Supplementary information

Host Potassiophilicity Strategy for Unprecedentedly Stable and Safe K Metal Batteries

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Experimental

1. Synthesis

Typically, the carbon cloth (W0S1011 CeTech) was cleaned with ethanol and deionized water under ultrasonic treatment and then dried in a vacuum oven at 80 °C for 48 h. The clean carbon cloth was then transferred to a muffle furnace for heat treatment at 450 °C in the air for 2 h with a heating rate of 5 °C min⁻¹. After the annealing treatment, the obtained carbon cloth was specified as O-CC. For comparison, carbon cloth with a similar method except for the heat treatment in the air was also obtained, which is defined as P-CC. For the full cell, the cathode material was obtained by annealing the pristine PTCDA (Sigma-Aldrich) at 450 °C for 4 h under Ar with a heating rate of 5 °C min⁻¹.

For the electrochemical testing, O-CC was contacted with molten metal K at 90 °C and then the metal K will be adsorbed on the O-CC electrode, which is named as O-CC@K. Compared to the electrochemical deposition methods, the combination of O-CC with K metal through the adsorption of molten K is a simple and reproducible process, making it more competitive for future large-scale applications. Therefore, we utilized the O-CC obtained the potassiophilicity strategy and combined it with molten K for testing the electrochemical performance. For the P-CC@K electrode, it was obtained by the flattening of metal K on the surface of P-CC. The Cu@K could be obtained by the flattening of metal K on the surface of Cu foil. For the PTCDA electrode, the PTCDA cathode, super P, and polyvinylidene fluoride with a ratio of 8:1:1 were mixed under grinding. After that, moderate 1-methyl-2-pyrrolidone was added to the mixed powder to form a homogeneous sizing. Subsequently, the homogeneous sizing was coated on the Al-C foil by a knife coating method. After drying, the obtained electrode was then cut into a disc with a diameter of 16 mm for full cells. The mass loading of PTCDA cathode is about 2 mg cm⁻². In K metal batteries, our metal anode can exhibit dendrite-free characteristics, allowing an excess of K to ensure stable battery operation. Therefore, we can use an excess of metal K in anode for the battery operation in O-CC@K//PTCDA full cell.

2. Characterization

The morphologies of the electrode were obtained by scanning electron microscope (SEM, FEI), transmission electron microscopy (TEM, TEOL), and optical microscope (Leica). The structures and surface properties were measured by X-ray diffraction (XRD, D8 Rigaku-9000), Raman spectrometer (Horiba T6400), and X-ray photoelectron spectroscopies (XPS, Thermo Scientific). For the in situ visualization observation, we used a portable optical microscope and cooperated with an electrochemical reaction cell to realize the in situ observation of the electrode.

3. Electrochemical measurement

The electrochemical performances of all the samples were tested with coin-type cells (CR2032), which were assembled in an argon-filled (O₂<0.1 ppm, H₂O<0.1 ppm) glove box (Etelus Lab2000). 5 M potassium bis(fluorosulfonyl)imide dissolve into dimethoxyethane (DME) was used as electrolyte. The symmetric cell was assembled by the same electrode at both ends of the cell. The half cell of Cu//P-CC@K and Cu//O-CC@K was assembled with one piece of Cu foil as the counter electrode and a work electrode of P-CC@K or O-CC@K. The full cell was assembled with one piece of PTCDA as the cathode and a P-CC@K or O-CC@K as the anode. The GCD curves were tested by the Neware battery test system (Neware BTS-4000). EIS and nucleation overpotential of the symmetric cells were recorded by Chenhua electrochemical workstation. A TENG system was introduced to charge for the fabricated O-CC@K//PTCDA full cell.

4. DFT computational methods

The density functional theory (DFT) computations were performed using the Vienna ab initio simulation package (VASP). The Perdew-Becke-Ernzerhof (PBE) functional and projector augmented wave (PAW) schemes were adopted for geometric optimizations. An energy cutoff of 500 eV for the plane wave basis set was used for the structure optimization and static self-consistent. All structures were optimized with a convergence criterion of 1×10^{-4} eV for the energy and 0.05 eV Å⁻¹ for the forces. A $3 \times 3 \times 1$ k-point mesh was used for the Brillouin zone sampling.

5. FEA computational methods

The tertiary current distribution, and the deformed geometry interface models were conducted on finite element method analysis. The mesh was triangular-based ultra-fine mesh which was controlled by the physical field. The electric field migration satisfied the Nernst-Einstein relation and the kinetics satisfied the Butler-Volmer equation. The average current intensity was set to 4 mA cm⁻² and the initial electrolyte concentration was 5 M. For P-CC and O-CC, the initial exchange current densities were set uneven and even, respectively. In the simulation process, the total current density and K metal deposition time used by two anodes were consistent.





Fig S1 Photographs of (a) P-CC and (b) O-CC.



Fig S2 Elemental mapping images of (a) P-CC and (b) O-CC.



Fig S3 XPS survey of P-CC and O-CC.



Fig S4 (a) FTIR and (b) enlarged FTIR of P-CC and O-CC.



Fig S5 The process of adsorbing molten potassium metal of (a) P-CC and (b) O-CC.



Fig S6 The digital microscope image of (a) P-CC@K and (b) O-CC@K; the SEM image of

(c) P-CC@K and (d) O-CC@K.



Fig S7 The process of adsorbing molten potassium metal of carbon felt.



Fig S8 The process of adsorbing molten potassium metal of carbon paper.



