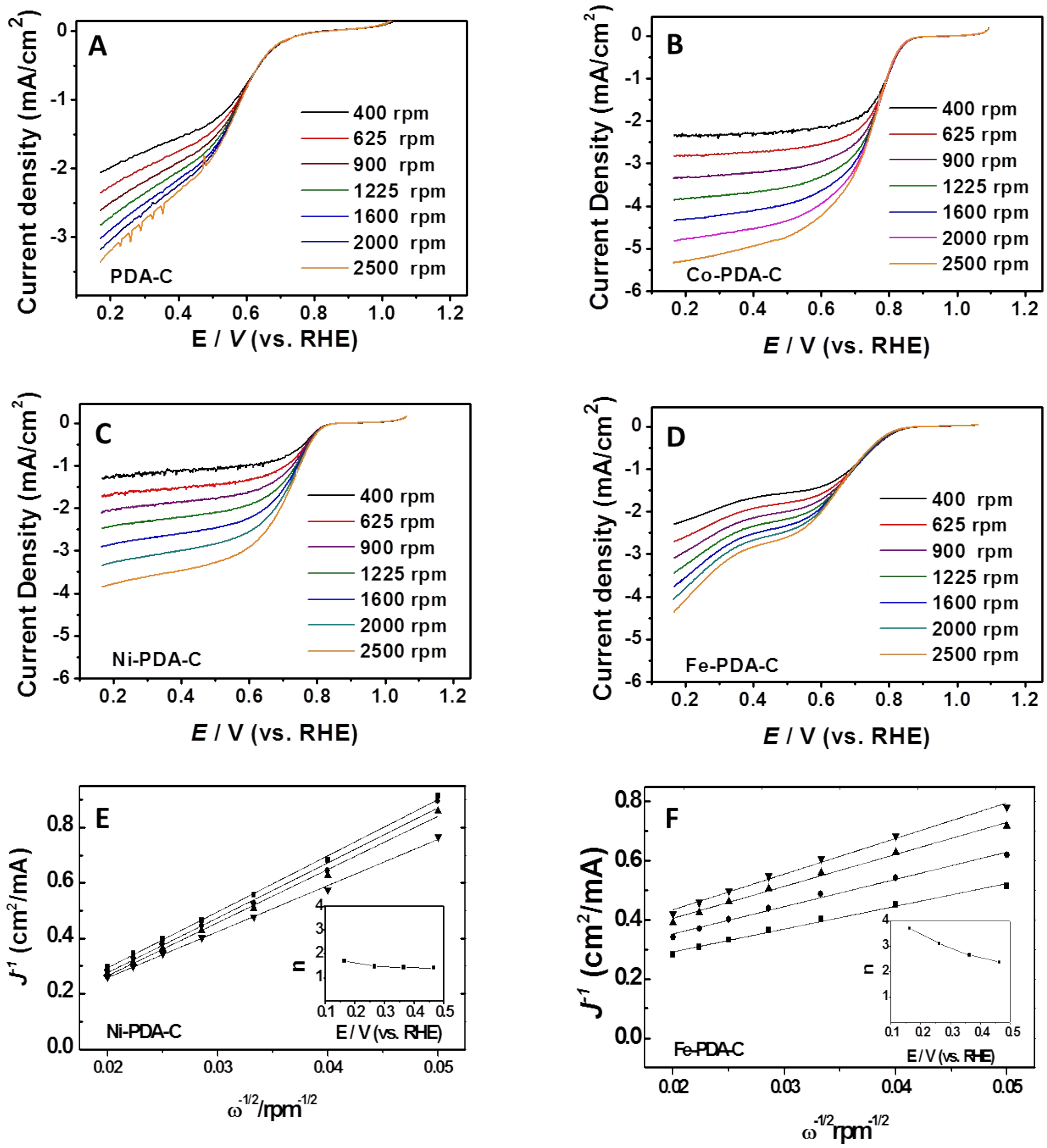


Fig. S5 RDE data of PDA-C (A), Co PDA-C(B), Ni- PDA-C(C) and Fe- PDA-C(D), respectively. (E) and (F) are the K-L plots and fitting curves of Ni- PDA-C and Fe- PDA-C, respectively.

