Electronic Supplementary Information

Boosting Potassium-ion Storage Performance of Carbon Anode by Chemically Regulating Oxygen-Containing Species

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Experimental methods

1.1 Synthesis of oxidizing-acid treated melamine foam carbons

Commercial melamine foams were firstly carbonized at 800 °C in N_2 flow atmosphere for 1 h, then the obtained melamine foam carbons were fully immersed in concentrated nitric and sulfuric acid mixed solution (1:3 in volume) for a certain time. After being washed with distilled water and ethanol for several times, the final products were dried at 80 °C. For convenience, the oxidizing-acid treated melamine foam carbons are labelled as OMFC-0, OMFC-30, OMFC-60 on the basis of soaking time (0, 30, and 60 min).

1.2 Characterization

The crystalline phases were determined by powder X-ray diffraction (XRD) using a Rigaku SmartLab 9 X-ray diffractometer (Cu Ka radiation). Raman spectra were obtained on a Monovista CRS500 Laser confocal Raman spectrometer (λ_{ex} = 532 nm). The morphologies were characterized by scanning electron microscopy (SEM, Zeiss Supra-40) and transmission electron microscopy (TEM, FEI Talos F200x). Element distribution mapping was carried out using an energy dispersive X-ray detector equipped on FEI Talos F200x. X-ray photoelectron spectroscopy (XPS) was studied on a Thermo Scientific ESCLAB 250Xi spectrometer.

1.3 Electrochemical measurements

The electrochemical performances of OMFCs as anode materials in PIBs were evaluated using CR2025 coin-type half cells. The working electrodes were prepared by mixing the active materials (70 wt%), carbon black (20 wt%) and polyvinylidene fluoride binder (10 wt%) to form a homogeneous slurry. N-methyl-2-pyrrolidone was employed to adjust the viscosity. The obtained slurry was coated on a copper foil and dried in a vacuum oven at 60 °C overnight to remove the solvent. The electrodes were punched into circular pieces (d = 12 mm) for coin-cell testing. The cell assembly was performed in an Ar-filled glove box (Mikrouna) with potassium metal as a counter/reference electrode, glass fiber (Whatman® GF/D) membrane as a separator and 0.8 M KPF_6 in ethylene carbonate (EC)-diethyl carbonate (DEC) (1:1 in volume) as an electrolyte. Galvanostatic charge-discharge (GCD) tests were performed on a LANHE CT2001A in the voltage window of 0.01–3.0 V (*vs.* K^+/K). Cyclic voltammetry (CV) measurements were conducted on a CHI 760E electrochemical workstation.

1.4 Calculation method

The K-adsorption on different carbon substrates were theoretically investigated by the density

functional theory (DFT) calculations. All calculations were performed using the PWSCF codes contained in the Quantum ESPRESSO package.[1] In all models, the vacuum layer was set to 15 Å, which was large enough such that the two successive slabs did not interact significantly. The generalized gradient approximation (GGA)[2] with the functional of Perdew–Burke–Ernzerhof (PBE) [3] was employed to describe the electron exchange-correlation interactions. An ultrasoft pseudopotential and a kinetic energy cutoff of 40 Ry were used to expand the electronic wave functions in the plane-wave basis. The first Brillouin zone was sampled using 4x4x1 Monkhorst–Pack k-points mesh. The K-adsorption energy on substrate was calculated according to the equation of $E_{ads} = E_{sub-K} - (E_{sub} + E_K)$, where E_{sub-K} is the total energy of the substrate with K adsorbed on it, E_{sub} is the total energy of the substrate, and E_K is the total energy of an isolated K adatom. According to this definition, a more negative binding energy implies a stronger bonding between K and substrate.

Reference：

[1] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S. Fabris, G. Fratesi, S.d. Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, *J. Phys.: Condens. Matter*, 2009, **21**, 395502.

[2] J.P. Perdew, Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244–13249.

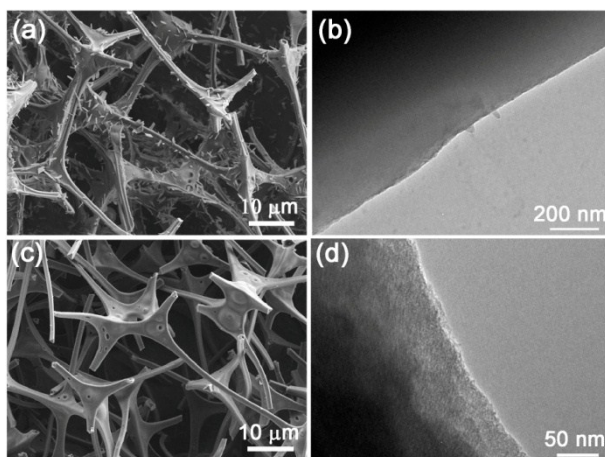[3] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, *1996,* **77**, 3865–3868.

