Supporting Information

Hollow Carbon Bowls with Cobalt Single-Atom Sites Enable Fast and Reversible Potassium Storage

Meng Zhang, Zizhu Fang, Zhaoyang Gao, Zhigang Pan, Huihua Min, Hsiang-Jung Chen, Han-Yi Chen, Hao Yang, Jin Wang**

M. Zhang, Z.Z. Fang, Z.Y. Gao, Prof. Z.G. Pan, Prof. H. Yang, Prof. J. Wang

College of Materials Science and Engineering, Nanjing Tech University, Nanjing 211816, PR China

E–mail: msejwang@njtech.edu.cn (Prof. J. Wang); mse_yanghao@njtech.edu.cn (Prof. H. Yang)

Prof. H. Min

Electron Microscope Lab, Nanjing Forestry University, Nanjing 210037, Jiangsu, PR China

Dr. H.J. Chen, Prof. H.Y. Chen

Department of Materials Science and Engineering, National Tsing Hua University, 101, Sec. 2, Kuang-Fu Road, Hsinchu 300044, Taiwan

1. Experimental section

1.1 Synthesis of SiO_2@SiO_2/PDA

In a typical synthesis, 3 mL of ammonia ($NH_3 \cdot H_2O$, 25%) was added to a mixed solution containing ethanol (70 mL) and deionized (DI) water (10 mL), and stirred for 10 min. Then, 2.8 mL of tetraethyl orthosilicate (TEOS) was dispersed into the above solution, and continuously stirring for 30 min. During the process, the solution was changed from transparent to white. Subsequently, 160 mL of aqueous dopamine hydrochloride (PDA, 2.5 mg mL^{-1}) was slowly added to the above mixed solution and stirred for 12 h at room temperature. Finally, the SiO_2@SiO_2/PDA precursor was obtained by centrifuging the supernatant and then drying it under vacuum overnight at 80°C.

1.2 Synthesis of Co/N-HCB and N-HCB

Firstly, SiO_2@SiO_2/PDA was placed in a tube furnace and carbonized at 900°C for 4 h under Ar atmosphere. And then, silica was removed using the 5 wt% hydrofluoric acid (HF) solution. After centrifugation and drying, the N-PCS powder was obtained. N-doped hollow bowl-liked porous carbon (N-HCB) was obtained by infiltrating N-PCS (50 mg) in DI water (200 mL) and drying at 80°C. Co/N co-doped hollow bowl-liked porous carbon (Co/N-HCB) was obtained by placing $CoCl_2 \cdot 6H_2O$ (200 mg) and N-HCB (60 mg) on both ends of a porcelain boat and annealing at 700°C for 2 h under Ar atmosphere.

1.3 Materials Characterization

X-Ray diffraction (XRD, Rigaku Smart Lab 3kw, Japan) was measured to determine the phase of the samples. Raman spectra were analyzed by a Raman spectrograph with a laser light wavelength of 532 nm. The X-Ray photoelectron spectra (XPS) were investigated by X-Ray photoelectron spectroscopy. Scanning electron microscopy (SEM, FEI, Quanta FEG 250, America) and transmission electron microscopy (TEM, FEI, Talos L 120C, America) were conducted to investigate the morphologies of all samples. The extended X-ray absorption fine structure (EXAFS) was analyzed at Taiwan Photon Source (TPS44A1, TLS17C1) beamline, at 44A Quick-scanning X-ray absorption spectroscopy (XAS), in National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The *in-situ* XRD measurement were recorded using an aluminum foil as the X-ray penetration window. For the *in-situ* XRD tests, the fabrication of cathode is similar to that of the half cells except that the slurries were coated onto an aluminum foil. The cell was assembled by a similar process to that of the half cell. For the measurements, the coin cells were galvanostatic charging and discharging at 0.1 A g^{-1}. The XRD patterns were collected at the diffraction angle (2θ) between 10° and 41.5°. For the *ex-situ* Raman, TEM and XPS measurements, the coin cells were disassembled in glove box after reaching the desired voltage. The electrodes were washed by diethyl carbonate (DEC) and thoroughly sealed to cut off from the air for the relevant ex-situ measurements.

