Suppoting information

Room-temperature liquid metal-based anodes for high-energy potassium-based electrochemcial devices

Lei Qin,‡[ab] Wei Yang,‡[a] Wei Lv,[a] Liang Liu,[c] Yu Lei,[a] Wei Yu,[a] Feiyu Kang,[a] Jang-Kyo Kim,[b] Dengyun Zhai*[a] and Quan-Hong Yang*[d]

[a] Engineering Laboratory for Functionalized Carbon Materials, Shenzhen Key Laboratory for Graphene-Based Materials, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

E-mail: zhaidy0404@sz.tsinghua.edu.cn

[b] Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China.

[c] Department of Physics, Tsinghua-Foxconn Nanotechnology Research Center, Tsinghua University, Beijing 100084, China

[d] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

E-mail: qhyangcn@tju.edu.cn

‡These authors contributed equally to this work.

Material preparation

Materials: Potassium hexafluorophosphate (KPF_6), sodium (Na), potassium (K) was purchased from Sigma Aldrich.

CM@NaK membrane preparation: The liquid Na-K alloy was prepared by mixing 33.3 wt% Na (99.9 %, Aldrich) and 66.7 wt% K (98 %, Aldrich), and slightly pestling with a glass rod in the argon-filled glove box with water content < 0.1 ppm and oxygen content < 0.1 ppm. The CM@NaK membrane was prepared by immersing a super-aligned carbon nanotube membrane (CM, supplied by Prof. Shoushan Fan's Group[1]) of 16 mm in diameter into the Na-K alloy at room temperature (RT). The CM of 7.9 mg was used to adsorb Na-K alloy and regarded as the anode in the symmetric cell, while the thinner CM of 1.5 mg was used to adsorb Na-K alloy and regarded as the anode in the asymmetric capacitor. In addition, another carbon nanotube membrane prepared by vacuum infiltration and the carbon paper (TGP-H-060, Toray) were used as reference samples to evaluate surface wettability with Na-K alloy.

Activated carbon electrode preparation: Activated carbon (AC) powder was prepared according to previous report.[2] A uniform slurry consisting of 80 wt% AC, 10 wt% carbon black and 10 wt% polyvinylidene fluoride (PVDF) was prepared by adding N-methyl-2-pyrrolidinone (NMP) solvent and thoroughly grinding the above mixture. The resultant slurry was uniformly coated onto Al foil, dried in vacuum at 110 ^{o}C overnight and cut into 16 mm disks with a typical AC loading of 2 mg for coin-cell tests.

Material characterization

X-ray diffraction (XRD) spectra were collected on a Rigaku D/MAX 2500/PC with a Cu Kα source (λ = 0.154 nm) and the step rate was 5 degrees per minute. The morphologies were observed using a scanning electron microscope (SEM, HITACHI SU8010) with an electron beam voltage at 10 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on PHI5000 XPS spectrometer using monochromatic Al Kα radiation at 1486.6 eV. All the XPS spectra were corrected by referencing the position of the C-C peak in C 1s spectra with a binding energy at 284.8 eV. Spectra curve fitting was finished with the help of the PHI-MultiPak software adopting a combined Gaussian-Lorentzian profile after a Shirley type background subtraction. Raman spectra were recorded from 200 to 3000 cm^{-1} with a confocal microprobe Raman system using 532-nm excitation laser (HORIBA LABRAM HR800) with 1% of the maximum power (50 mW). Nitrogen adsorption/desorption experiments were conducted on an ASAP 2020M+C. The samples were degassed in vacuum at 200 ^{o}C for 12 h in prior to the adsorption measurements. The specific surface area was determined from the Brunauer-Emmett-Teller (BET) method and the corresponding pore size distribution by density function theory (DFT). ^{1}H NMR (Bruker AVANCE Ⅲ 400) was used to identify the electrolyte component and the $CDCl_3$ was selected as the solvent.

