

## Supporting Information

# Highly Concentrated Electrolytes for High-Efficiency Potassium Metal Batteries

Wenxin Xu, ‡<sup>a</sup> Huwei Wang, ‡<sup>b</sup> Junyang Hu,<sup>a</sup> Haodong Zhang,<sup>b</sup> Biao Zhang,<sup>d</sup> Feiyu Kang<sup>\*abc</sup> and Dengyun Zhai <sup>\*a</sup>

<sup>a</sup> Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China.

<sup>b</sup> Shenzhen Environmental Science and New Energy Technology Engineering Laboratory, Tsinghua-Berkeley Shenzhen Institute (TBSI), Tsinghua University, Shenzhen 518055, China.

<sup>c</sup> Shenzhen Key Laboratory for Graphene-Based Materials and Engineering Laboratory for Functionalized Carbon Materials, Shenzhen Geim Graphene Center, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China.

<sup>d</sup> Department of Applied Physics, The Hong Kong Polytechnic University Kowloon, Hong Kong, China.

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

## Experimental

**Materials:** Potassium bis(fluorosulfonyl)imide (KFSI) (>99.9%, Fluolyte) was dried under vacuum at 95 °C for 24 h before using. Diethylene glycol dimethyl ether (DEGDME) (>99%, Sigma-Aldrich) was stored over 3 Å molecular sieves (Sigma-Aldrich).

Preparation of electrodes and assembling of batteries. Cu foil (MTI) was cut into circular pieces with the diameter of 14 mm and pretreated with hydrochloric acid solution to clear oxidized surface. All electrochemical testing studies are based on 2032-type K||Cu half cells. Each half cell was consisted of K metal as the counter electrode and Cu foil (diameter of 14 mm) as the working electrode. The K metal (>98%, Sigma-Aldrich) was pressed into circular sheets and placed on stainless steel sheets. The separators used were Celgard2320 (polypropylene-polyethylene-polypropylene, 25 µm thickness) and glass fiber (GF/A, Whatman). The trilayer celgard separator was close to Cu foil to avoid GF/A sticking with K metal, which would destroy the deposition morphology. 100 µl electrolytes were added into each cell. All the cells were assembled in an argon filled glove box with oxygen and water contents below 0.1 ppm.

Prussian blue power was synthesized according to a modified co-precipitation method. Concretely, 4 g potassium citrate and 0.8 g FeCl<sub>2</sub> were dissolved into 100 mL deionized water under nitrogen atmosphere followed by adding 3 mmol potassium ferrocyanide aqueous solution dropwise with vigorous stirring. After stirring the solution for 10 h and centrifugal treatment, the precipitation was vacuum-dried overnight under 120 °C.

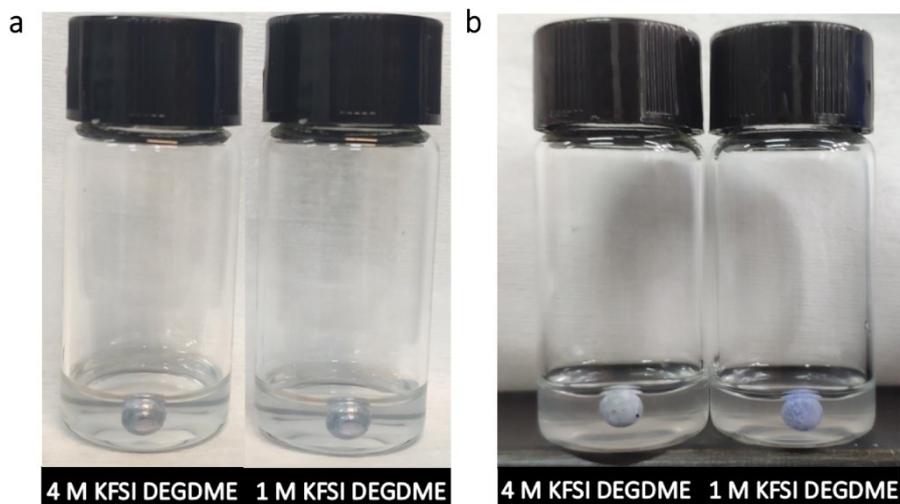
Then the Prussian blue cathode was prepared by mixing the KPB powder, carbon black (Sinopharm Chemical Reagent Co., Ltd) and polyvinylidene difluoride binder (PVDF, Canrd) at a weight ratio of 7:2:1. Stirring the mixture with N-methylpyrrolidone (AR, Sinopharm Chemical Reagent Co., Ltd) for 6 h to form uniform slurry followed by pasting it on an Al foil (MTI) and dried in a vacuum oven at 110 °C for 12 h. After drying, the coated foil was cut into circular pieces with the diameter of 12 mm. And the mass loading of the Prussian Blue active material in the electrodes was ~0.88 mg per cm<sup>2</sup>.

