

Eggplant-Derived Microporous Carbon Sheets: Towards Mass Production of Efficient Bifunctional Oxygen Electrocatalyst at Low Cost for Rechargeable Zn-Air Batteries

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1. Materials and Methods

1.1 Preparation of eggplant carbons (EPCs)

Eggplant was obtained from a local supermarket (NTUC Fairprice Co-operative Ltd. Singapore). After its skin was peeled using a penknife, the flesh without seeds was freeze-dried and stored in a dry box prior to the carbonization whereby the freeze dried eggplant flesh was simply heated under N₂ atmosphere inside a Quartz Tube Furnace (Elite Thermal Systems Limited) at a heating rate of 10 °C min⁻¹ to temperatures of 600 °C, 700 °C, 800 °C, 900 °C or 1000 °C, respectively, and kept at the temperature for about 1.5 h. The obtained eggplant carbons are denoted as EPC-600, EPC-700, EPC-800, EPC-900 or EPC-1000 accordingly.

1.2 Preparation of activated EPC-900 (A-EPC-900)

The EPC-900 was activated following the KOH method¹⁻³ with some modifications. Briefly, 4.5 g EPC-900 was dispersed into 40 mL of 12 mol L⁻¹ KOH solution to form a uniform black slurry which is kept at 80 °C in oven for 8 h. The sample was then transferred into a Quartz Tube Furnace in an alumina crucible and heated under N₂ atmosphere at a heating rate of 10 °C min⁻¹ to 700 °C, and kept at the temperature for 30 min. The obtained black mixture was washed with 2 mol L⁻¹ HCl and then DI water, and dried for further use.

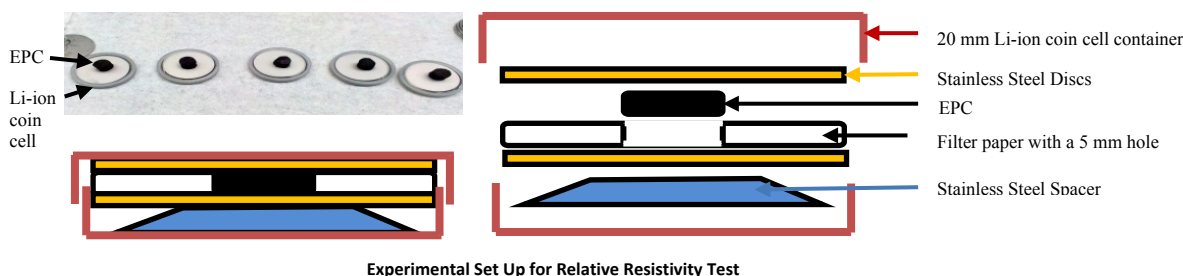
2. Material Characterizations:

The morphology of the samples was captured on a JSM-7600F field emission scanning electron microscope (FESEM) (JEOL Ltd, JP) at an operating voltage of 2 kV. The energy dispersive X-ray (EDX) spectrum and elemental mapping were recorded with an EDS detector (Oxford INCA) equipped on the SEM. The specific surface area and the N₂ adsorption and desorption isotherms were measured using an Automated Surface Area and Pore Size Analyzer of Quadrasorb SI (Quantachrome Instruments, USA). Thermogravimetric analysis (TGA) was performed on TGA Q500 (TA instruments) under air atmosphere. X-ray photoelectron spectroscopy (XPS) data was collected with a Theta Probe electron spectrometer (VG ESCALAB200i-XL, Thermo Scientific). The binding energies were calibrated using C 1s peak at 284.8 eV. Raman spectrum data was collected using a Renishaw inVia Raman microscope with an Ar ion laser ($\lambda = 514$ nm).