Electrochemical measurement

CM@NaK or K electrodes were assembled into symmetric cells respectively, which were tested at 0.05, 0.1, 0.25, 0.5 and 1 mA cm^{-2} with the deposition/stripping time of 2 h. An asymmetric capacitor was evaluated with R2032 coin-type cells, consisting of a CM@NaK or K anode, a AC cathode and two pieces of glass fiber separators (GF/A, Whatman) with ~70 μL electrolyte added in cell. The K anode has a typical mass of 30 mg with 16 mm in diameter by pressing K chunks on the stainless steel sheet. The electrolyte is 0.5 M KPF_6 in diethylene glycol dimethyl ether (DEGDME). The cells were galvanostatically cycled on a LAND battery tester. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) tests were conducted on an electrochemical workstation (Bio-Logic VMP3, France).

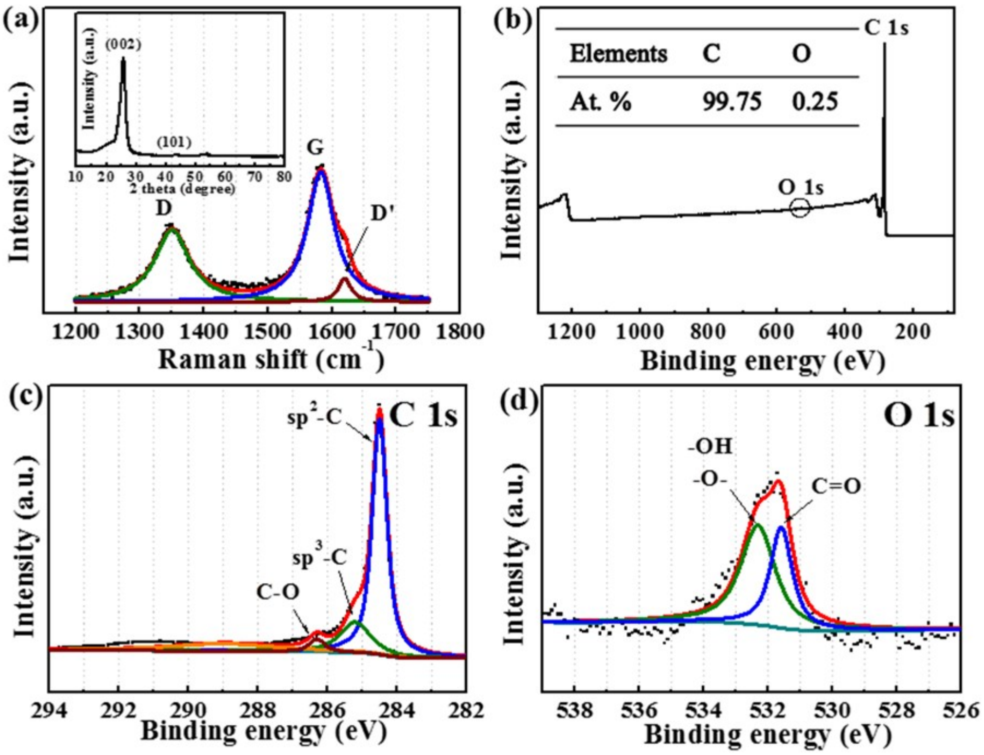


Fig. S1 (a) Raman spectrum and XRD pattern, and (b) XPS spectrum of CM (inset: the chart shows the percentages of carbon and oxygen). High-resolution (c) C 1s and (d) O 1s XPS spectra of CM.

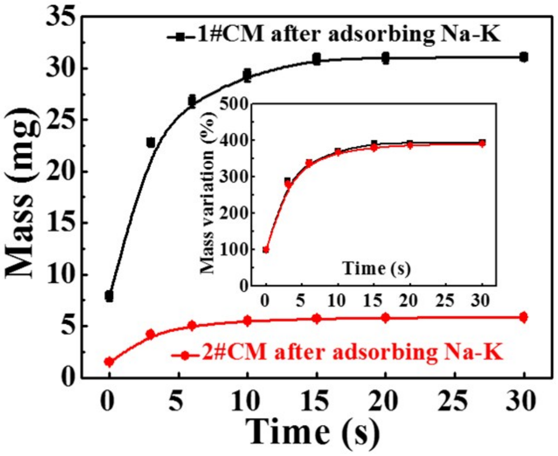


Fig. S2 Mass variation of CM with two typical initial weight after adsorbing liquid Na-K upon time.