**Electrochemical measurements:** The galvanostatic discharge/charge tests of K||Cu and K||KPB coin cells were conducted on a standard eight-channel battery tester (CT2001A, Wuhan LAND Electronics Co., Ltd.). The charge cutoff voltage of K||Cu cell is 1.0 V (vs. K<sup>+</sup>/K). The CE was defined as the ratio of K stripping to that plating on the Cu substrate. The discharge and charge cutoff voltages of K||KPB cell is 2.5 V and 4.0 V (vs. K<sup>+</sup>/K), respectively. Ionic conductivities were measured on a FE38-Standard conductivity meter (Mettler Toledo, Switzerland) at 25 °C. The anodic limits of KFSI-DEGDME electrolytes was measured by LSV at the scan rate of 0.5 mV/s. Al was used as the working electrode and K was used as counter electrode and reference electrode.

Materials characterization: Raman spectra were performed on HORIBA HR800 spectrometer (785-nm Ar-ion laser) with the electrolytes storing in cuvettes. Morphological observation was conducted on a scanning electron microscopy (SEM, HITACHI SU8010, Japan). X-ray photoelectron spectroscopy (XPS) analysis was

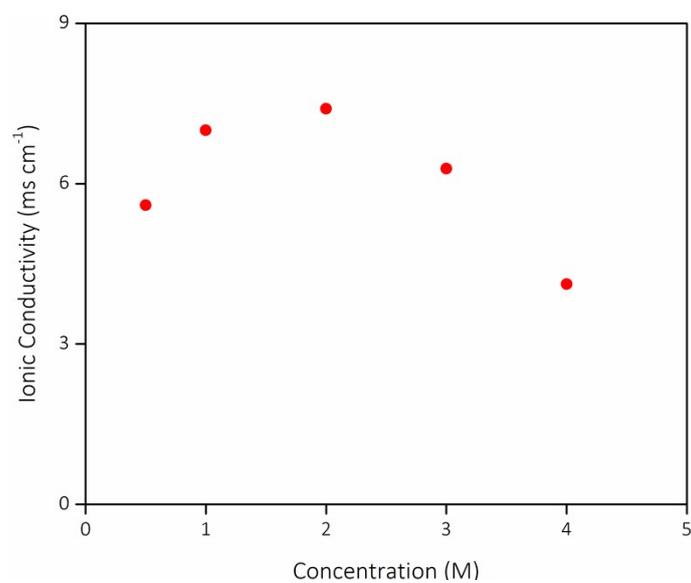
obtained on a PHI 5000 VersaProbe II (Ulvac-Phi, Japan) spectrometer with monochromatic Al-K $\alpha$  X-ray source. The obtained XPS data was calibrated with respect to the C-C speak at 284.8 eV in C1s spectrum. For SEM, K metal with 2.5 mAh cm<sup>-2</sup> was deposited on the Cu substrate for further characterization. All coin cells were disassembled in the argon glove box to obtain the samples for SEM and XPS characterizations. The potassium electrodes to be characterized were washed by solvent of DEGDME followed by DME for several time and then transported from the argon-filled glove box to characterization instruments in an air-free transfer vessel. Electrochemical impedance spectroscopy (EIS) was conducted using a Solartron workstation, with a frequency range of 100 KHz to 100 mHz and an AC voltage amplitude of 10 mV.