1.4 Cell Assembly and Electrochemical Measurements

All the electrodes for half-cells and potassium-ion hybrid capacitors were manufactured by mixing active materials of Co/N-HCB or N-HCB, polyvinylidene fluoride (PVDF) in N-Methyl-pyrrolidone (NMP) and super P with a weight ratio of 8:1:1. After thorough stirring, the slurries were coated on copper foil and vacuum dried at 100°C for 12 h. The mass loading of active material is about 0.8~1.04 mg cm^{-2}. The CR-2032 half-cells were assembled with potassium metal as the anode, glass fiber membrane as the separator, and 0.8 M KPF_6 in ethyl carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) as electrolyte. All the galvanostatic discharge/charge and galvanostatic intermittent titration (GITT) measurements were tested by a battery tester (Neware). A typical GITT measurement is followed by a current pulse of 0.1 A g^{-1} for 10 min with a relaxation of 1 h. The VMP3 electrochemical workstation is carried out to measure cyclic voltammetry (CV) with a voltage range at 0.01-3 V and electrochemical impedance spectroscopy (EIS) with a frequency range at 0.01-10^5 Hz. For the typical assembly of potassium-ion hybrid capacitors (PIHCs), Co/N-HCB acts as anode, and the commercial (AC) acts as cathode. Before the assembly of PIHCs, half coin cells ran 5 cycles at 0.2 A g^{-1} in advance, which were finally ended in a full discharging state for pre-potassiation and activation. The obtained pre-potassiated electrode served as anode, which was further matched with AC cathode according to a proper mass ratio (1:2). The measured voltage ranges were set between 0.01-4.1 V (vs. K/K^+). The energy and power density of PIHCs can be calculated by the reported equations:

$$P=\triangle V\times i \tag{1}$$

$$E=P\times t/3600 \tag{2}$$

$$\triangle V=(V_{max}+V_{min})/2 \tag{3}$$

E, P, t, and i are energy density, power density, the discharge time and current density. V_{max} and V_{min} represents the maximum and minimum potential, respectively.

1.5 Density Functional Theory (DFT) Calculations

The Vienna ab initio simulation software package was employed for the DFT calculation. In brief, the optimization and calculation of the structure and electronic structure were performed using the projector‐augmented plane‐wave method. The exchange–correlation energy was described by generalized gradient approximation of the Perdew–Burke–Ernzerhof functional. A kinetic energy of 500 eV was set as the cutoff for the plane wave. The geometric structure was fully optimized when the force on each atom and the energy were below 0.01 eV/Å and 1×10^{-5}/cell, respectively. The K^+ absorption energy (ΔEa) was calculated using:

$$\Delta Ea = E_{GK} - (E_G + E_K) \tag{4}$$

where E_{GK}, E_G, and E_K are the energies of the doped carbon models after K adsorption, without K adsorption, and the energy of isolated K atoms, respectively. A Brillouin zone with an 8 × 8 × 1 k-point grid was used to optimize the geometric structure and density of states.

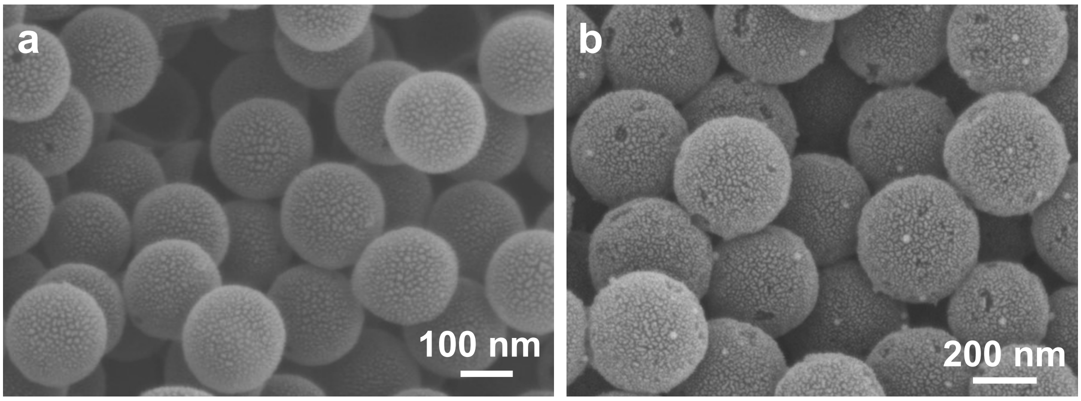

Figure S1 (a)-(b) SEM images of N-PCS.

