
Supplementary Information

Interface Chemistry Engineering towards Layer-structured Oxide for Potassium-Ion Batteries

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Experimental section

Materials Synthesis

Synthesis of $K_{0.5}MnO_2$: Using the traditional solid-phase synthesis method, 2 mmol of anhydrous potassium carbonate (K_2CO_3) and 4 mmol of Mn_2O_3 were weighed and milled in an onyx ball mill jar at 400/rpm for 8 h. After removal, the powdered material was dried in a vacuum oven, pressed into flakes by a press, and then calcined in a tube furnace at 800 °C for 8 h. The powdered material was cooled down naturally to 200 °C,

and transferred to a glove box with AR for storage. P3-KMO was used as a cathode material for PIB.

Preparation of electrolytes

The electrolyte was prepared using the following procedure: A 0.8 mol potassium hexafluorophosphate (KPF_6) EC/PC was prepared using a mixture of ethylene carbonate (EC) and diethyl carbonate (PC) in a 1:1 volume ratio as the solvent. A 0.8 M KPF_6 EC/DEC electrolyte was prepared using a mixture of EC and diethyl carbonate (DEC) in a 1:1 volume ratio as the solvent. 3 M potassium bis(fluorosulfonyl)imide (KFSI) was dissolved in ethyl methyl carbonate (EMC) to form a 3 M KFSI EMC electrolyte. A 3 M KFSI EC/PC was prepared using a mixture of EC and PC in a 1:1 volume ratio as the solvent. A 3 M KFSI EC/DEC was prepared using a mixture of EC and DEC in a 1:1 volume ratio as the solvent, and a 3 M KFSI EC/DEC/EMC was prepared using a mixture of EC, DEC and EMC in a 1:1:1 volume ratio as the solvent.

Electrode preparation

The test cathode was prepared by coating an aluminum foil with a slurry made by mixing 70% active material, 20% super P, and 10% polyvinylidene fluoride (PVDF) in N-methylpyrrolidone (NMP), and then drying the slurry in a vacuum oven at 120 °C overnight.

Materials Characterization

Raman spectroscopy were acquired using a customized LabRAM HR800 confocal Raman microscope (Horiba Jobin Yvon). The microscope was equipped with an 18 mW He: Ne 633 nm laser source for excitation, a 1800 or 600 lines/mm grating to disperse the scattering light with different resolutions, and a long working distance objective lens (Nikon 50 x 0.45 NA). All MS data were acquired on an LTQ Orbitrap XL hybrid mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). The Orbitrap ion transfer capillary was held at 285 °C, and the resolution was set to 30,000 for all analyses. All data were analyzed using the Qual Browser feature of the Xcalibur TM program (Thermo Fisher Scientific, San Jose, CA). The structure analysis was collected by XRD (SHIMADZU, XRD7000). The chemical states of the elements in the electrode sheets before and after cycling were characterized using XPS (KRATOS),

and the data were corrected with the C 1s binding energy (284.8 eV). (284.8 eV) as the energy standard correction data. The detailed morphology changes of the electrodes were characterized by TEM (Titan G2 60-300 with image corrector). Ex-situ Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet iS5 iD7 ATR spectromete. *In-situ* FTIR reflectance spectra were collected using a Nicolet iS-50 spectrometer (Thermo Fisher Scientific Co.) equipped with a liquid nitrogen-cooled MCT (HgCdTe) detector and a silicon trigonal prism with a gold-plated surface as an IR window. The corresponding electrochemical data were measured using sp-200 electrochemical workstation. In the in situ three-electrode cell, the gold-plated surface was used as the working electrode, excess AC was used as the counter electrode, and a K metal electrode was used as the reference electrode. IR spectra of electrolyte reduction were collected in different electrolyte systems with a scan number of 32 and a resolution of 4 cm⁻¹. For the CV tests, the electrolyte was scanned from open circuit potential to 3.9 V at a scan rate of 1 mV s⁻¹ and then returned to 1.5 V for 2 cycles. Before each in-situ test, the spectrum without electrolyte was collected at the open circuit potential as the background spectrum.