3. Relative Resistivity Test of EPC

To quickly yet reliably ascertain the optimum carbonization temperature of eggplant flesh, the relative resistance of EPC obtained at different temperature was examined and compared. For a better comparison, the samples were

prepared by using a punch with a diameter of 5 mm, thereby giving a uniform cylindrical shape. The sample weight was kept at a constant 2.3 mg and assembled into coin cell type as schematically shown below:



Briefly, EPC samples were contained within a fixed circular surface area of 0.196 cm² punched out from a filter paper. With fixed cross sectional area, the standardized mass of 2.3 mg was used across all samples to minimize the deviation in length of the samples upon compression. The additional spacer and stainless steel discs were meant to establish good electrical contact between the components of the cell. A force of 1000 kg cm⁻² was applied using a Manual Coin Cell Crimping Machine (MTI Corporations) to compress the cells evenly, before they were measured by a multimeter (179 True RMS, Fluke). The experiment was performed in quintuplicates to ensure the consistency and reliability of the results.

4. Electrochemical Measurements

Cyclic voltammetry (CV), linear sweep voltammetry (SLV) and rotating disk electrode (RDE) measurements were carried out on an Autolab Potentiostat Galvanostat 302N electrochemical workstation (Metrohm Autolab B.V., NL) with a standard three-electrode cell in O₂-purged aqueous solution of 0.1 mol L⁻¹ KOH. All experiments are conducted at room temperature. The standard three-electrode cell consists of a 5 mm glassy carbon (GC) working electrode, an Ag/AgCl reference electrode and a Pt foil counter electrode. In this work, the onset potential is defined as the potential at which the current density is 10 % of that at the potential of -0.4 V.

To prepare the working electrode with catalyst, 6.8 mg of active material (e.g. EPC or A-EPC or Pt/C) was dispersed in a mixture solution containing 500 µL of DI water and 120 µL of 5 wt.% Nafion solution. It was then sonicated for at least 30 minutes to ensure the formation of a homogenous ink. Next, the prepared ink was carefully drop-casted onto the GC and dried naturally in air at room temperature.

The electron transfer number (*n*) per O₂ molecule in the ORR was calculated using the slopes of the linear best fit lines based on the Koutecky-Levich (KL) equations as bellows:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B \omega^{1/2}} + \frac{1}{J_K} \text{ ---- (1)}$$

$$B = 0.62 n F C_0 (D_0)^{2/3} \nu^{(-1/6)} \text{ ---- (2)}$$

$$J_k = n F k C_0 \text{ ---- (3)}$$

where *J* is the measured current density, *J_k* and *J_L* are the kinetic limiting and diffusion limiting current densities respectively, *ω* is the angular velocity, *F* is Faraday constant, *C₀* is the bulk concentration of O₂, *D₀* is the diffusion coefficient of O₂, *ν* is the kinematic viscosity of the electrolyte and *k* is the electron-transfer rate constant.^{4, 5}

5. Zn-Air battery assembly and tests

ZnABs were assembled with a home-made Zn-Air cell⁵ using the air cathode with A-EPC-900 or a commercial Pt/C (20% Pt) as the catalyst. The battery performance was evaluated at ambient air conditions without introducing additional O₂ sources⁶ (e.g. the oxygen supplied only from environment). Polished zinc plate was used as the anode, and 6 M KOH (containing 0.2 M ZnCl₂ to facilitate the reversible Zn electrochemical reactions by forming zincate) was used as the electrolyte. The current density used for battery test was normalized by geometric surface area of the catalyst film.