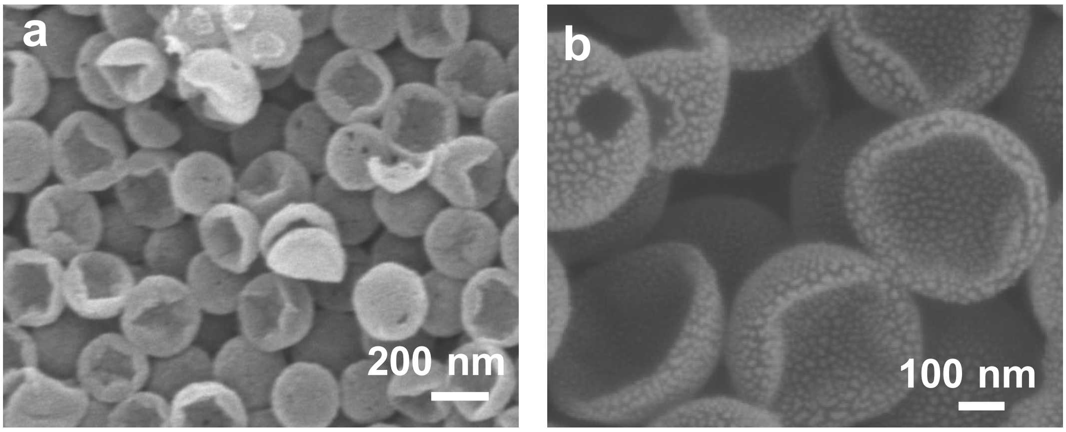

Figure S2 (a)-(b) SEM images of N-HCB.

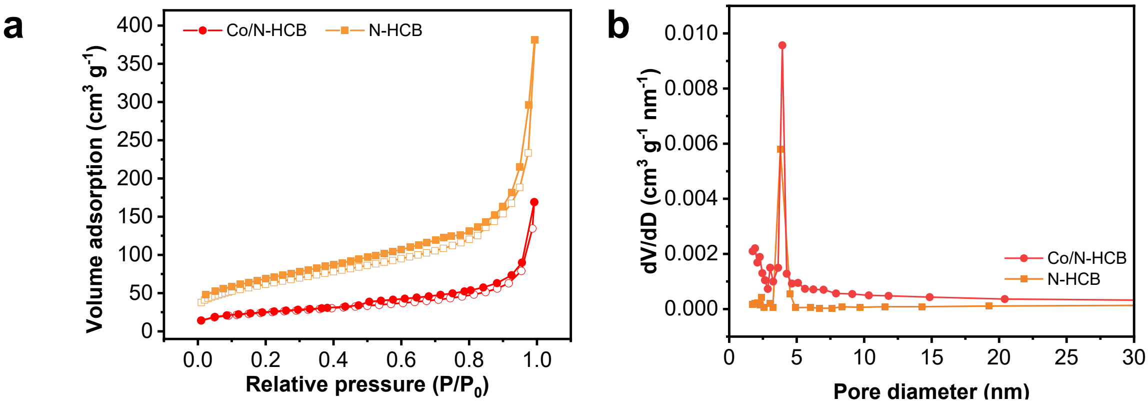

Figure S3 (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of Co/N-HCB and N-HCB.

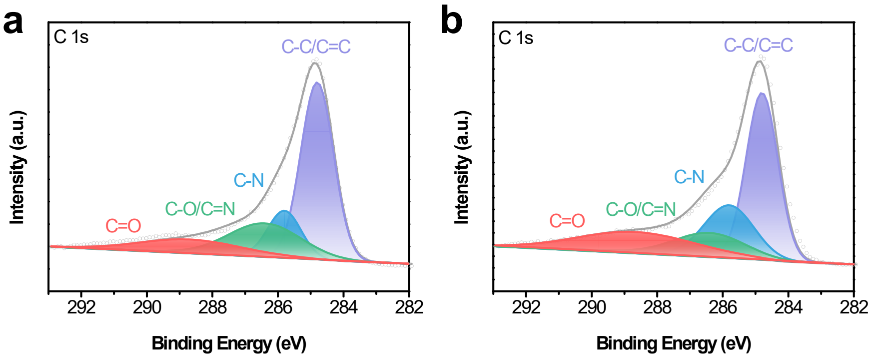

Figure S4 High-resolution C 1s XPS spectra of (a) Co/N-HCB and (b) N-HCB.