## List of Supporting Figures and Tables



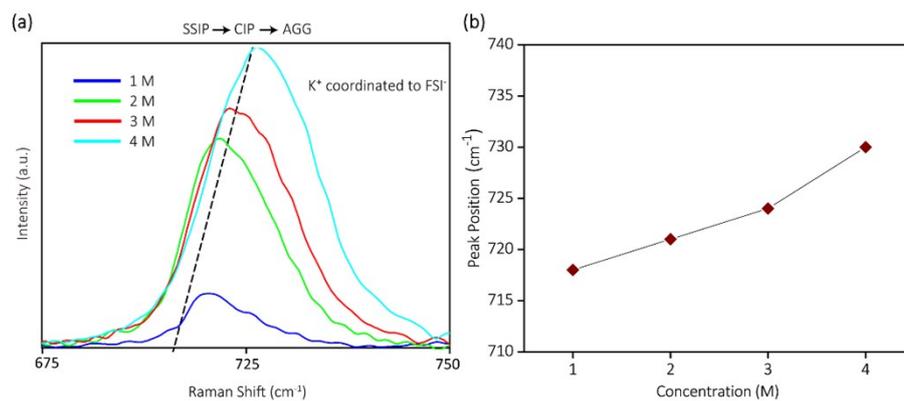
**Fig.S1** The compatibility test between the electrolytes with K metal. Photographs of K metal in electrolytes with different concentration (a) after the K metal was dropped in and (b) after 10 days.

Both the surfaces of K metal in different electrolytes were shiny after the K metal was dropped in. After 10 days, the surfaces of K metal in the diluted electrolyte of 1 M KFSI DEGDME became dark blue obviously, indicated that side reaction have occurred. While in the HCE of 4 M KFSI DEGDME electrolyte, the surfaces of K metal just became a little gray.



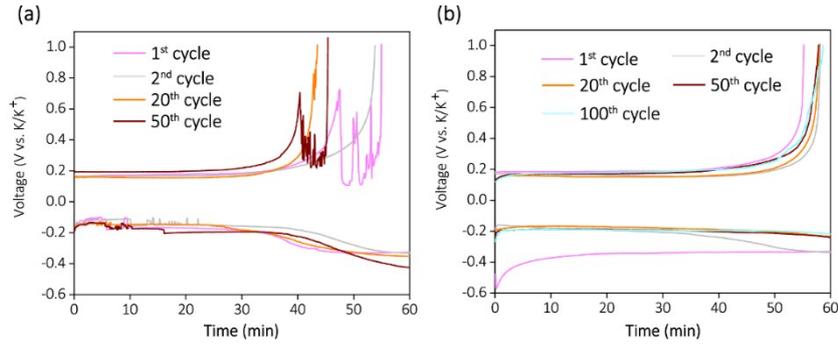
**Fig. S2** Change of ionic conductivity with the increase of electrolyte concentration.

The maximum ionic conductivities ( $7.4 \text{ mS cm}^{-1}$ ) is achieved when the concentration is around 2 M. Although the increase in salt concentration leads to the increasing of the electrolyte viscosity, the ionic conductivity of 4 M electrolyte can still reach  $4.1 \text{ mS cm}^{-1}$ .



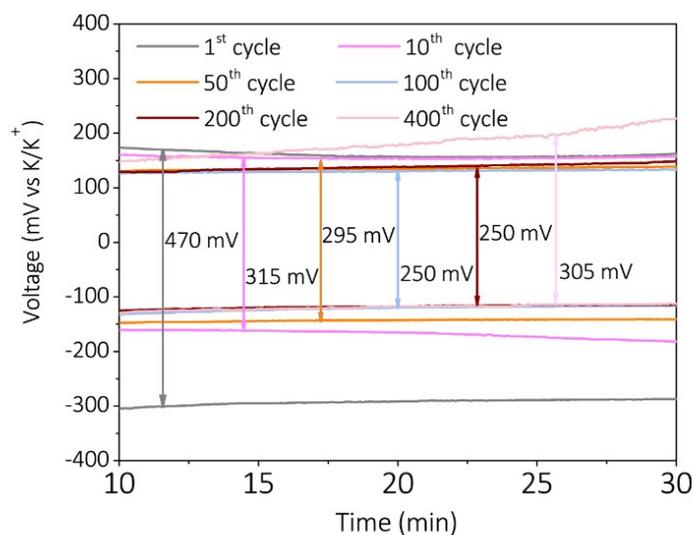
**Fig. S3** Raman spectra of K<sup>+</sup> coordinated to FSI<sup>-</sup>.

The most intense peak shifts from 718 cm<sup>-1</sup> at 1 M to 730 cm<sup>-1</sup> at 4 M, implying that contact ion pairs (CIPs, FSI<sup>-</sup> coordinates with one K<sup>+</sup> ion) and AGGs (FSI<sup>-</sup> coordinates with two or more K<sup>+</sup> ions) are formed in the HCE.



