Supporting Information

Al-MOF derived porous carbon modified Pt/C catalyst for constructing high-performance super fuel cell via ORR + EDLC parallel discharge mechanism

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Experimental

Chemicals

1,3,5-Benzenetricarboxylic acid ($C_9H_6O_6$, AR) was received from Tianjin Fuchen Chemical Reagent Limited, China. Aluminium nitrate ($Al(NO_3)_3 \cdot 9H_2O$, AR), ethanol (99.7%) and melamine ($C_3H_6N_6$, AR) was provided by Beijing Chemical Works, China. Polytetrafluoroethylene (PTFE, 60%) was purchased from Shanghai Micro-technology Co. Limited, China. All of the above chemicals were AR grade and utilized directly. Potassium hydroxide with high purity grade (KOH, 95 %) was supplied by Beijing Huarong Chemical Factory, China.

Electrochemical analysis

The Galvanostatic charge and discharge (GCD) tests and Cyclic voltammetry (CV) test were run on the battery test stations (CT3001A, LAND, Wuhan, China) and the Electrochemical Workstation (CHI760D, Chenhua, China Shanghai), respectively.

The specific capacitances of samples were calculated with the parameters from the GCD curve according to the following formula:

$$C_m = I \times \Delta t / (\Delta V \times m) \quad \text{(S1)}$$

Here, C_m represents the specific capacitance of the active sample per unit mass (F g^{-1}), *I* represents the current value during discharge (A), Δt represents the time spent in a discharge cycle (s), ΔV represents the voltage change window (V), and m represents the active sample mass in the electrode (g).

For the capacitance calculation, energy density and power density of the two EDLCs are calculated via the following formulas S2-S4.

$$Cs = I\ \Delta t / (\Delta V \times m_T) \quad (S2)$$

$$E = 0.5\ Cs \times (\Delta V)^2/3.6 \quad (S3)$$

$$P = 3600 \times E/\Delta t \quad (S4)$$

Here, C_s represents the SC of the symmetric supercapacitor (F g^{-1}), m_T represents the total mass of the active material in the electrode (g), E represents the energy density of a symmetric supercapacitor (Wh kg^{-1}) and P indicates the power density of a symmetric supercapacitor (W kg^{-1}).

Redox tests were completed in a three-electrode system by CHI760D at room temperature. The disc electrode (RDE, diameter 5.0 mm) was used as the working electrode, Hg/HgO as the reference electrode, a Pt wire (with a salt bridge) as the auxiliary electrode, and 0.1 M KOH as the electrolyte, which was continuously passed through N_2 or O_2 for 20 min to ensure nitrogen-saturated or oxygen-saturated atmospheres prior to the use of the electrolyte. In addition, the test potentials were all converted to relative reversible hydrogen RHE potentials according to the following formulas S5.

$$E_{RHE} = E_{Hg/HgO} + 0.0592 \times pH + 0.098\ V \quad (S5)$$

Linear linea voltammetry (LSV) tests were performed at a scanning speed of 5 mV s^{-1}, speeds of 400-2500 rpm, and voltage intervals of 1.2-0.2 V. The LSV polarisation curves of the catalysts were obtained by subtracting the current of the N_2 atmosphere background from the LSV curves of the O_2 atmosphere. The data of onset potential (E_0), half-wave potential ($E_{1/2}$) can be read from the LSV obtained at 1600 rpm. In addition, the number of transferred electrons was obtained by fitting the Koutecky-Levich (K-L) equation (S5 and S6) to the limiting current density values obtained at different rotational speeds in the kinetic region.

$$j^{-1} = j_L^{-1} + j_K^{-1} = B^{-1} \times \omega^{-0.5} + j_K^{-1} \quad (S6)$$

$$B = 0.62\ n\ f\ C_0 D_0^{2/3} v^{-1/6} \quad (S7)$$

Zn-Air fuel cell testing was performed according to the following procedure. 5 mg of catalyst was weighed and dispersed in a mixture of 20 μL Nafion, 730 μL isopropanol, and 250 μL deionised water, and then sonicated for 40 min until the catalyst formed a homogeneous slurry. The 800 μL slurry was applied dropwise onto a 2 × 2 cm^2 carbon paper with a diffusion layer (loading capacity of about 1.0 mg cm^{-2}), and then left to dry naturally. The catalyst electrode was used as the cathode, the Zn plate as the anode, and the electrolyte was a mixed solution of 0.2 M ZnO and 6 M KOH.

Zn-Air cell open-circuit voltages were obtained using an electrochemical workstation for testing, and LSV curves were obtained by sweeping from 1.4 V to 0.4 V at a scan rate of 5 mV s^{-1}.

