

Supporting Information

Optimal utilization of fluoroethylene carbonate in potassium ion batteries

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Experimental section

Materials and method:

KClO₄ (99% purity), and K metal (99.5%) were purchased from Sigma-Aldrich. Fluoroethylene carbonate (FEC) and propylene carbonate (PC) were purchased from DuoDuoChem. The glass fiber separator (GF/F, 420 μm thickness) was purchased from Whatman.

The based organic electrolyte solutions were prepared by dissolving the KClO₄ into PC with a 0.1 M concentration in an Ar-filled glove box. 5 % FEC additives (V/V) were added in this based organic electrolyte for forming SEI. For comparison, electrochemical tests were further conducted in 5% FEC-based and FEC-free electrolyte.

Besides, we also adopted the other method to treat the potassium foil. The potassium foil was dipped into pure FEC for 2 minutes, and then was rinsed by PC for three times to remove the redundant FEC prior to use. The cycling performance for this 2-min sample was also studied.

Electrochemical measurements:

Electrochemical tests were carried out using 2032 type coin cells. The cell consists of two potassium metal electrodes separated by a glass fiber membrane. 100 μL electrolyte was added into coin cells. Galvanostatic cycling was performed in a LANHE battery testing system at a current density of 0.1 mA cm^{-2} .

EIS measurements and DRT analysis

Electrochemical impedance spectroscopy (EIS) was performed on the potentiostat (VMP3, Biologic). The potentiostatic EIS of the potassium symmetric cell was measured after certain cycles. To be specific, the impedance was tested in the frequency range from 100kHz to 0.01Hz with an amplitude of 10 mV. In addition, six sample points were selected per decade frequency, each of which was repeated twice for average.

In the case of the DRT calculation, we adopted the open matlab code shared online by prof. Francesco Ciucci^{1,2}. It is based on the Tikhonov regularization, and we took 0.005 as the regularization parameter in our calculations. Moreover, the range of DRT fit was based on the frequency range from 100 kHz to 0.01Hz after the Kramers-Kronig validity test.

Characterizations:

The SEI composition was confirmed by X-ray photoelectron spectroscopy (PHI5000 VersaprobeIII XPS, ULVAC-PHI.INC). The surface topography was characterized by scanning electron microscope (Regulus 8100). ICP-MS was performed on Thermo XSeries 2. TOF-SIMS 5-100 (ION-ToF GmbH, Germany) was employed to analyze depth profiling. The sample was transferred under inert gas. A Bi_1^+ beam was used for depth profiling analysis and the typical sputtering area was $200 \mu\text{m} \times 200 \mu\text{m}$. A Cs^+ ion beam was used for the sputtering of the immersed K foil.