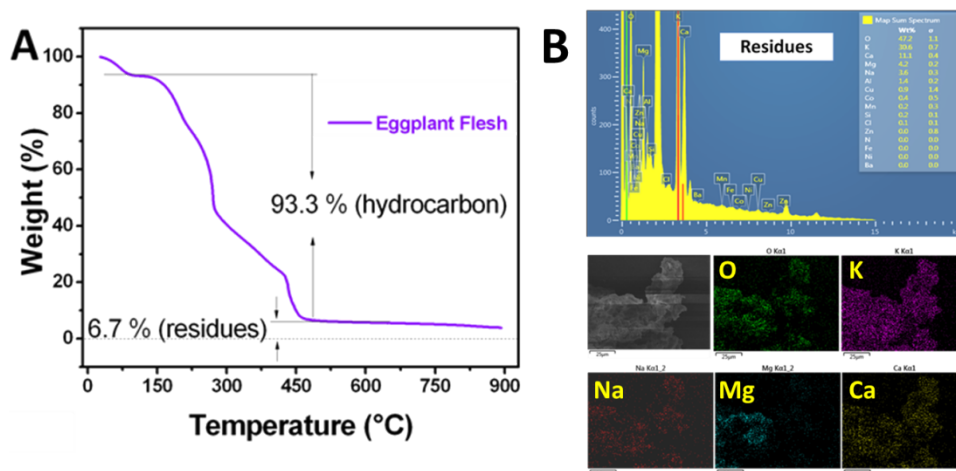


Fig. S1 A) A typical TGA curve of eggplant flesh measured in air atmosphere from 30°C to 900°C at a heating rate of 10°C per minute. B) EDX spectrum and SEM image and corresponding elemental mappings of eggplant flesh residual after TGA test. The results show that O, K, Na, Mg and Ca species are homogeneously distributed across the sample, and no obvious N and Cl signals were detected.

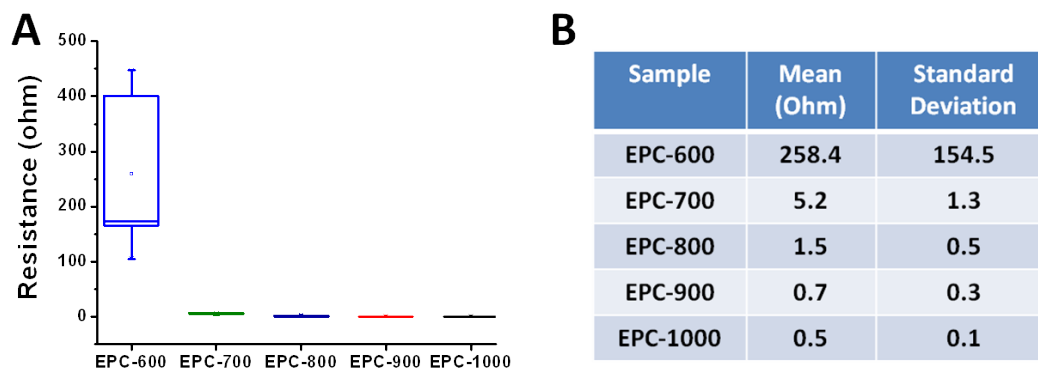


Fig. S2 Relative Resistivity of EPCs. A) Box Plot of the resistance of EPC-600, EPC-700, EPC-800, EPC-900, EPC-1000 measured using aforementioned method. B) A summary table derived from (A) showing the average resistance and the standard deviation of EPCs. From the results it can be concluded that the EPC-900 has a comparable resistance to that of EPC-1000, which is significantly lower (means higher conductivity) than that those EPCs obtained at lower temperatures.