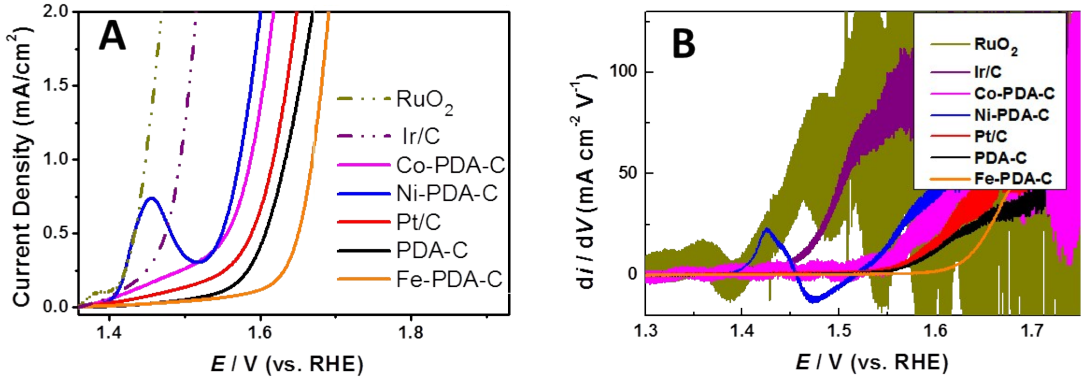


Fig. S6 Comparison of OER activities of different catalysts after (A) deducting the background current or (B) taking the first derivative of current with respect to voltage, d*i*/d*V*, based on the original data shown in Fig.4D.

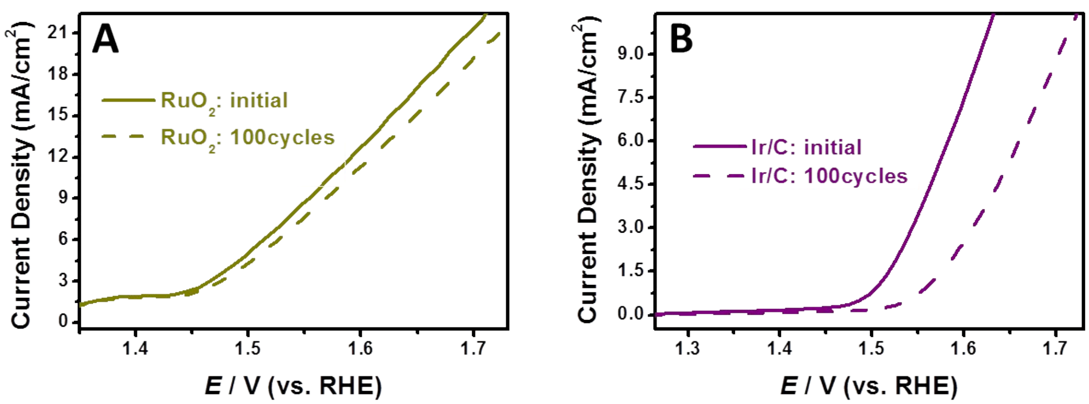


Fig. S7 ADT results of RuO_2 (A) and Ir/C (B) before (solid lines) and after 100 cycles (dashed lines) at electrode rotating speed of 400 rpm for OER. Scan rate: 5 mV s^{-1}.