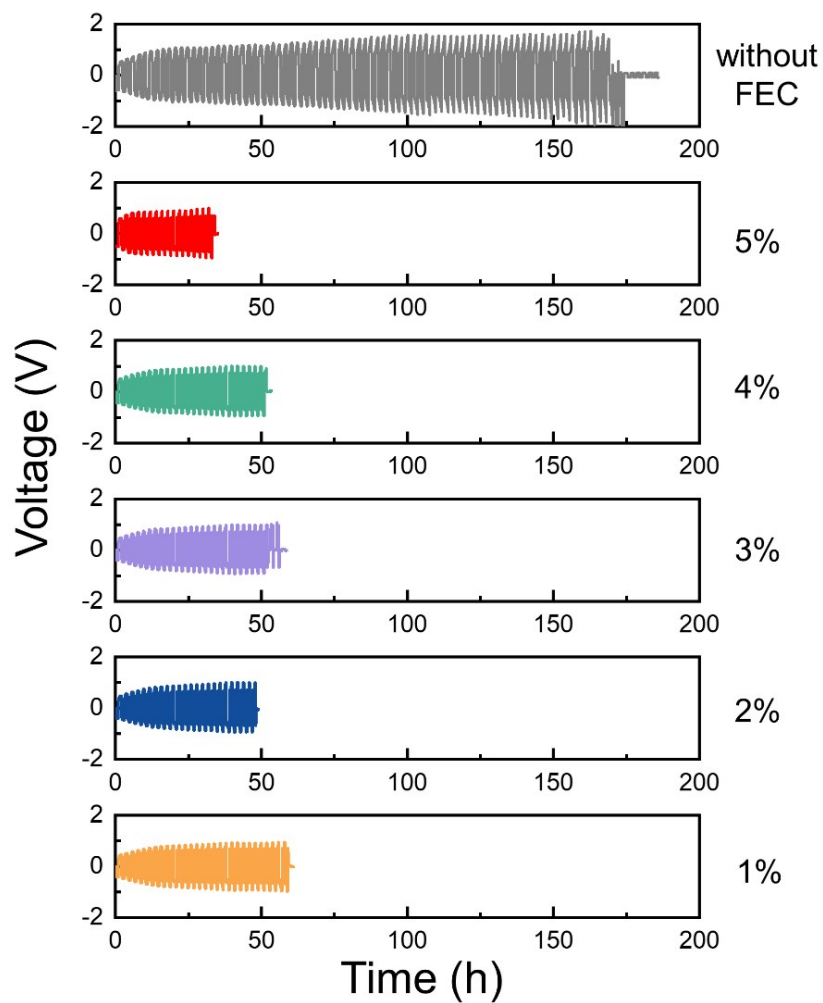


Figure S1 Galvanostatic cycling performance of K-K symmetric cells in electrolyte with different FEC concentrations.

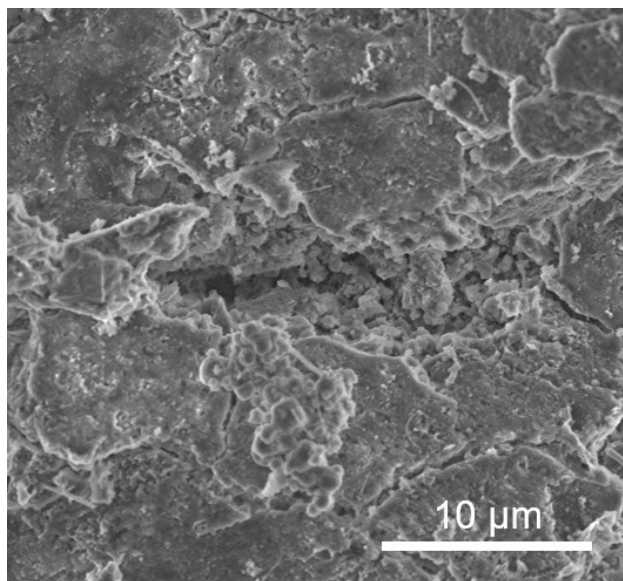


Figure S2 SEM image of the surface of K metal anode after cycling 174 hours in the KClO₄ electrolyte without FEC.

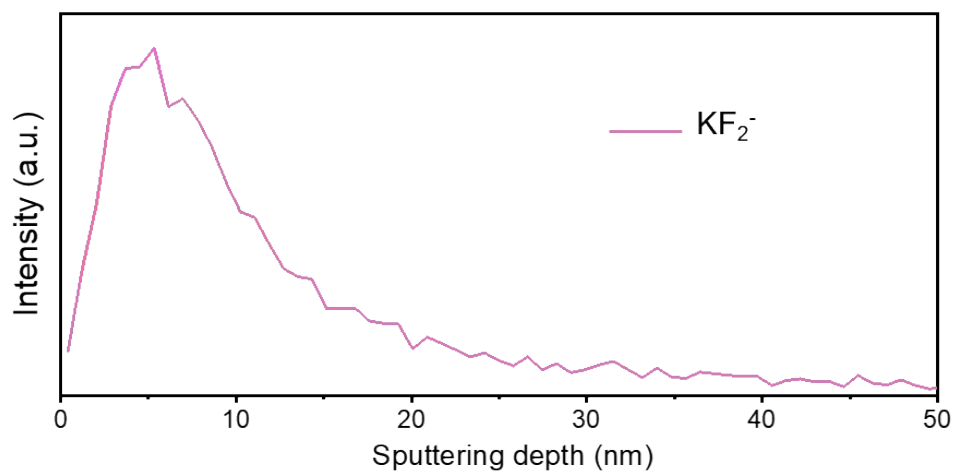


Figure S3 TOF-SIMS depth profile of KF_2^- collected on K metal anode after 2min-immersion. (The thickness of the SEI section containing KF component is about 20 nm.)