Fig. S3 Illustration of the flexible CM and CM@NaK with diverse shapes.

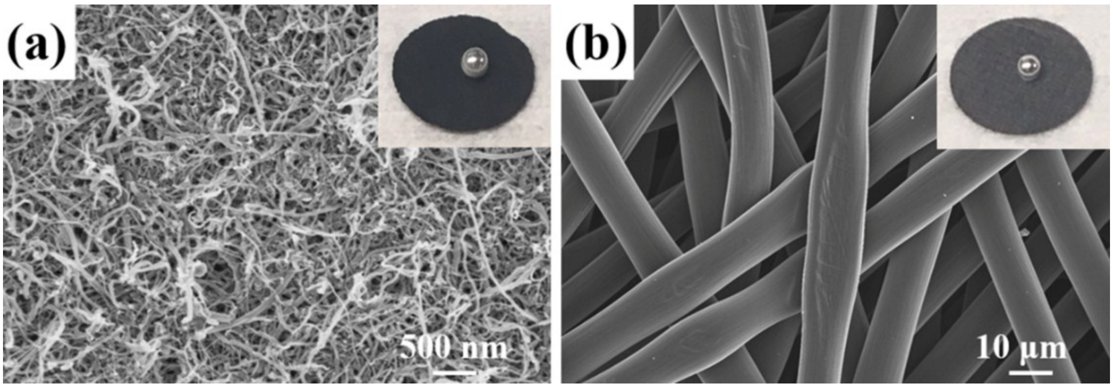


Fig. S4 Representative SEM image of (a) a CNT membrane prepared by vacuum filtration and (b) a carbon paper. The insets are the photos of a Na-K droplet on them at RT.

Table S1 The estimated contact angle of liquid Na-K alloy on different substrates.

Substrates	Carbon fiber	Vacuum filtrated CNT membrane	Super-aligned CNT membrane
Contact angle (°)	115°	130°	40°