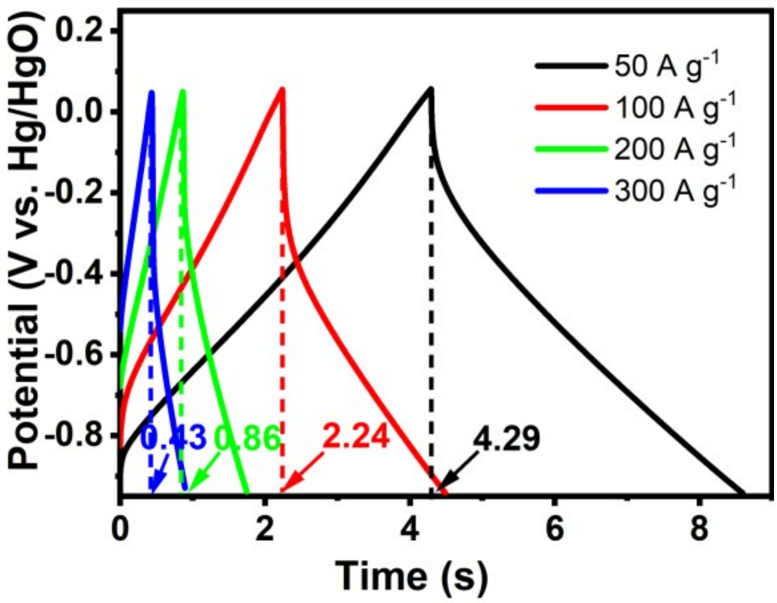

Figure S1. GCD curves at high current densities (50-300 A g^{-1}) of BTCC-2.

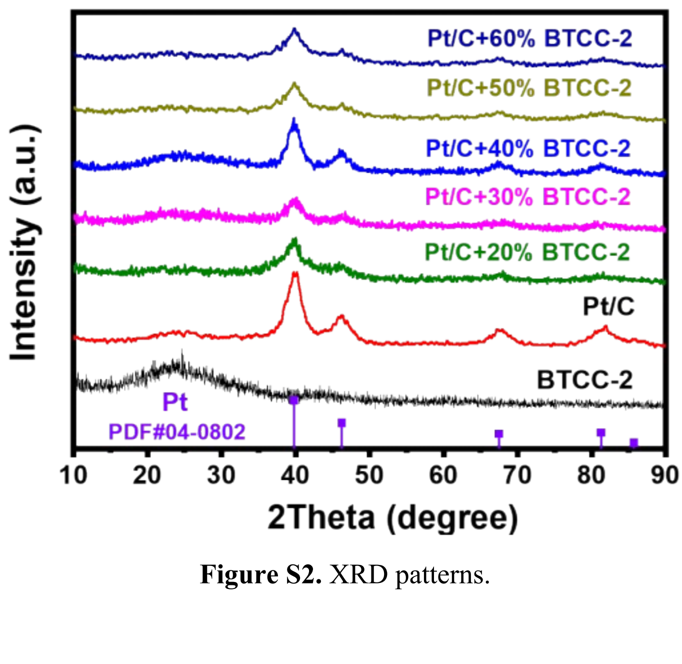

Figure S2. XRD patterns.