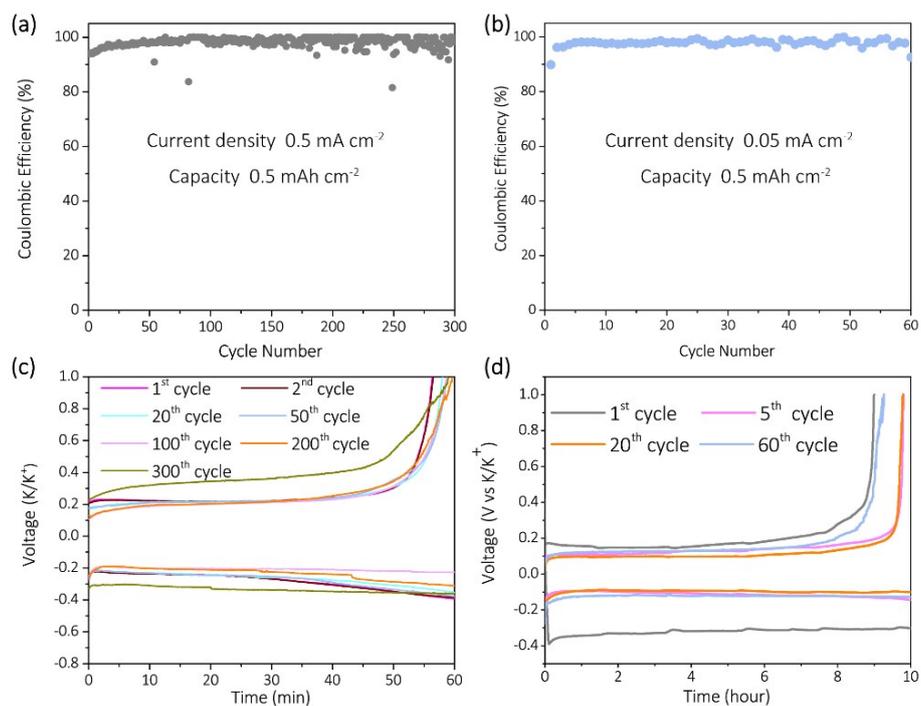
**Fig. S4** Voltage profiles for the cell cycled at a current of  $0.25 \text{ mA cm}^{-2}$  in (a) 2 M KFSI DEGDME and (b) 3 M KFSI DEGDME.

The voltage profiles of charge and discharge in 2 M KFSI DEGDME are fluctuated severely, indicating serious side reactions between electrolytes and K metal anode. The fluctuations in CE are clearly alleviated with further increasing the concentration to 3 M. However, the CE is still lower than 97% and it can only maintain about 100 cycles. The continuous accumulation of side reaction products increases the interfacial impedance, leading the unstable charge-discharge process. As a result, the K||Cu cell paired with this electrolyte suffer from sudden CE decay.

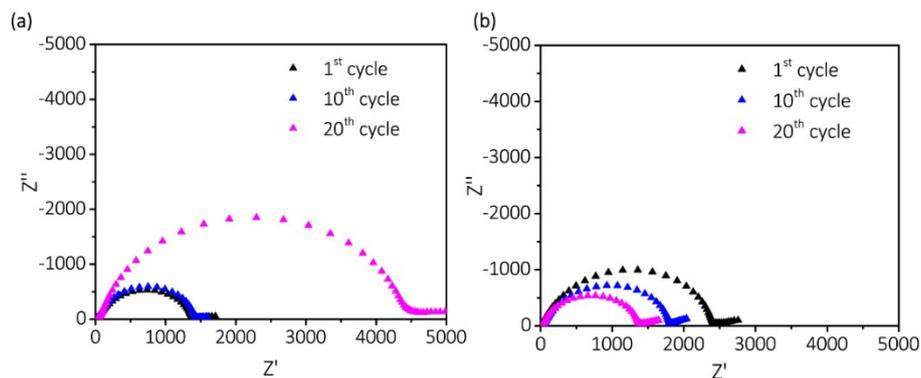


**Fig. S5** Polarization of the K plating/stripping for 4 M KFSI DEGDME electrolyte at different cycles.

The polarization of the first K plating/stripping is relatively large, which is attributed to the large deposition overpotential of K on bare Cu substrate. While the well-maintained polarization during the next 400 cycles demonstrates that a stable interface is formed during the initial cycles.