Electrochemical tests

The KMO cathode is stamped into a 12 mm diameter electrode and assembled into a CR2032 coin cell. The KMO cathodes are stamped into 12 mm diameter electrodes and assembled into CR2032 coin cells. Cycle and rate performance of half and full batteries is measured by the Neware Test System (CT-4008Tn-5V20mA-164). Ex-situ EIS of continuous deposition process was performed by Donghua electrochemical workstation (DH7006, Jiangsu Donghua Analytical Instruments Co., Ltd.). Galvanostatic intermittent titration technique (GITT, Neware tester) were conducted to calculate the impedance data and K⁺ diffusion kinetics.

Theoretical calculation

Electrolyte structure simulations: The Lee-Yang-Parr correlation functional (B3LYP) combined with 6-31G* basis set was used to perform Density Functional Theory (DFT) calculations for solvent and electrolyte in a Gaussian 16W program package.¹ The hybrid density functional B3LYP with the 6-31G* basis sets has been used for the

structure optimization as well as the electronic structures calculation. The SMD implicit solvation model² was used to describe the solvation effect. Visualization of the atomic and electronic structures were made by using Multiwfn software.³ The desolvation energy of clusters is defined as follows: $E_{des} = E[\text{K-solvent}_n]^+ + E[\text{solvent}] - E[\text{K-solvent}_n]^+$. The Molecular dynamics (MD) results were subsequently calculated at 100 ps of NPT (canonical) ensemble and 500 ps of NVT (constant-pressure, constant-temperature) ensemble with a Compass II force field and a 0.001 step length as well as a Berendsen pressure-controlling method. The coordination number is obtained from the radial distribution function (RDF) and is calculated as follows: $CN(r) = \sum 4\pi r^2 \rho g(r) \delta r$.