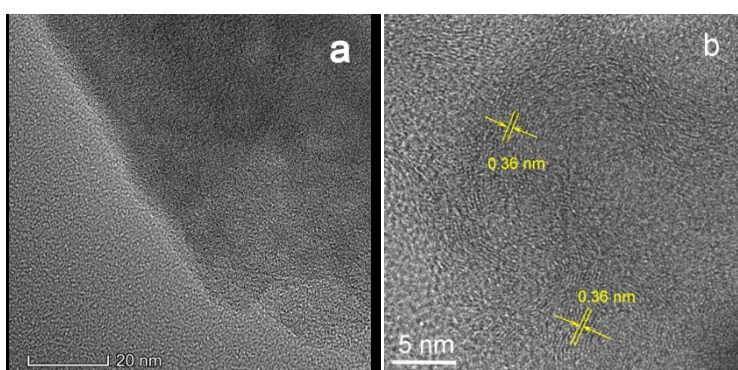**Fig. S1** SEM and TEM images of (a,b) OMFC-0 and (c,d) OMFC-60.

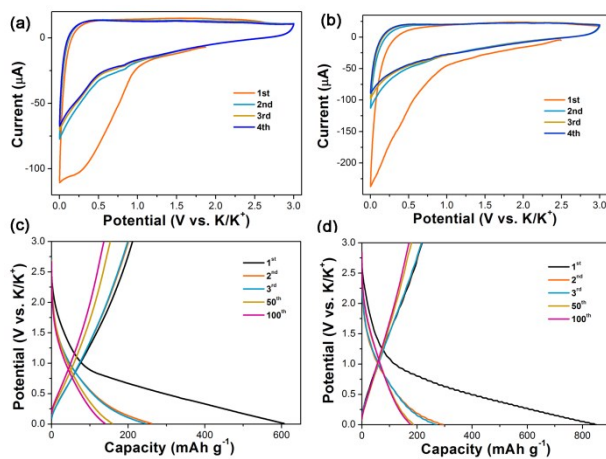

Fig. S2 HRTEM images of OMFC-30.

Fig. S3 CVs of (a) OMFC-0 and (b) OMFC-60 at 0.1 mV s^{-1}. The 1st, 2nd, 3rd, 50th, and 100th

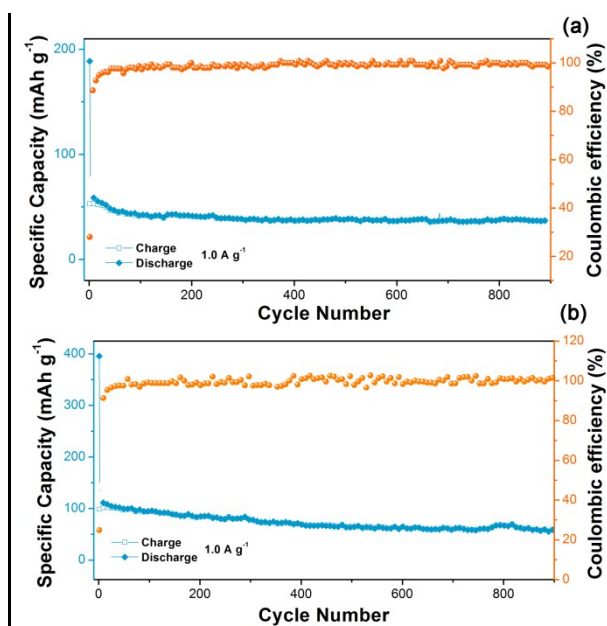charge-discharge profiles of (c) OMFC-0 and (d) OMFC-60 at 50 mA g^{-1}.