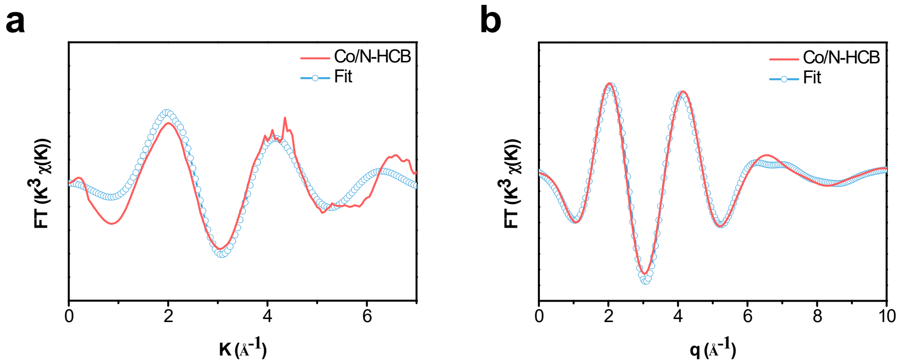

Figure S5 The EXAFS fitting curves of Co/N-HCB in (a) K-space and (b) q-space.

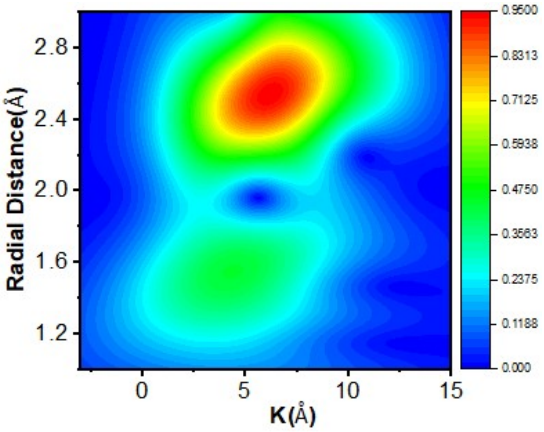

Figure S6 Wavelet transform (WT) analysis of the k^3-weighted Co K-edge EXAFS signals for CoO.

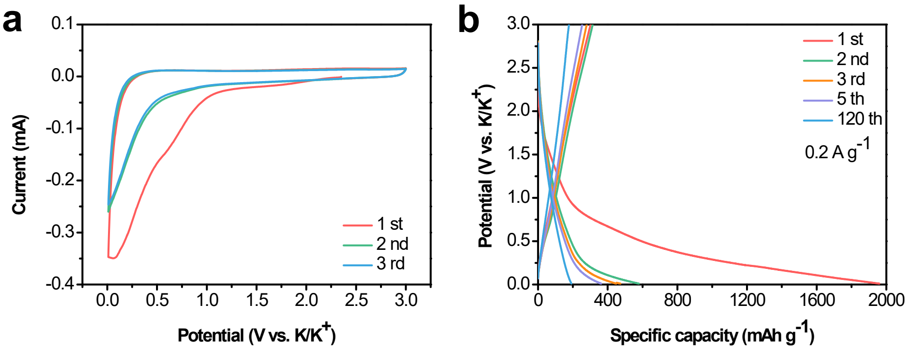

Figure S7 (a) CV curves of N-HCB for the first three cycles at 0.1 mV s^{-1}, (b) Charge-discharge curves for the first 120 cycles at 0.2 A g^{-1} of N-HCB.