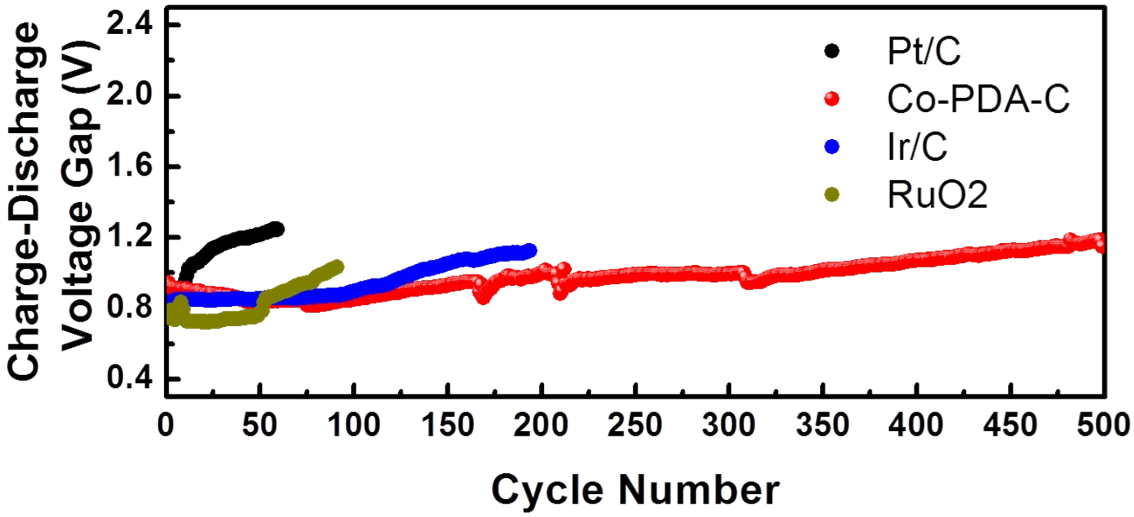


Fig. S8 The voltage gaps during the cycling of ZnABs with different catalysts in air-cathode over an extended period. It clearly shows the superior durability of Co-PDA-C based ZnABs as compared to its counterparts using catalysts of Pt/C. Ir/C or RuO_2 in their air cathodes.

Table S1. A comparison of cycling performances of the ZnABs based on Co-PDA-C and Pt/C catalyst in terms of charge/discharge (Ch/Disch) voltage and Ch/Disch voltage gap at different cycles as well as the degradation rate in charge and discharge, respectively. All the values were extracted according to the Fig.5.

Catalyst	Initial cycle		Cycle 10		Cycle 60		Cycle 90		Cycle 180		Cycle 500		Degradation rate in Ch/Disch (mV/cycle)
	Ch/Disch Voltage (V)	Voltage gap (V)	Ch/Disch Voltage (V)	Voltage gap (V)	Ch/Disch Voltage (V)	Voltag e gap (V)	Ch/Disch Voltage (V)	Voltage gap (V)	Ch/Disch Voltage (V)	Voltage gap (V)	Ch/Disch Voltage (V)	Voltage gap (V)	
Co-PDA-C	2.15/1.21	0.94	2.14/1.24	0.9	2.10/1.24	0.86	2.08/1.24	0.84	2.12/1.15	0.97	2.18/1.01	1.17	0.06/0.40
Pt/C	2.03/1.27	0.76	2.12/1.20	0.92	2.40/1.15	1.25	---	---	---	---	---	---	6.20/2.00
RuO_2	1.98/1.20	0.78	1.95/1.21	0.74	1.93/1.04	0.89	1.93/0.91	1.02	---	---	---	---	---/2.00
Ir/C	2.05/1.21	0.84	2.06/1.21	0.85	2.07/1.20	0.86	2.07/1.19	0.88	2.19/1.08	1.11	---	---	0.78/0.72

Fig. S9 A photograph of a ZnAB after long time discharging showing electrolyte leakage problem. The electrolyte turned to brown color indicating the degradation of carbon.

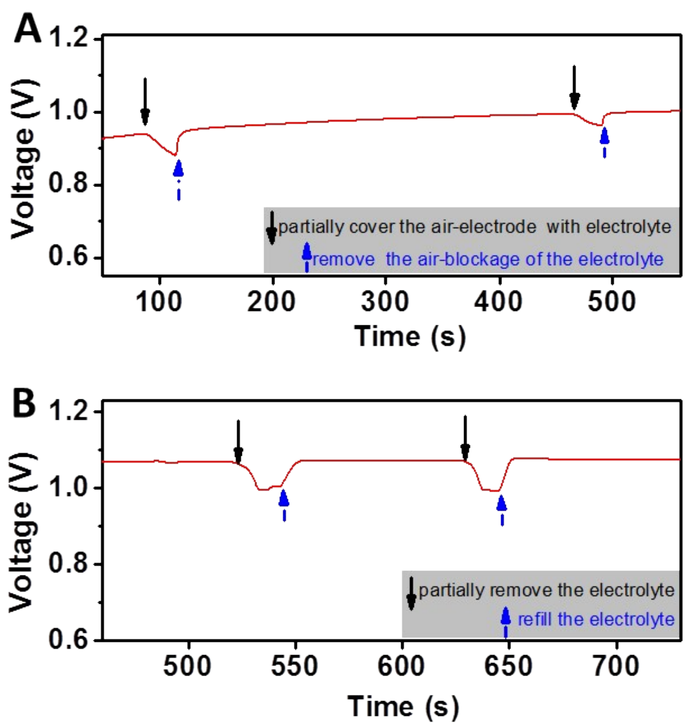


Fig. S10 Chronopotentiometric tests of a ZnAB at constant discharge current, showing that the discharge voltage drop caused by air blockage or electrolyte shortage can be resumed by removal of air-blockage or refilling of the electrolyte. **A)** Voltage profile of a ZnAB at constant discharge current with air-electrode partially blocked by adding electrolyte on the air-cathode as indicated by black arrows, and removal of the air blockage electrolyte at the points indicated by blue arrows. Also see the supplementary video 1. **B)** Voltage profile of a ZnAB at constant discharge current with partially removal of electrolyte as indicated by black arrows, and refilling of the electrolyte at the points indicated by the blue arrows. Also see the supplementary video 2.