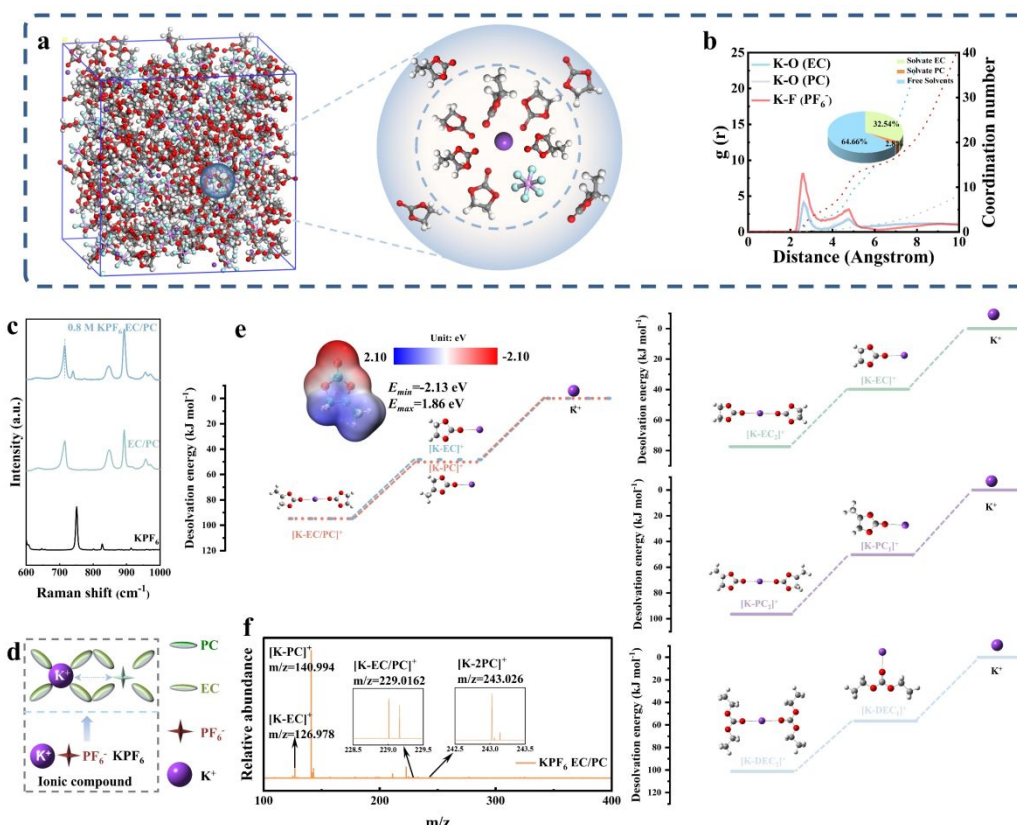


Figure S1. a) Snapshots of 0.8 M KPF₆ EC/PC. b) Radical distribution functions and coordination numbers of 0.8 M KPF₆ EC/PC. c) Raman spectra of 0.8 M KPF₆ EC/PC. d) Schematic interaction of ions (K⁺, PF₆⁻). e) Electrostatic potential energy (ESP) mapping of PC the desolvation energies of different solvated molecule's structures and the desolvation energies of different solvated molecule's structures (including [K-EC/PC]⁺; [K-EC₂]⁺; [K-PC₂]⁺ and [K-DEC₂]⁺). f) Electrospray ionization mass spectroscopy (ESI-MS) spectra (positive mode) in 0.8 M KPF₆ EC/PC. The peak intensities are normalized.

In the electrolyte, the interaction between cations and solvent molecules is primarily achieved through Coulombic forces, i.e., electrostatic forces. When two solvents compete for coordination with cations, each solvent molecule attempts to form coordination bonds with the cations to stabilize them and reduce their charge density. When a solvent molecule is removed from the system, the remaining solvent molecules will readjust to adapt to the new environment. Since the charge of the cation remains unchanged and the number of coordinating solvent molecules is reduced, the coordination interaction between the remaining solvent molecules and the cation is enhanced. This enhancement occurs because, with fewer competitors, the interaction force between each solvent molecule and the cation increases.

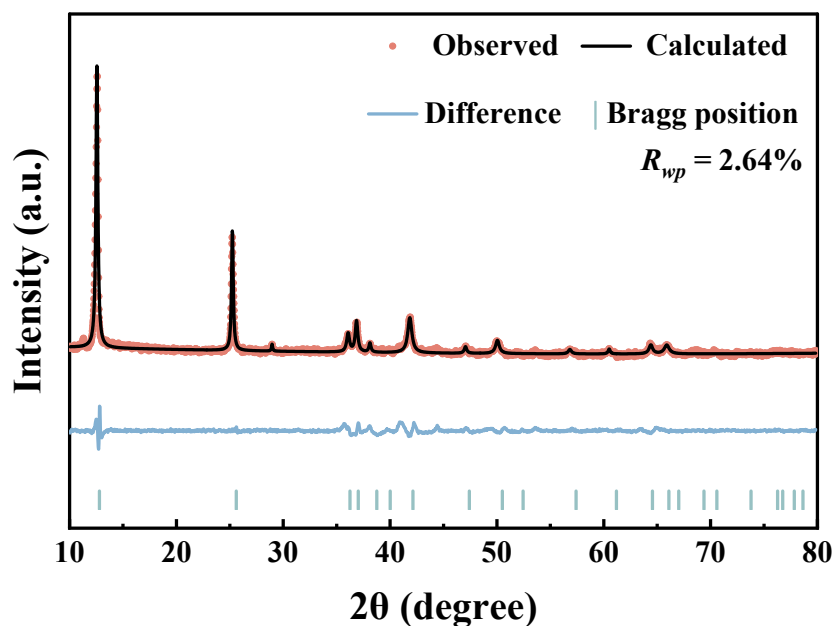


Figure S2. XRD Rietveld analysis of $K_{0.5}MnO_2$ electrode.

By Rietveld refinement, we determined the crystal structure of the $K_{0.5}MnO_2$ material to be a hexagonal crystal system P3 phase with cell parameters $a = b = 2.88$ nm, $c = 19.08$ nm, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. These parameters are consistent with the standard cell parameters of $K_{0.5}MnO_2$ reported in the literature, which verifies the successful synthesis of the material. The Rietveld analysis also provides information on the atomic coordinates and occupancies. The Mn atoms are located in octahedral sites and the K atoms are located in trigonal prismatic sites, which is consistent with the expected structure of $K_{0.5}MnO_2$.