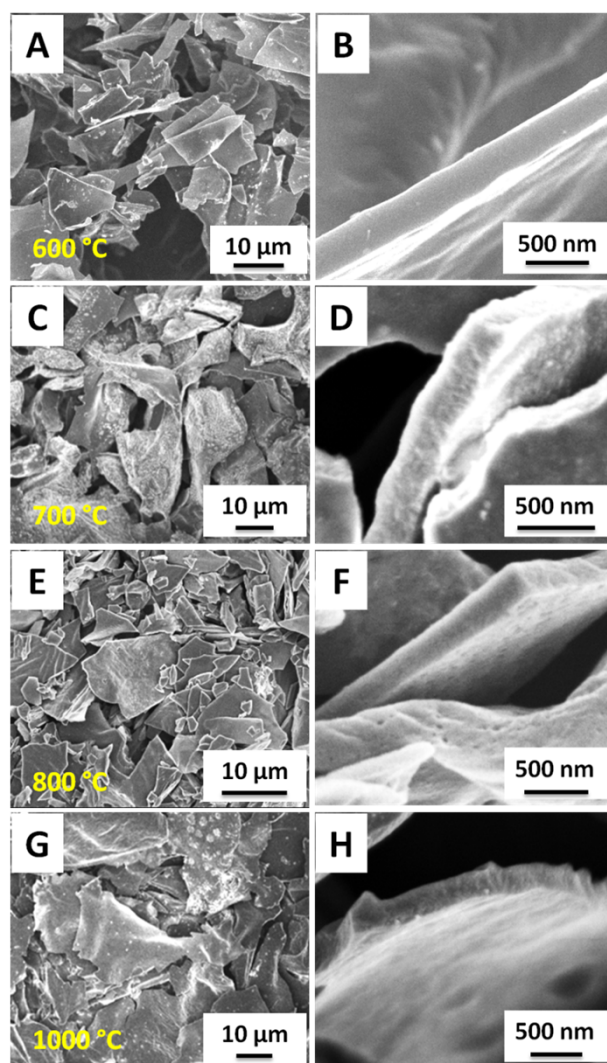


Fig. S3 SEM images of eggplant carbons produced at different temperatures. (A) and (B) EPC-600, (C) and (D) EPC-700, (E) and (F) EPC-800, (G) and (H) EPC-1000 produced at 600, 700, 800 and 1000°C, respectively.

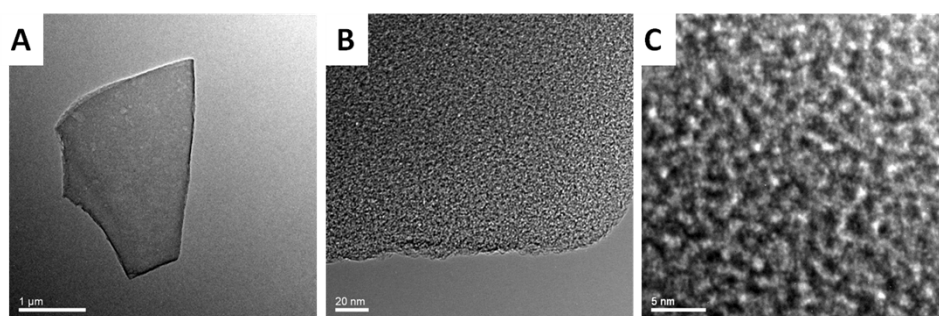


Fig. S4 Typical TEM images of A-EPC-900 at different magnifications.

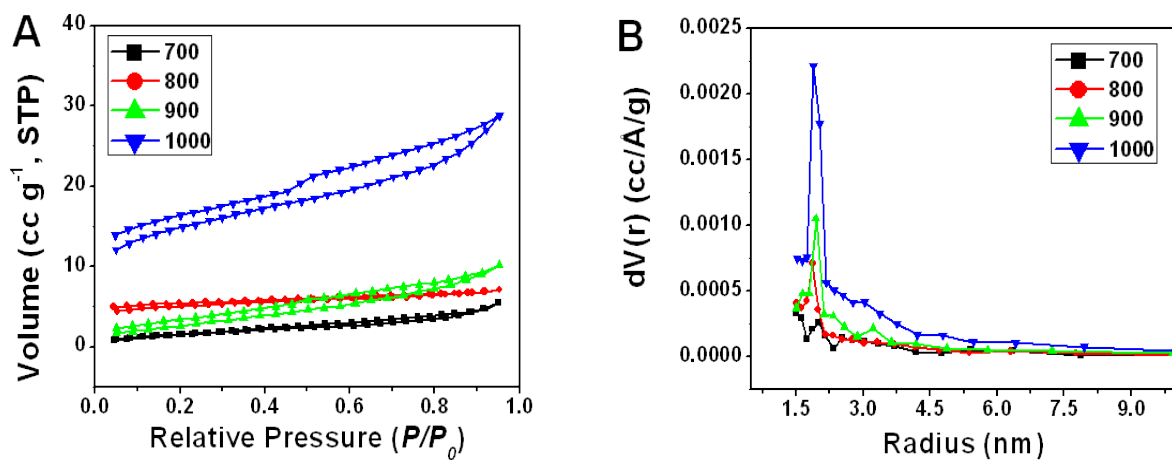


Fig. S5 N₂ adsorption-desorption isotherms (A) and pore size distributions (B) of EPC-700(black), EPC-800(red), EPC-900(green) and EPC-1000 (blue), respectively.