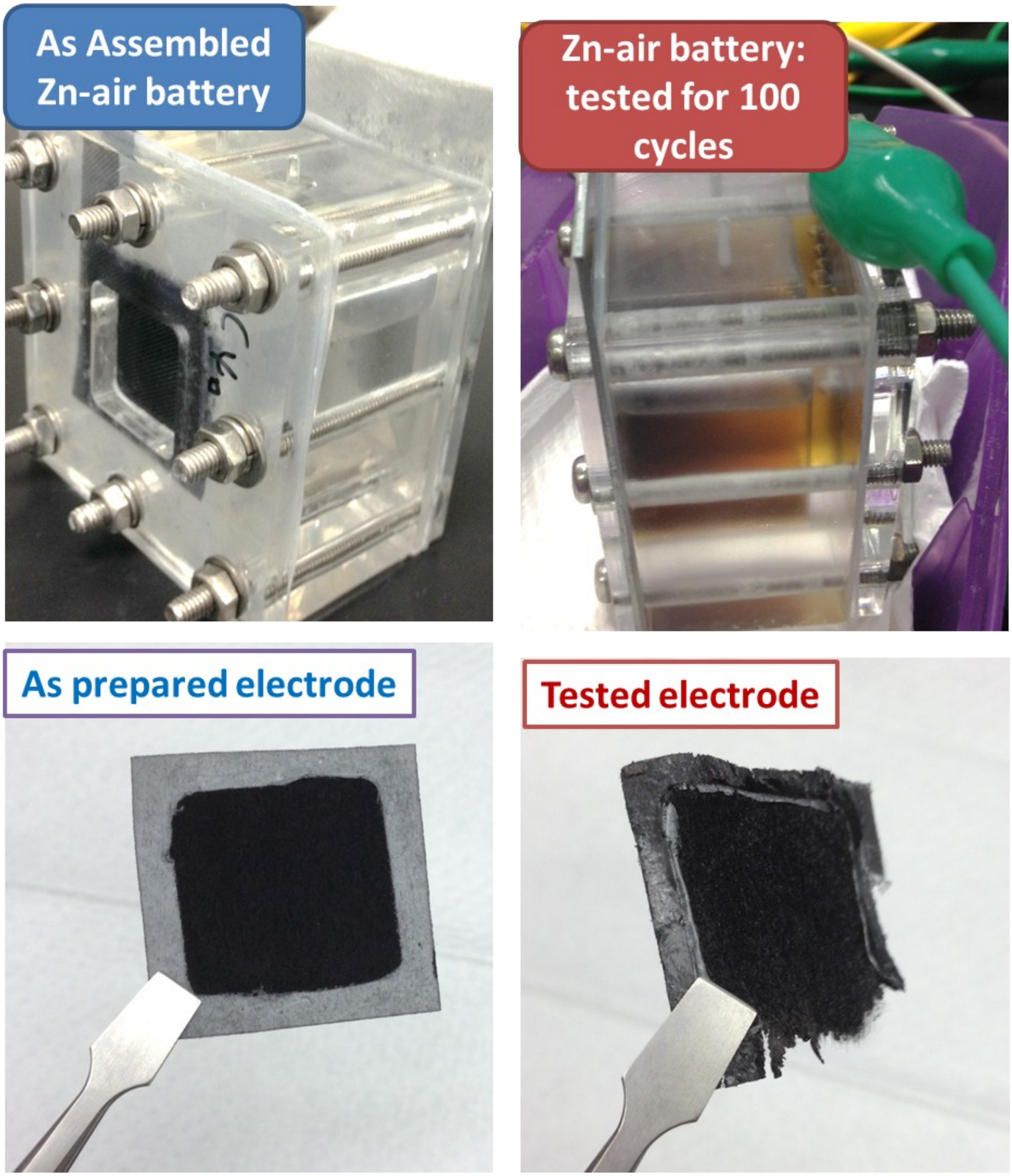


Fig. S11 Photos of as-assembled ZnAB (top left), tested ZnAB (top right), as prepared electrode (down left) and tested electrode (down right), also see video 3. The dark brown colour of the electrolyte in tested ZnAB and the softening in the tested electrode suggesting the carbon paper underwent corrosion in concentrated KOH electrolyte during the battery testing.