Fig S9 The initial galvanostatic cycling performance of Cu@K, P-CC@K, and O-CC@K composite anodes in symmetric cells at 0.5 mA cm⁻²~0.5 mAh cm⁻² in 500 h.



Fig S10 The EIS spectra of (a) O-CC@K composite anodes in symmetric cells at 0.5 mA cm⁻²~0.5 mAh cm⁻² after different times ;(b) P-CC@K composite anodes and bare K symmetric cells.

It is observed that the O-CC exhibits higher impedance compared to P-CC before cycle (Fig. S10). We suggest that the introduction of epoxy groups leads to reduced electronic conductivity. However, after cycling, the interface behavior of electron migration is effectively improved, resulting in a significant reduction in impedance.



Fig S11 The partial galvanostatic cycling performance of P-CC@K and O-CC@K composite anodes in symmetric at different current densities with areal capacities of 0.5 mAh cm⁻².



Fig S12 (a) Corresponding curve of potential specific capacity profiles of O-CC//K from Fig 2e; (b) CEs curves for O-CC//K and P-CC//K asymmetric cells at 0.5 mA cm⁻²/1 mAh cm⁻² and (c) corresponding curve of potential specific capacity profiles; (d) CEs curves for Cu//O-CC@K and Cu//P-CC@K asymmetric cells at 0.5 mA cm⁻²/0.5 mAh cm⁻² and corresponding curve of potential specific capacity profiles of (e) Cu//O-CC@K and (f) Cu//P-CC@K.



Fig S13 The Raman spectra of the primary electrolyte, the electrolyte filtered by P-CC

and O-CC.



Fig S14 The adsorption energy (E_a) of P-CC and O-CC with DME electrolyte.



Fig S15 Electrolyte immersion test of (a) P-CC and (b) O-CC.



Fig S16 XPS survey of SEI layers for P-CC and O-CC after 1 cycle.



Fig S17 XPS spectra of SEI layers for (a-b) P-CC and (c-d) O-CC after 1 cycle.



Fig S18 The photograph of in-situ optical microscope observation device.



Fig S19 Schematic of O-CC@K//PTCDA full batteries.



Fig S20 CEs of O-CNF@K//PTCDA full cell at the current density of (a) 20 mA g^{-1} and (b) 100 mA g^{-1} .



Fig S21 GCD curves of O-CNF@K//PTCDA full cell at 20 mA $\rm g^{-1}.$



Fig S22 GCD curves of O-CNF@K//PTCDA full cell at 100 mA g⁻¹.



Fig S23 Photograph of LED bulbs (6 V 1 W) and O-CC@K//PTCDA batteries.

Table S1 Galvanostatic cycling performance of all the host materials for K metal anodein symmetric cells.

Host	Combination	Cell	Current	Cycle	Over	Ref
	method	construction	capacity	life	poten	
			density	(h)	-tial	
			(mA		(mV)	
			cm2@mAh cm-2)			
Oxygen-modified	Adsorption (90°C/0.	symmetric	0.5@0.5	5500	~30	This
carbon cloth (O-CC)	7s)		1@0.5	3500	~50	wor
Carbonized	Adsorption(100°C/2	symmetric	0.5@0.5	1400	45	[S1]
Bacterial Cellulose	s)		1@1	1200	55	
(CBC)						
Co–CNFs	Adsorption(100°C/1	symmetric	0.5@0.5	1300	~100	[S2]
	.5s)		2@1	500	~100	
MSCNF	Adsorption(150°C/1	symmetric	1@1	800	~100	[S3]
	s)					
Ag-CC	Electrodeposition	symmetric	0.5@0.5	700	~200	[S4]
Carbon-cloth-based	Adsorption(80°C/4s	symmetric	1@1	350	~200	[S5]
potassium)					
composite anode						
(K@CC)						
Graphite	facile mixing and	symmetric	0.4@0.4	700	~200	[S6]
intercalation	stirring process					
compound of K (K-						
GIC)						
DN-MXene/CNT	Adsorption(80°C/10	symmetric	0.5@0.5	>300	~150	[S7]
	Os)					
rGO@3D-Cu	Adsorption(300°C/6	symmetric	0.5@0.5	~200	~45	[S8]
	s)					
Sn@3D-K	Electrodeposition	symmetric	0.2@1	~50	9	[S9]

			1@1	~50	31	
ACM	Adsorption(100°C)	symmetric	1@1	230	~100	[S10]
Al@Al	Electrodeposition	asymmetric	0.5@0.5	440		[S11]
Al@G	Rolling	asymmetric	0.5@0.5	1000		[S12]
Cu3Pt–Cu	Punch	symmetric	0.5@1	300	~500	[S13]
Pd/Cu foam	Punch	symmetric	1@1	130	~500	[S14]
SA-Co@HC	Adsorption	symmetric	0.5@0.5	2500	~200	[S15]
Cu@SKS	Electrodeposition	symmetric	1@1	900	66	[S16]
hoCNT	Electrodeposition	asymmetric	0.5@4	1000		[S17]
Bi ₈₀ /NrGO	Adsorption	Symmetric	0.2@0.1	3000	~50	[S18]
OPCMs	Electrodeposition	Symmetric	1@1	800	~40	[S19]
rGCA	Adsorption	Symmetric	0.5@0.5	400	~400	[S20]
NiCo@NOGC	Electrodeposition	Symmetric	3@0.5	~190	310	[S21]
RGO	Fuse-mixing	Symmetric	0.5@0.5	500	50	[S22]

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