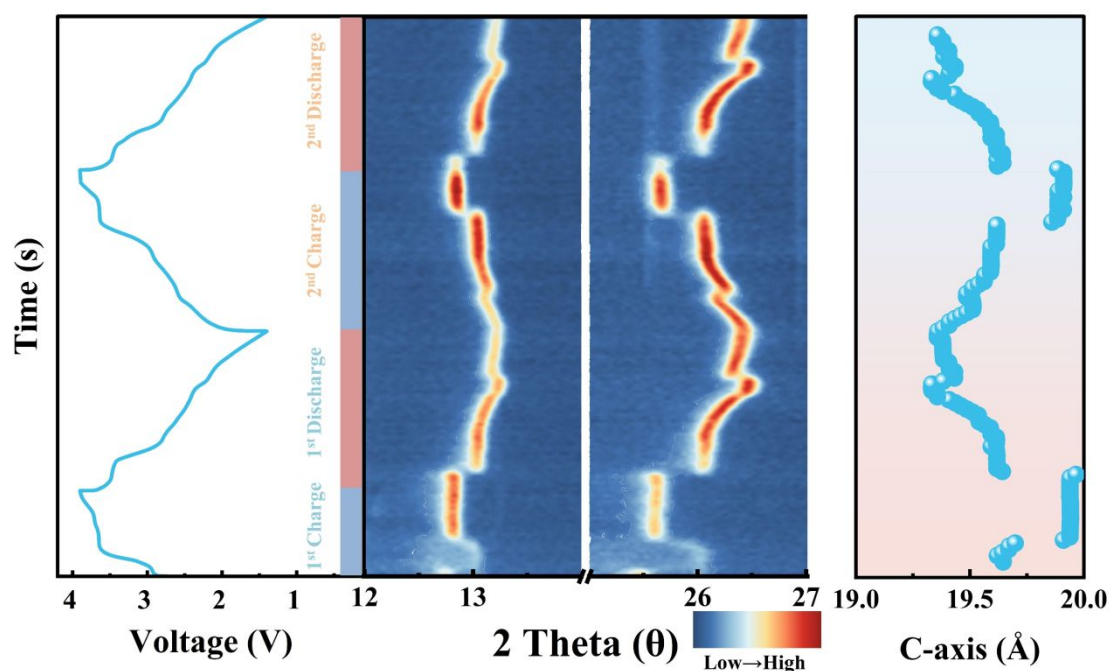


Figure S3. *In-situ* XRD image, charge/discharge curves and *c*-axis distance change curve of KMO.

The figure illustrates the evolution of the (003) and (006) peaks during the initial charging process of KMO. Initially, these peaks shift to lower angles, indicating an increase in the interlayer face-to-face spacing of the [TMO₂] sheets along the *c*-axis. This is attributed to the deintercalation of K⁺ ions, which serve as an electrostatic shielding between adjacent O ions within the [MnO₆] sheets. As the K⁺ ions deintercalate, the shielding effect diminishes, allowing the electrostatic repulsion between adjacent O ions to become dominant, leading to an increase in the distance between the [TMO₂] sheets.⁴ However, during further charging, due to additional potassium removal, the (003) and (006) peaks shift to higher angles. This phenomenon correlates with the transition of the KMO electrode from the P3 phase to the O3 phase, accompanied by a sliding of the transition metal layers, which reduces the interplanar spacing between them.