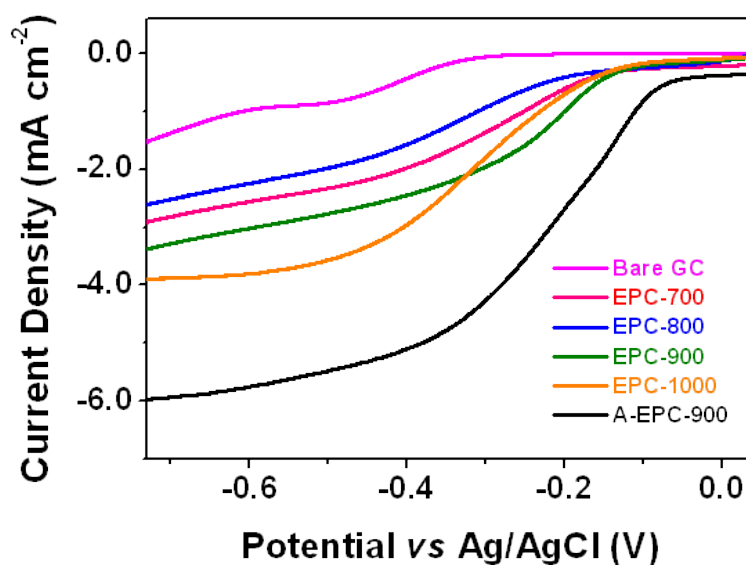


Fig. S6 Comparison of RDE polarization curves of EPC-Ts in O₂-saturated KOH at 1600 rpm.

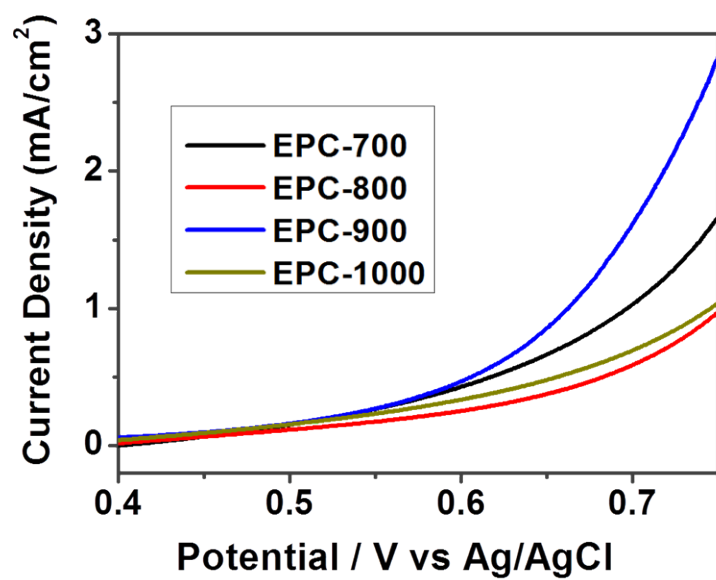


Fig. S7 Comparison of OER RDE polarization curves of EPC-Ts in 0.1 M KOH.