electrolyte	cycling performance	reference
<i>half-cell</i>		
0.05 M KClO ₄ PC	200 cycles	3
KClO ₄ PC containing 10% FEC	100 cycles	4
<i>symmetric cell</i>		
KPF ₆ ECDEC+5% FEC	97 h	5, 6
KPF ₆ ECDEC	125 h	
KFSI ECDEC+5% FEC	180 h	
KFSI ECDEC	208 h	
1 M KPF ₆ PC	200 h	7
ECDEC	220 h	8
2 M KFSI TEP	750 h	9
KPF ₆ ECDEC (K-ACM electrodes)	230 h	10
0.1 M KClO ₄ PC	1200 h	<i>this work</i>

Table S1 Comparison of cycling performance with various electrolytes previously reported for PIBs.

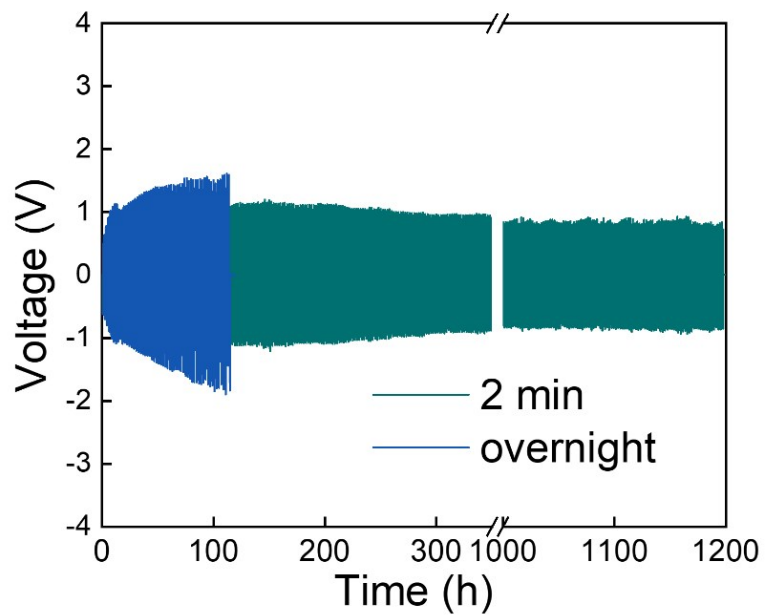


Figure S4 Cycling performance of K-K symmetric cells with immersing the K foil into the pure FEC for different time.

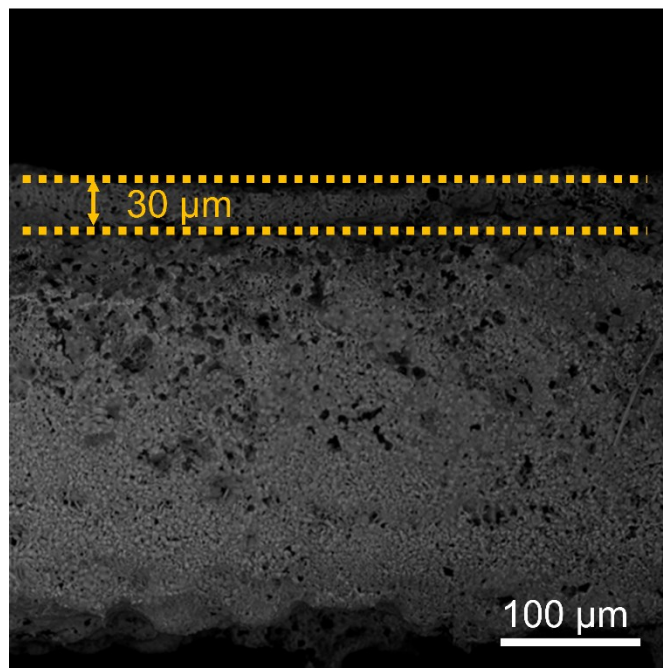


Figure S5 Cross-section SEM image of K metal anode after cycling with a 2 min-immersing pretreatment.