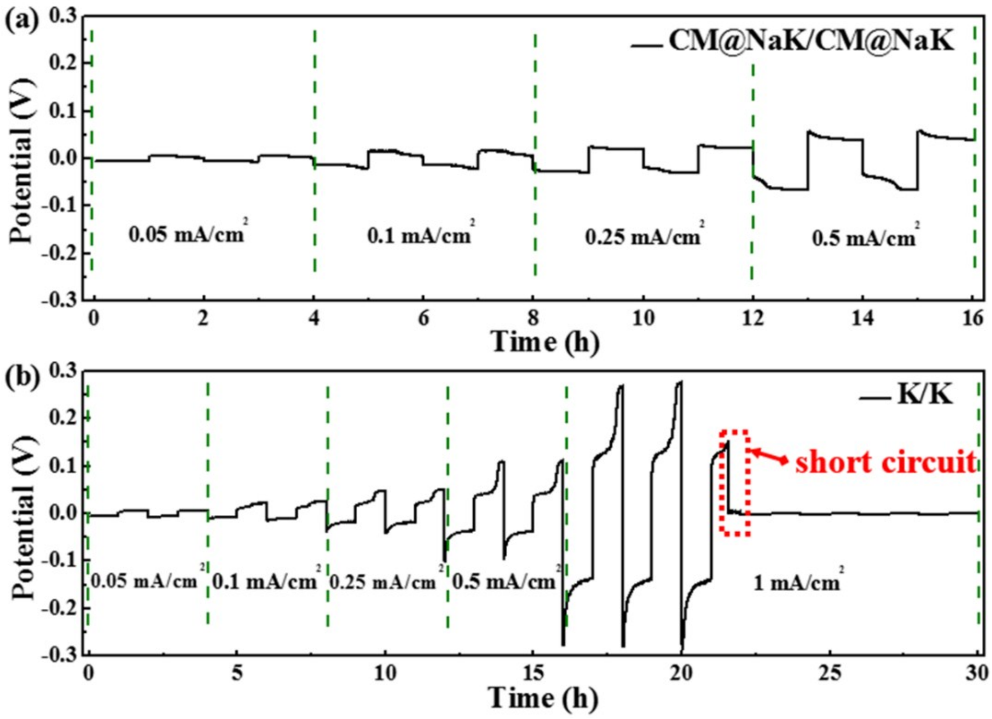
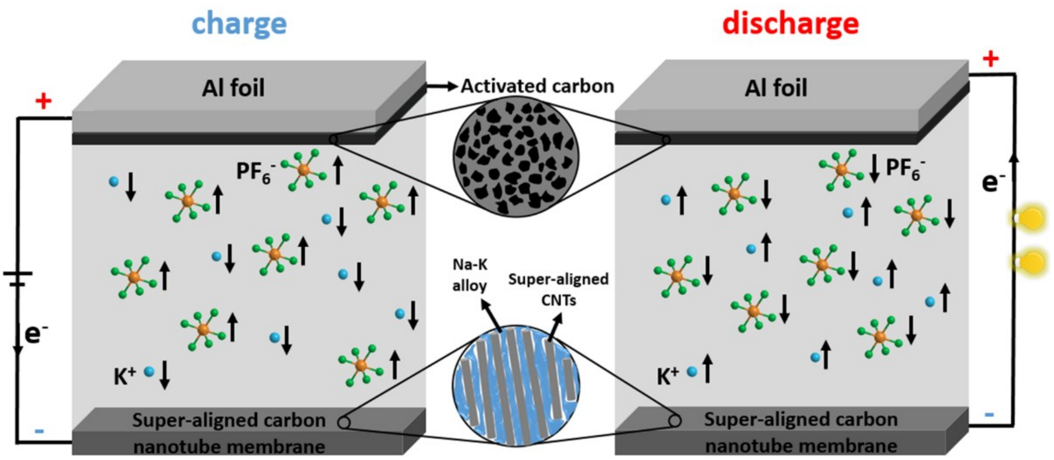


Fig. S5 Electrochemical performance of the symmetric cells. Voltage versus time of a symmetric (a) CM@NaK/CM@NaK and (b) K/K cell cycled at various current densities with the stripping/plating time of 2 h. The electrolyte is 0.5 M KPF_6 in DEGDME.



Scheme 1. Schematic illustration of charging/discharging mechanism of the asymmetric PIC, composed of CM@NaK anode and AC cathode. The electrolyte is 0.5 M KPF_6 in DEGDME.