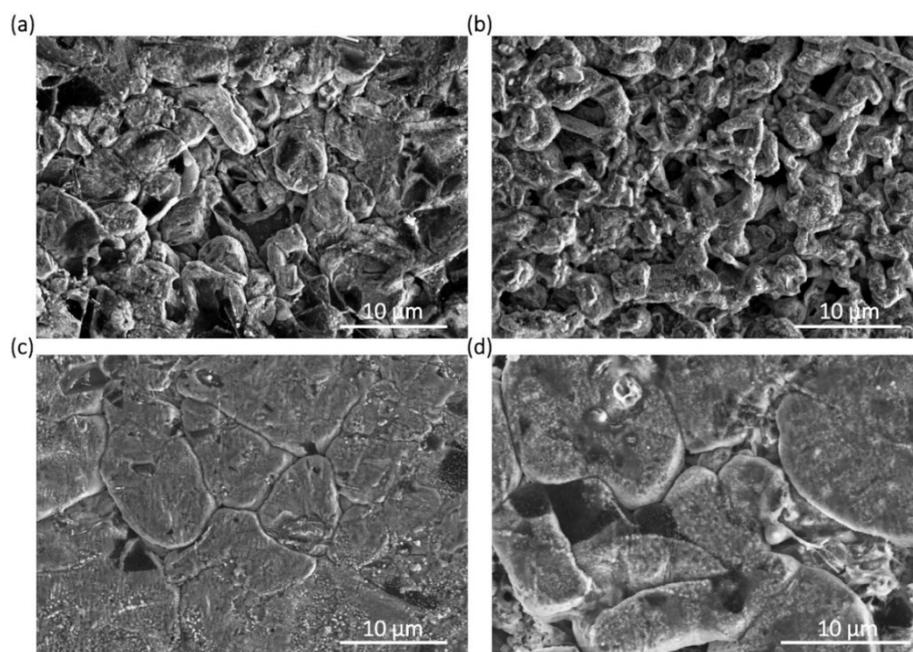


**Fig. S6** Cycling performance of K || Cu coin cell at different current densities. CE of K deposition–stripping in 4 M KFSI DEGDME at current density of (a)  $0.5 \text{ mA cm}^{-2}$  and (b)  $0.05 \text{ mA cm}^{-2}$ . The voltage profiles of charge and discharge in 4 M KFSI DEGDME at current density of (c)  $0.5 \text{ mA cm}^{-2}$  and (d)  $0.05 \text{ mA cm}^{-2}$ .

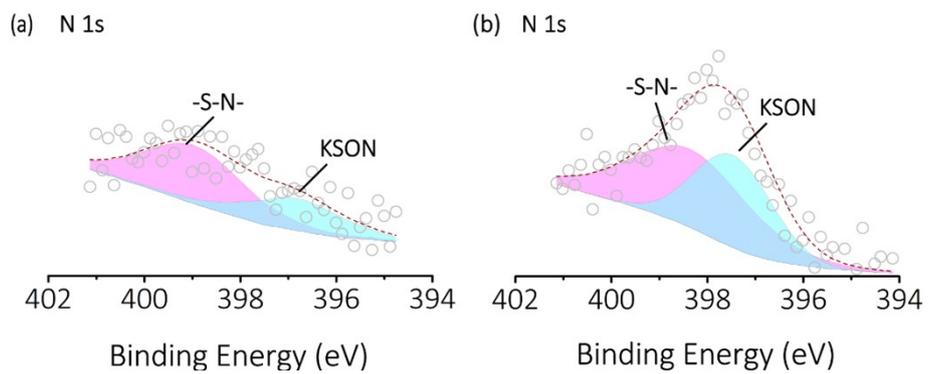


**Fig. S7** Nyquist plots of K||Cu coin cells after different cycle numbers in (a) the diluted electrolytes and (b) the HCE.