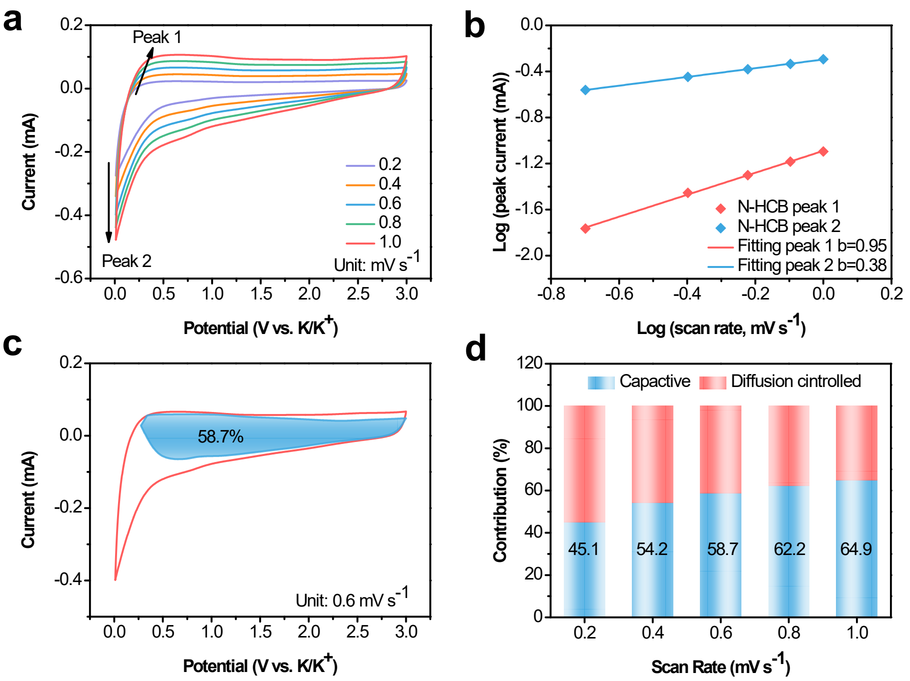

Figure S8 (a) CV curves at 0.2-1.0 mV s^{-1}, (b) relation diagram of log(v) and log(i) at corresponding scan rate, (c) capacitive contribution at 0.6 mV s^{-1}, (d) pseudocapacitance contribution ratios at different scanning rate of N-HCB.

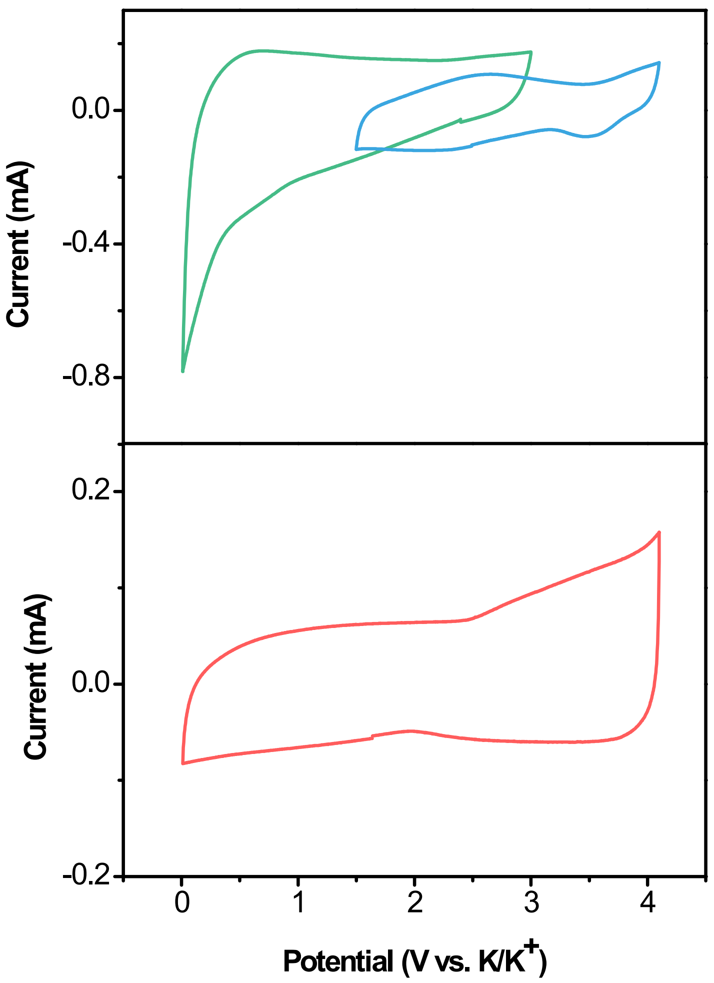

Figure S9 CV curves of Co/N-HCB anode and AC cathode in half batteries (top) and Co/N-HCB//AC (bottom) at 0.6 mV s^{-1}.