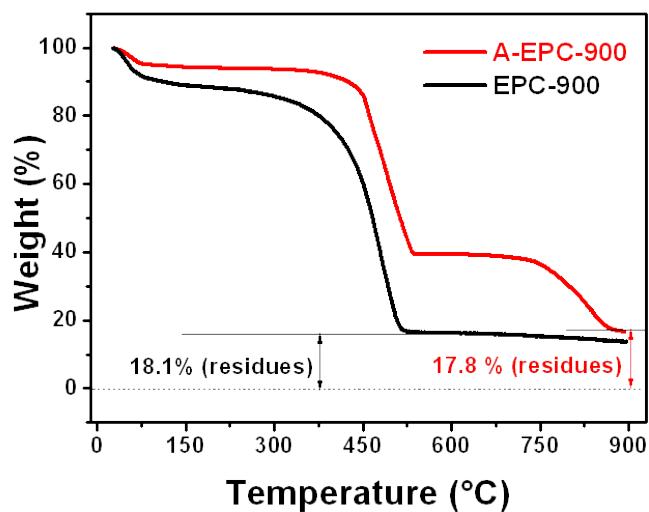


Fig. S8 TGA curves of EPC-900 and A-EPC-900 measured in air atmosphere from 30°C to 900°C at a heating rate of 10°C per minute. The residues were about 18.1 and 17.8 wt. % of the total weight (exclude water) of EPC-900 and AEPC-900, respectively.

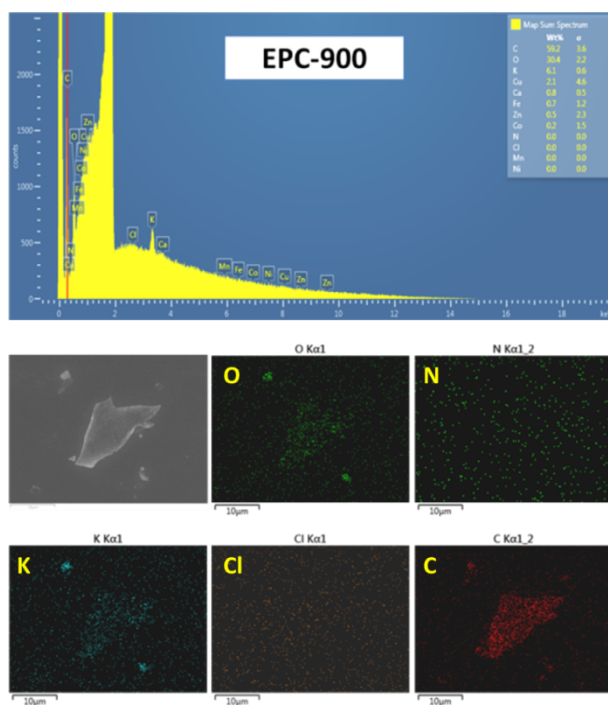


Fig. S9 A) EDX spectrum of the EPC-900, SEM image of a representative individual EPC-900 sheet and the corresponding elemental mapping for O, N, K, Cl and C of the same EPC-900 sheet.

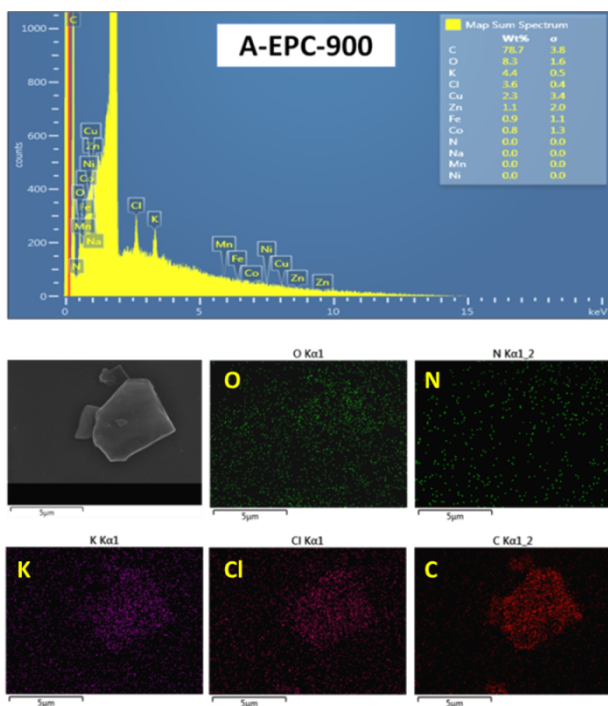


Fig. S10 A) EDX spectrum of the A-EPC-900, SEM image of a representative individual A-EPC-900 sheet and the corresponding elemental mapping for O, N, K, Cl and C of the same A-EPC-900 sheet.