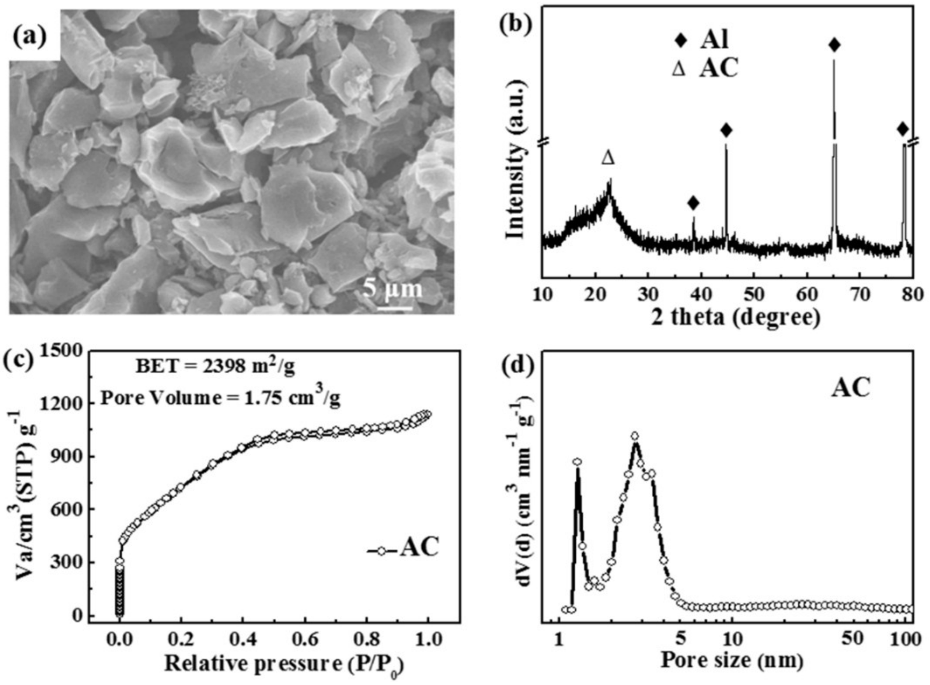


Fig. S6 (a) SEM image of AC, (b) XRD pattern of AC coated on the Al current collector, (c-d) Nitrogen adsorption/desorption isotherm of AC and its corresponding pore size distribution.

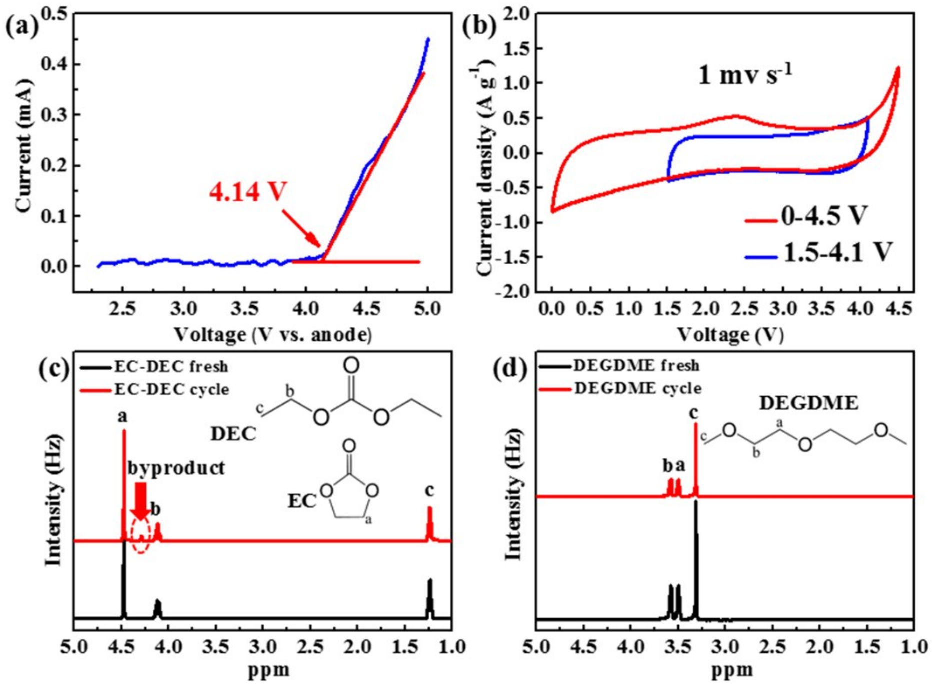


Fig. S7 (a) LSV of PIC with CM@NaK anode scanning from the open circuit voltage to 5.0 V, (b) CV curves of PIC with CM@NaK anode in the voltage range of 1.5-4.1 V and 0-4.5 V, (c-d) Electrolyte stability evaluation of EC-DEC and DEGDME in the presence of CM@NaK anode based on ^{1}H NMR spectra.

The newborn byproduct can be identified as potassium ethyl (C_2H_5K) from NMR results in **Figure S7**c, indicating that the EC-DEC electrolyte occur decomposition in the presence of liquid Na-K.