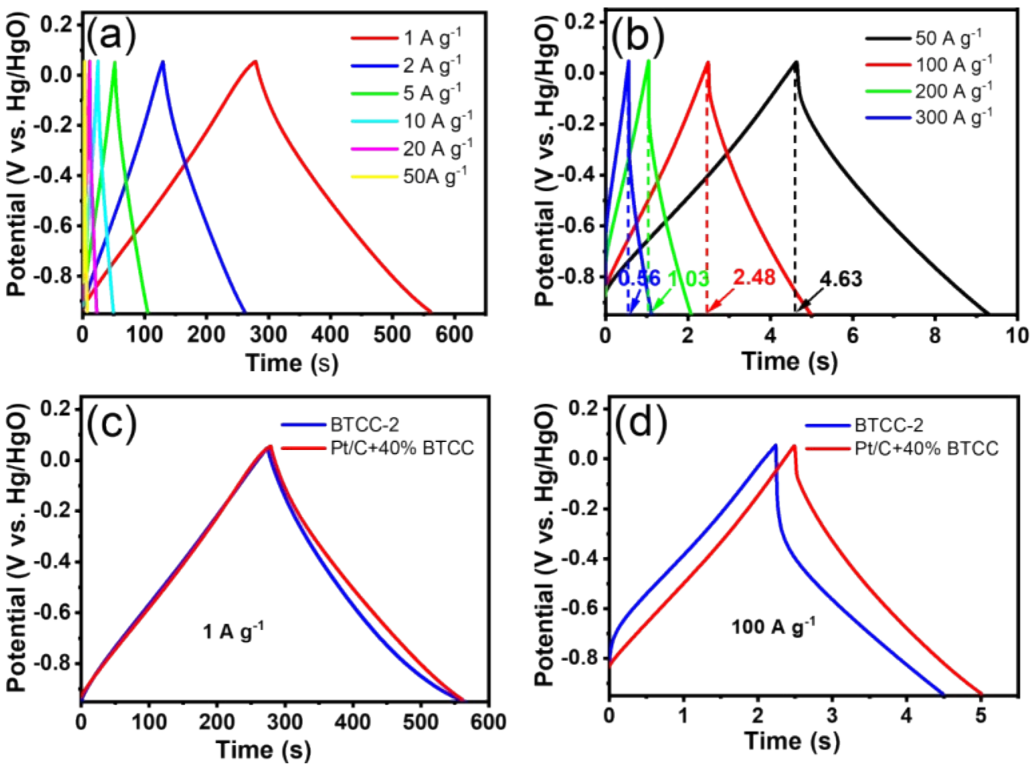

Figure S3. GCD curves: BTCC-2 electrode at 1-300 A g^{-1} (a, b); BTCC-2 and Pt/C+40% BTCC at (c) 1 A g^{-1} and (d) 100 A g^{-1}.

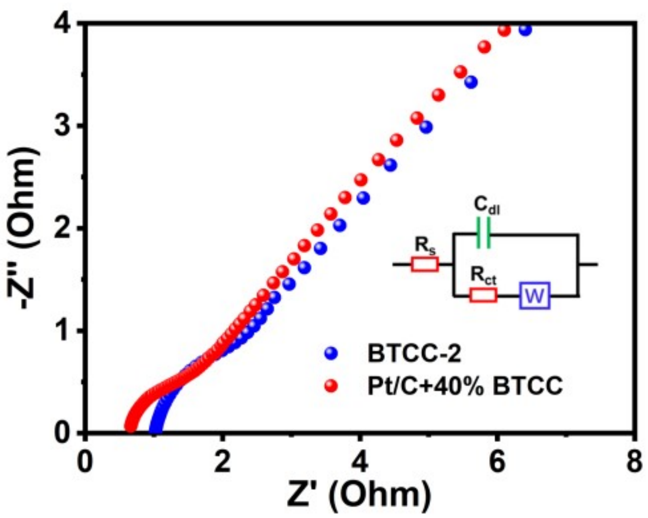

Figure S4. Nyquist plots of BTCC-2 and Pt/C+40% BTCC electrode, and the inset is its equivalent electrical circuit.

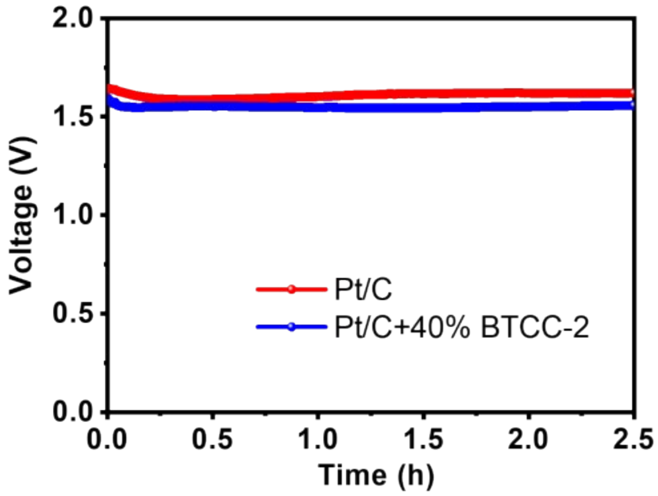

Figure S5. Open circuit voltage test of Zn-Air battery.

Table S1. The specific information of the instruments used in this work.

Technique	Model	Company/Country	Condition
Field-Emission Scanning Electron Microscopy (FSEM)	SUPRA 55 SAPPHIRE	Carl Zeiss/Germany	Operating voltage of 20 kV
High-Resolution Transmission Electron Microscopy (HR-TEM)	H-800 JEOL JEM-2100F	JEOL/Japan	Operating volage of 300.0 kV.
X-ray Diffraction (XRD)	XRD-6000	Shimadzu/Japan	2θ range from 5 to 80° at scan rate 10° /min (40 kV, 200 mA)
Brunauer Emmett Teller (BET)	Belsorp-max Micromeritics ASAP2020H	Micromeritics/USA	
Raman Spectroscopy	Renishaw inVia Reflex	Renishaw/UK	Scan rate from 500 to 2500 cm^{-1} at wavelength $\lambda = 514$ nm
X-ray Photoelctron Spectroscopy (XPS)	ESCALAB 250	ThermoFisher Scientific, USA	Operating voltage of 200 eV for the survey and 30 eV for high resolution at Al K radiation

Table S2. Electrochemical data of catalysts.

PC	$\boldsymbol{J_0}$ (mA cm^{-2})	$\boldsymbol{v_{1/2}}$ (V vs. RHE)	$\boldsymbol{v_0}$ (V vs. RHE)
Pt/C	-5.096	0.835	0.998
Pt/C+20% BTCC-2	-5.096	0.826	1.002
Pt/C+30% BTCC-2	-5.189	0.830	1.020
Pt/C+40% BTCC-2	-5.236	0.833	1.021
Pt/C+50% BTCC-2	-5.084	0.829	1.040
Pt/C+60% BTCC-2	-5.026	0.827	1.022