Table S1 Summary of elemental content in EPC-900 and A-EPC-900 based on EDX tests.

Sample	O (wt%)	N (wt%)	K (wt%)	Cl (wt%)	Ca (wt%)	C (wt%)	O/C Weight ratio
EPC-900	30.4	---	6.1	---	0.8	59.2	0.51
A-EPC-900	8.3	---	4.4	3.6	---	78.7	0.11

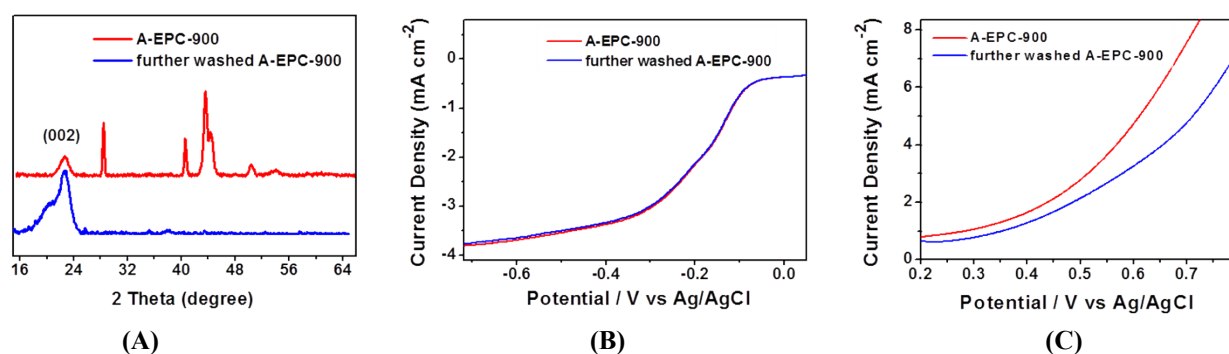


Fig. S11 A) XRD spectrum of A-EPC-900 before (red) and after (blue) additional washing steps. B) The corresponding LSV data for ORR activity. C) The corresponding LSV data for OER activity. The scan rate was 50 mV S⁻¹ with electrode rotating speed of 625 rpm.

Table S2 Summary of BET surface area, pore size, pore volume, ORR onset potential, ORR current density at given potentials of the obtained EPCs and A-EPC-900. The electrocatalytic performance of Pt/C at given potentials are also listed for comparison.

Sample	BET surface area (m ² g ⁻¹)	Pore radius D _{v(r)} (Å)	Pore volume (cm ³ g ⁻¹)	ORR Onset potential (mV)	Current density @ -0.35V** (mA cm ⁻²)	Current density @ -0.40 V** (mA cm ⁻²)	Current density @ -0.65V** (mA cm ⁻²)
EPC-900	9.5	19.4	0.011	-116	-2.23	-2.45	0.85
A-EPC-900	1051.5	19.2	0.076	-69	-4.78	-5.10	6.09
EPC-700	6.3	15.1	0.007	-96	-1.70	-1.97	0.65
EPC-800	14.2	18.6	0.009	-121	-1.26	-1.56	0.37
EPC-1000	44.6	20.1	0.022	-141	-2.42	-2.96	0.47
Pt/C	N.A.	N.A.	N.A.	-22	-4.67	-4.74	0.41