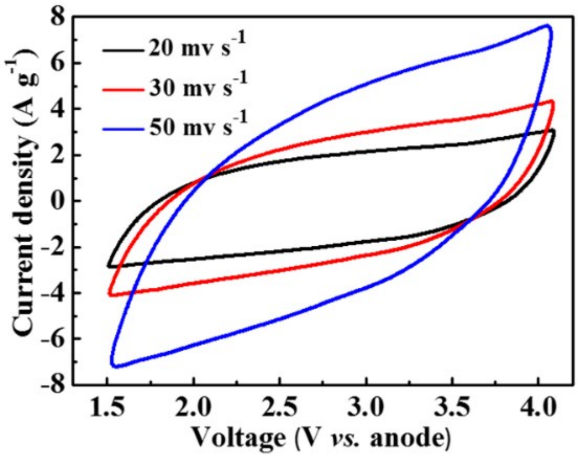


Fig. S8 Cyclic voltammograms of CM@NaK/AC at high scan rates.

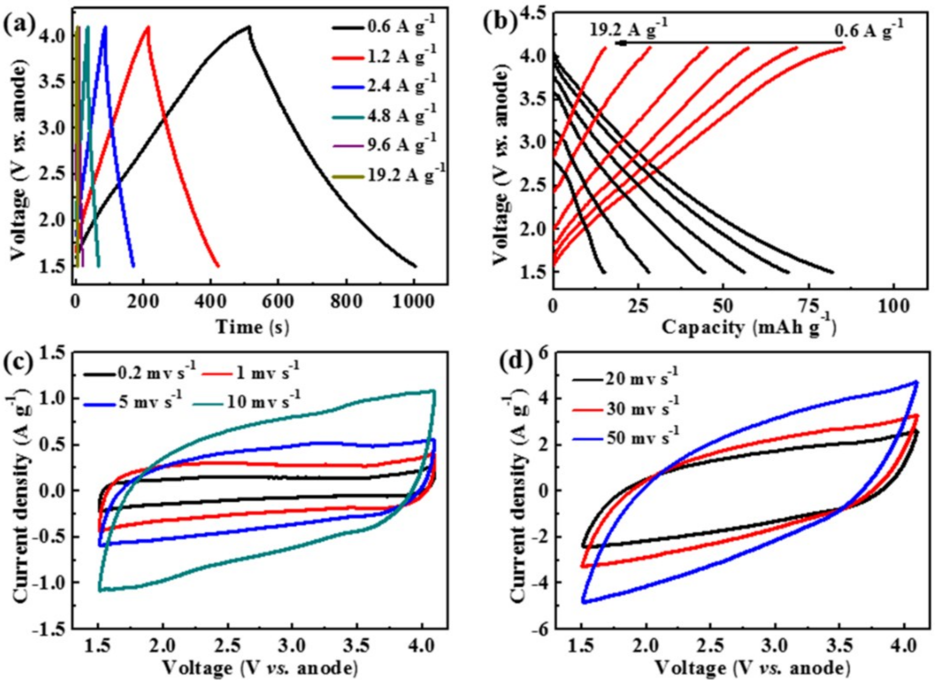


Fig. S9 Electrochemical performance of the asymmetric PIC with K anode and AC cathode, tested between 1.5-4.1 V. The applied current densities are calculated based on the mass of AC electrode. (a-b) Galvanostatic discharge/charge profiles of PIC, at current densities from 0.6 to 19.2 A g^{-1}, The capacities are calculated based on AC electrode. (c-d) Cyclic voltammograms of PIC at various scan rates.

References

1 X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, J. Kong, T. Zhang, Q. Li and S. Fan, *Adv. Mater.*, 2006, **18**, 1505-1510.

2 D. Zhai, H.-H. Wang, J. Yang, K. C. Lau, K. Li, K. Amine and L. A. Curtiss, *J. Am. Chem. Soc.*, 2013, **135**, 15364-15372.