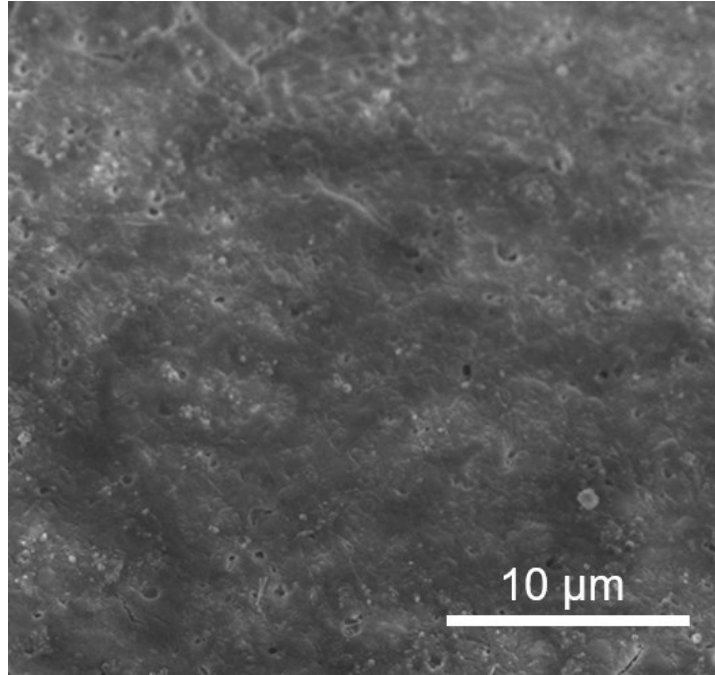


Figure S6 SEM images of the surface of K metal anode treated with FEC for 2 min after cycling 174 hours.

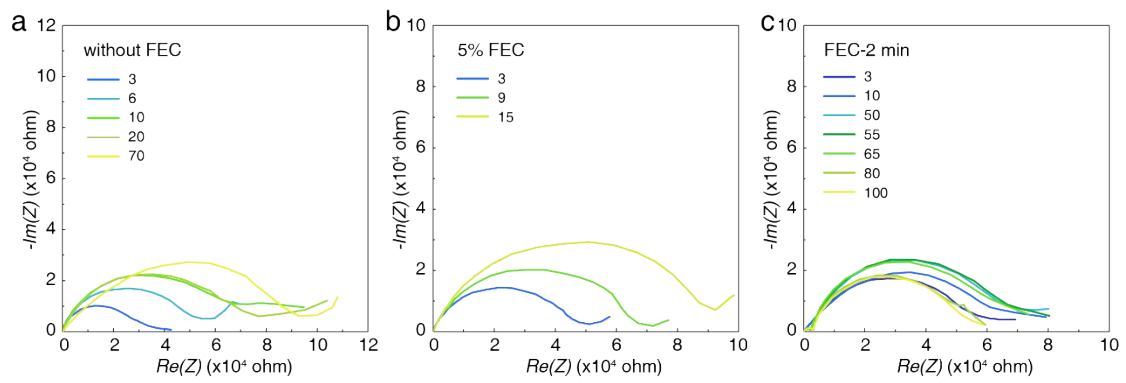


Figure S7 *In-situ* EIS results of the K-K symmetric cell with 0.1 M KClO_4 -PC electrolyte after various cycles: (a) without FEC, (b) electrolyte with 5% FEC, and (c) K metal anode treated with FEC for 2 min.

References

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