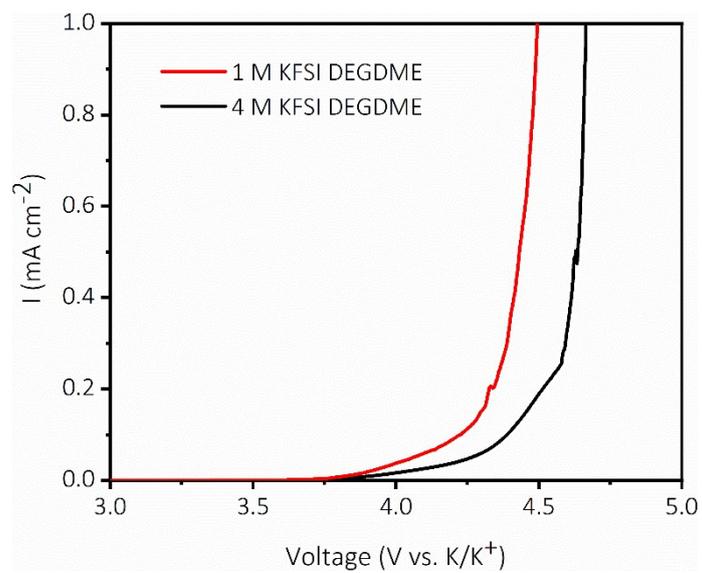
The interfacial resistance increased sharply from 1400 to over 4000  $\Omega$  from initial 10 cycles to 20 cycles during the cycling in diluted electrolyte, revealing that the unstable SEI on K metal is continuously accumulated. (Fig. S7a) As for the HCE (Fig. S7b), the impedance shows a gradual decrease with the cycle, which suggests the SEI formed in HCE is gradually stabilized. Meanwhile, the impedance in the HCE is much lower than that in the diluted electrolyte. Such stable SEI with reduced interfacial resistance promised the high CE and cycling stability of K metal battery.



**Fig. S8** SEM images of K metal deposited on Cu electrodes at  $0.25 \text{ mA cm}^{-2}$  with capacity of  $0.25 \text{ mAh cm}^{-2}$  after (a) 1 cycle and (b) 20 cycles with 1 M KFSI DEGDME. SEM images of K metal deposited on Cu electrodes at  $0.25 \text{ mA cm}^{-2}$  with capacity of  $0.25 \text{ mAh cm}^{-2}$  after (c) 1 cycle and (d) 20 cycles with 4 M KFSI DEGDME.



**Fig. S9** XPS spectra of N 1s peak of K metal anode cycled in (a) 1 M KFSI DEGDME and (b) 4 M KFSI DEGDME.



**Fig. S10** LSV curves of K||Al coin cells with Al as working electrode and K metal as counter and reference electrode.

**Table S1.** Physical properties of DEGDME and DME.

Solvent	Boiling Point (T <sub>b</sub> )[°C]	Flash Point (T <sub>f</sub> ) [°C]	Viscosity ( $\eta$ ) at 25°C [cP]	Dielectric constant( $\epsilon$ ) at 25°C
DME	84	0	0.46	7.18
DEGDME	162	57	1.06	7.4

**Table S2.** The cycling performance of K metal battery reported in recent studies.

architecture	electrolyte	Current densities (mA cm <sup>-2</sup> )	Capacity (mAh cm <sup>-2</sup> )	CE	Cyclic Stability
K  Cu	0.8M KPF <sub>6</sub> in 1:1 v/v EC-DEC <sup>1</sup>	0.05	0.15	< 50%	20 cycles for 120 hours
K  Cu	1M KFSI	0.05	0.15	~99%	200 cycles for 1200 hours
K  Cu	DME <sup>1</sup>	0.5	0.15	~99%	100 cycles for 60 hours
K  Cu	2M KFSI TEP <sup>2</sup>	0.5	0.12	99.6%	500 cycles for 240 hours
K  Cu	4 M KFSI DEGDME	<b>0.25</b>	<b>0.25</b>	98.3%	<b>400 cycles for 800 hours</b>
K  Cu	<b>This work</b>	<b>0.5</b>	<b>0.5</b>	~98%	<b>300 cycles for 600 hours</b>

**Table S3.** Total amount of elements in the SEI layer at the K metal anode.

Elements	1 M KFSI DEGDME	4 M KFSI DEGDME
F	8.75%	12.92%
S	2.35%	3.10%
N	0.28%	2.77%
O	61.51%	43.10%
C	27.11%	38.11%

## References

1. N. Xiao, W. D. McCulloch and Y. Wu, *J. Am. Chem. Soc.*, 2017, **139**, 9475-9478.
2. S. Liu, J. Mao, Q. Zhang, Z. Wang, W. K. Pang, L. Zhang, A. Du, V. Sencadas, W. Zhang and Z. Guo, *Angew. Chem., Int. Ed.*, 2020, **59**, 3638-3644.