**Potential vs Ag/AgCl

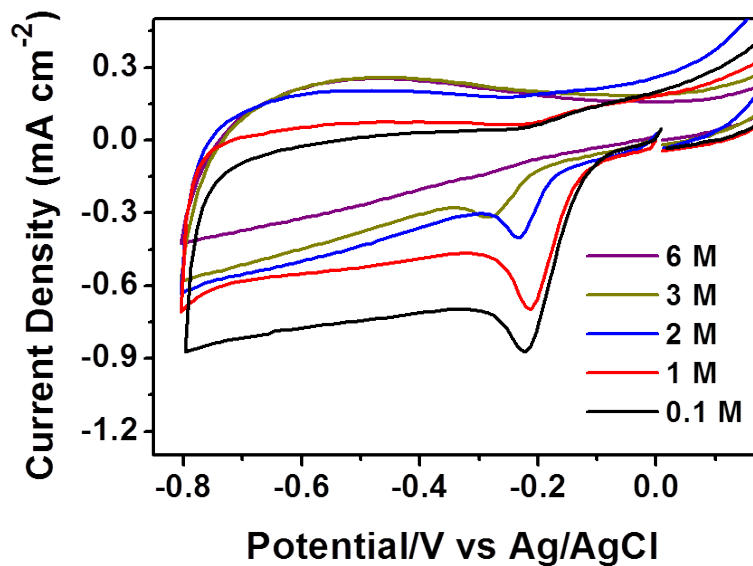


Fig. S12 CV curves of A-EPC-900 in different concentration O_2 - saturated KOH electrolytes.

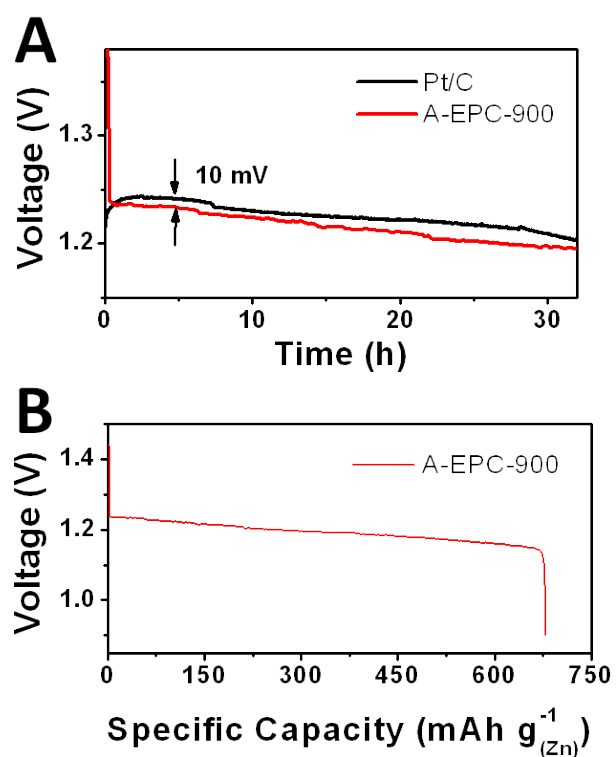


Fig. S13 A) Discharge curves (at $5\ mA\ cm^{-2}$) of the ZnABs using A-EPC-900 (red) and Pt/C (black) the catalysts, respectively. B) The typical deep discharge curve (at $5\ mA\ cm^{-2}$) and specific capacity of the ZnAB using A-EPC-900 as the catalyst.

References:

1. J. Wang and S. Kaskel, *Journal of Materials Chemistry*, 2012, **22**, 23710-23725.
2. Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach and R. S. Ruoff, *Science*, 2011, **332**, 1537-1541.
3. L. Qie, W. Chen, H. Xu, X. Xiong, Y. Jiang, F. Zou, X. Hu, Y. Xin, Z. Zhang and Y. Huang, *Energy & Environmental Science*, 2013, **6**, 2497-2504.
4. Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat Mater*, 2011, **10**, 780-786.
5. B. Li, X. Ge, F. W. T. Goh, T. S. A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu and Y. Zong, *Nanoscale* 2015, **7**, 1830-1838.
6. Y. Li, M. Gong, Y. Liang, J. Feng, J.-E. Kim, H. Wang, G. Hong, B. Zhang and H. Dai, *Nat Commun*, 2013, **4**, 1805.