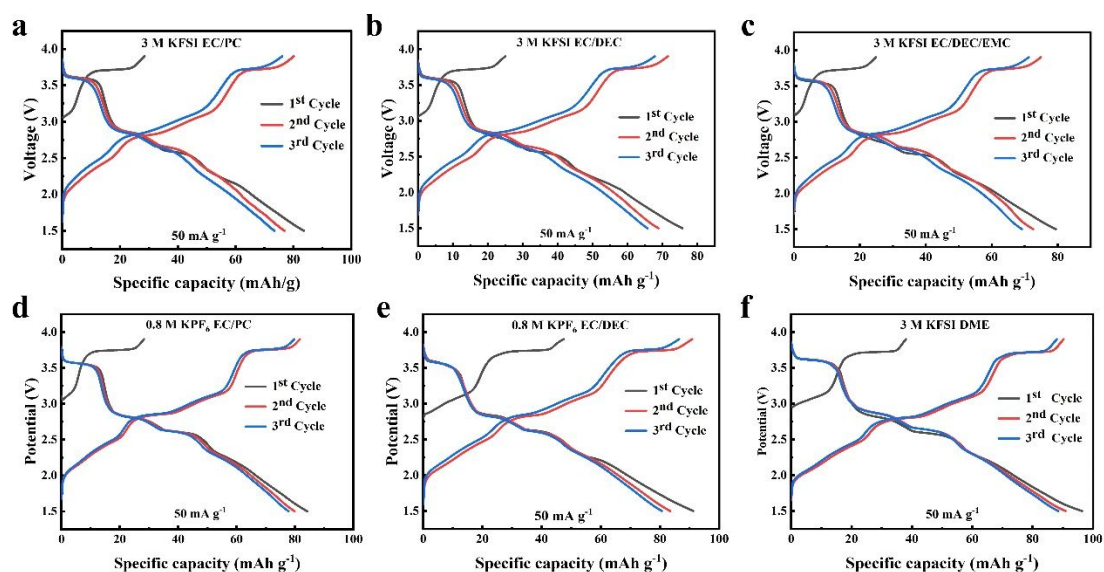


Figure S4. Electrical charge/discharge curves for the first three cycles of different electrolytes: a) 3 M KFSI EC/PC. b) 3 M KFSI EC/DEC. c) 3 M KFSI EC/DEC/EMC. d) 0.8 M KPF₆ EC/PC. e) 0.8 M KPF₆ EC/DEC. (f) 3 M KFSI DME.

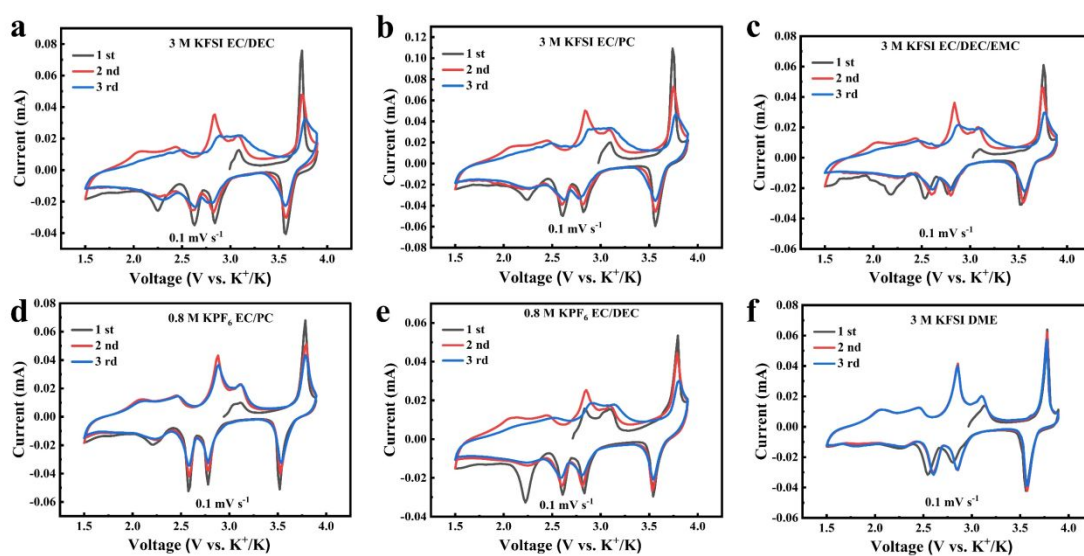


Figure S5. CV curves of different electrolytes: a) 3 M KFSI EC/PC. b) 3 M KFSI EC/DEC. c) 3 M KFSI EC/DEC/EMC. d) 0.8 M KPF₆ EC/PC. e) 0.8 M KPF₆ EC/DEC. f) 3 M KFSI DME.