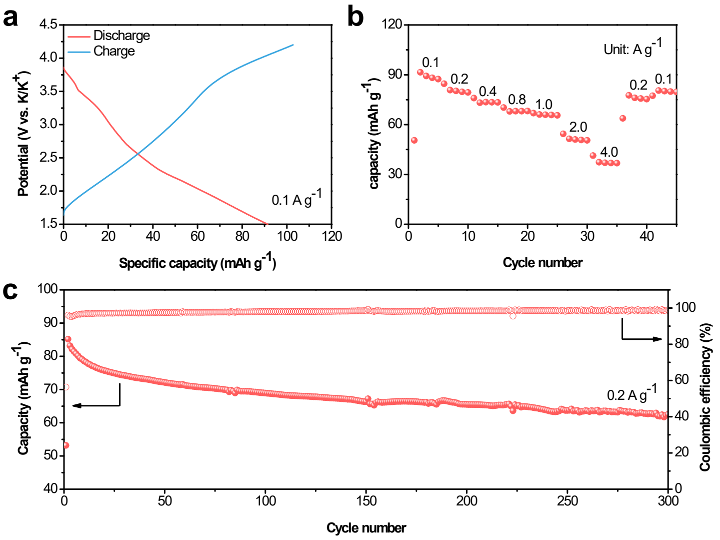

Figure S10 (a) Charge-discharge curve of AC at 0.1 A g^{-1}, (b) rate performance of AC at 0.1-4.0 A g^{-1}, (c) Cycle performance of AC at 0.2 A g^{-1}.

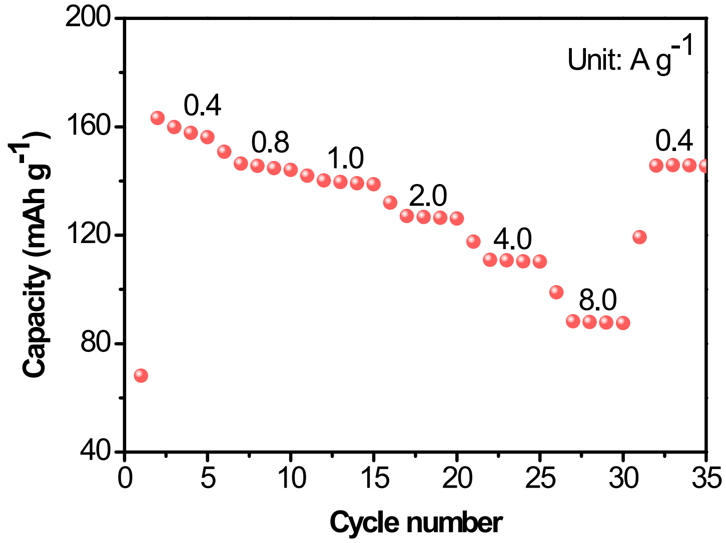

Figure S11 Rate performance of Co/N-HCB//AC at 0.4-8.0 A g^{-1}.

Table S1 Physical parameters of Co/N-HCB and N-HCB obtained from the XRD patterns.

Samples	**2θ (°)**	**d (nm)**
Co/N-HCB	21.7	0.41
N-HCB	23.8	0.37

Table S2 The contents of nitrogen and cobalt elements in Co/N-HCB measured by the XPS measurements.

Elements	**Element Content (at%)**
Nitrogen	5.15
Carbon	86.64
Cobalt	0.19
Oxygen	8.02

Table S3 Structural parameters of the sample obtained from the XAFS fitting.

Sample	**Path**	**CN**	**R(Å)**	**σ^2 (Å^2)**	**ΔE_0 (eV)**	**R-factor**
Co/N-HCB	Co-N	4	2.02	0.0023	-0.5	0.018

The calculation of potassium ion diffusion coefficients form EIS

$$\omega = 2\pi f \tag{5}$$

$$Z_{re} = R + \sigma\omega^{-1/2} \tag{6}$$

$$D_{K^+} = \frac{R^2T^2}{2A^2n^2F^4C_K^2\sigma^2} \tag{7}$$

Where f is the frequency; A is the area of electrodes; C is the molar concentration of K^+; n is the electronic transfer number per molecule; σ is the Warburg coefficient; and R, T, and F are constant.[1]

References

[1] W. Xu, H. Li, X. Zhang, T. Y. Chen, H. Yang, H. Min, X. Shen, H. Y. Chen, J. Wang, *Advanced Functional Materials* **2023**, 34, 2309509.