Fig. S4 Long-term cycle stability and Coulombic efficiency of (a) OMFC-0 and (b) OMFC-60 at 1.0 A g^{-1}.
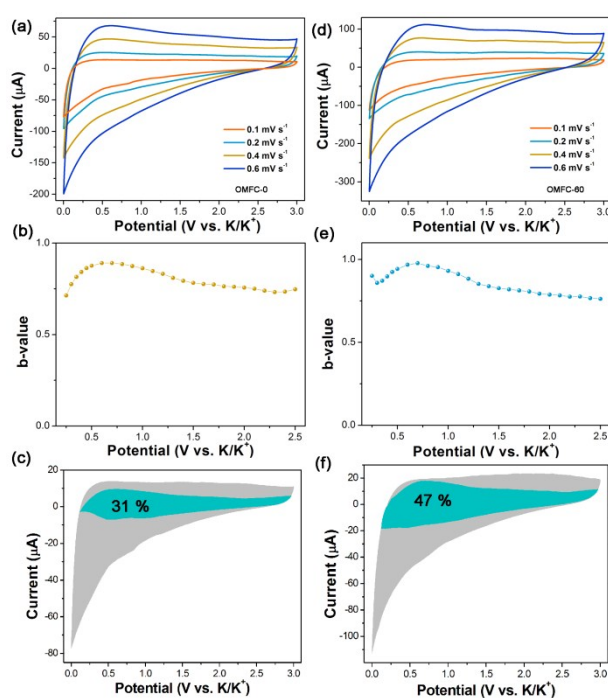

Fig. S5 CV curves of (a) OMFC-0 and (d) OMFC-60 at different scan rates. The calculated *b*-value of (b) OMFC-0 and (e) OMFC-60. Capacitive contribution ratio of (c) OMFC-0 and (f) OMFC-60 at 0.1 mV s^{-1}.

Table S1 Relative atomic contents of oxygen species obtained by fitting O1s XPS spectra

O species	OMFC-0 at%	OMFC-30 at%	OMFC-60 at%
O-I	4.7	5.3	5.7
O-II	5.0	3.6	3.5
O-III	0.2	0.6	1.6
O-IV	3.9	1.0	1.0
Total	13.8	10.5	11.8
O-I + O-III	4.9	5.9	7.3
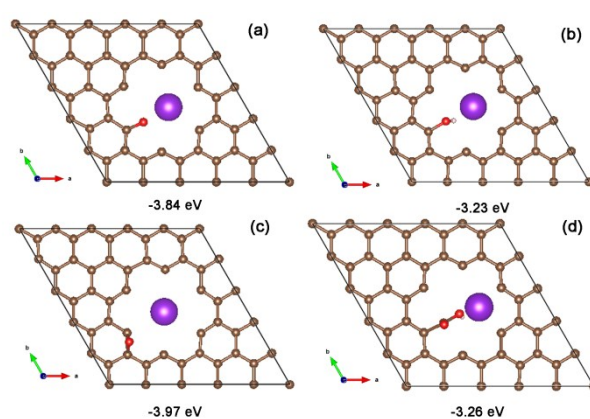
Fig. S6 Top views and K-adsorption energies on carbon substrates containing (a) quinone-type, (b) phenol-type, (c) ether-type, and (d) carboxyl-type oxygen species. Brown balls represent carbon atoms, red balls represent oxygen atoms, white balls represent hydrogen, and purple balls represent potassium atoms.
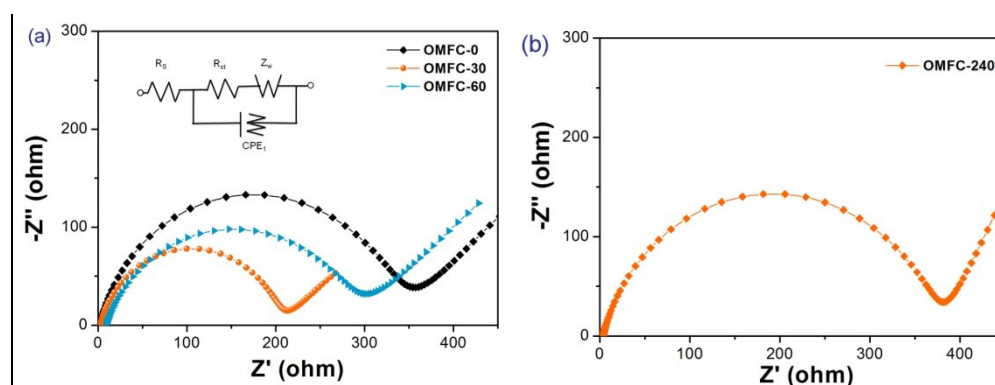
Fig. S7 (a) The Nyquist plots of OMFC-0, OMFC-30, and OMFC-60 electrodes. The inset shows the corresponding equivalent electrical circuit. (b) The Nyquist plots of OMFC-240.