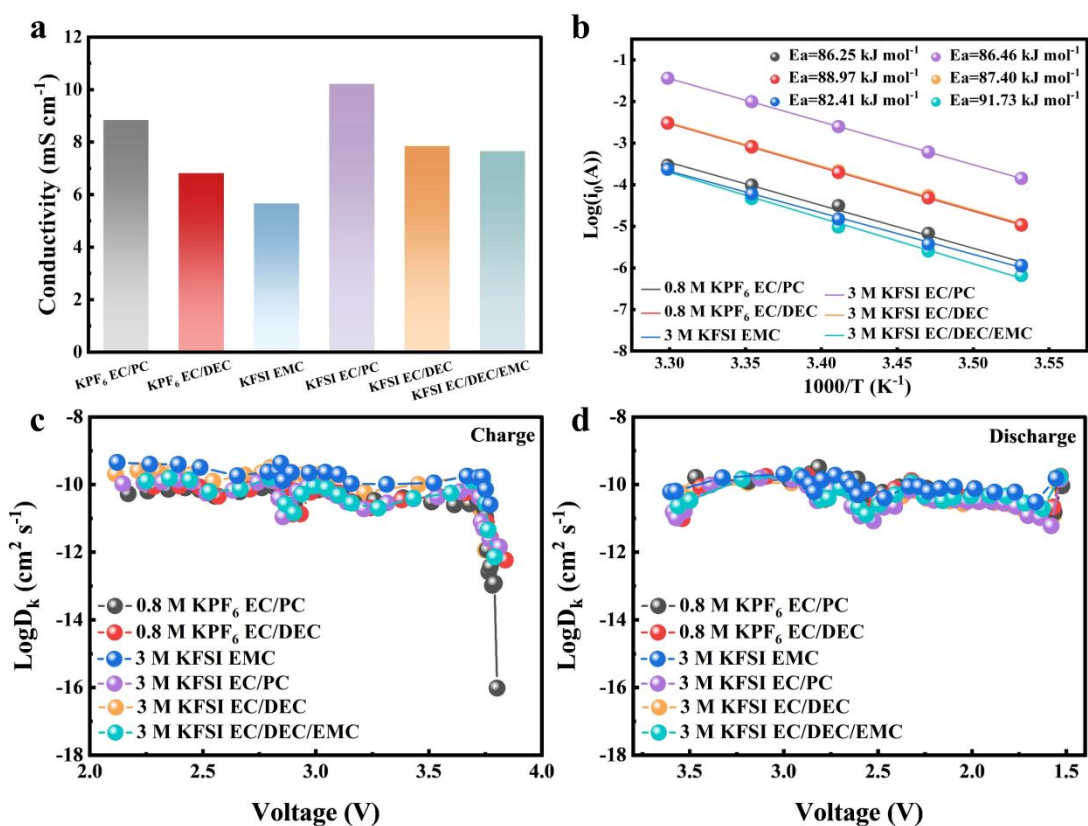


Figure S6. a) Ionic conductivity of different electrolytes at room temperature. b). Activation energy calculations of the EIS test at variable temperatures. The variation curve of K⁺ (D_{K^+}) diffusion coefficient during charge c) and discharge d) processes.

Figure S6a shows the ionic conductivity of various carbonate electrolytes, and the results show that the ionic conductivity of 3 M KFSI EMC is relatively low. However, we also observed that while the weakly solvated structure may have some impact on the ion transport process in the electrolyte, it also exhibits excellent desolvation capabilities. These abilities have a clear positive effect in promoting the formation of a stable CEI layer and improving the reaction kinetics at the electrolyte interface.

The results of activation energy (**Figure S6b**) and electrostatic intermittent titration technique (GITT) (**Figure S6c, d**) tests indicate that the activation energy and diffusion coefficient of the 3 M KFSI EMC are at a high level. This suggests that the kinetic performance of the cell was not significantly affected despite the low ionic conductivity. Although the weak solvation structure may lead to a decrease in the efficiency of the ion transfer process in the electrolyte, its advantages in forming a stable CEI and improving the reaction kinetics at the electrolyte interface are more critical.

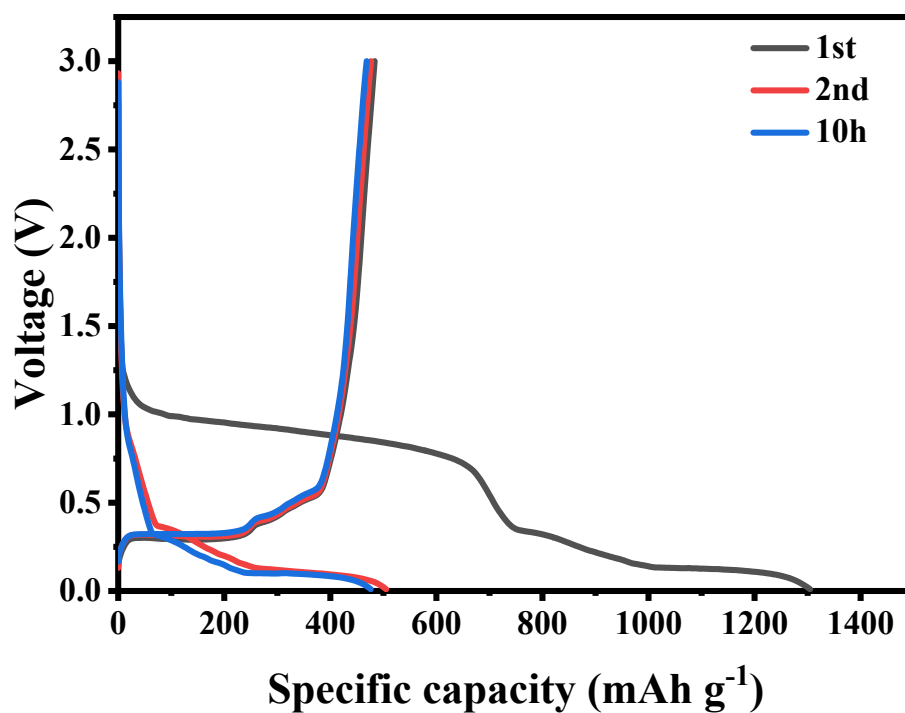


Figure S7. Electrochemical performance of Nano-graphite in half-cells.

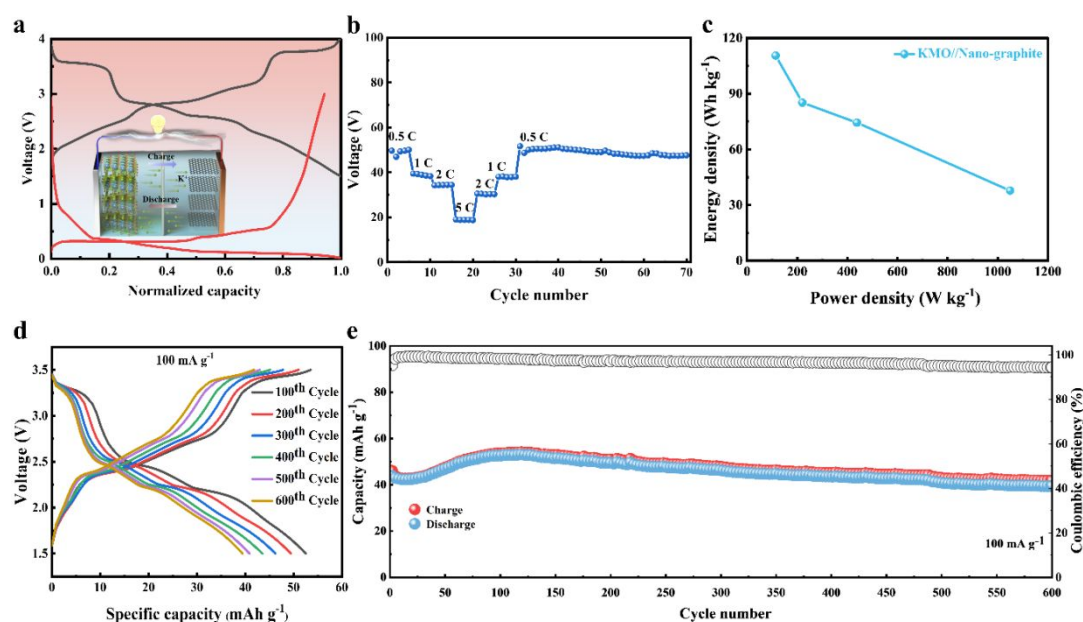


Figure S8. Demonstration of PIBs based on KMO//Nano-graphite configuration: a) Schematic of PIBs based on KMO//Nano-graphite configuration and charge/discharge curves of KMO and Nano-graphite in half-cells. b). Rate and cycling performance at 50 mA g⁻¹. c) Ragone plots. d) Electrochemical charge/discharge curves of PIBs at 100 mA g⁻¹ e) cycling performance at 100 mA g⁻¹.

We paid special attention to the effect of current density on the activation effect of electrode materials. In our experiments, we found that the activation treatment at lower current densities can effectively improve the long-term cycling stability.

Finally, regarding the use of NP ratios, in our battery design, the selection of NP ratios takes into account the multiplier performance and cycle stability of the battery. We found that when the NP ratio is between 1.1 and 1.5, the overall performance of the battery is optimal.

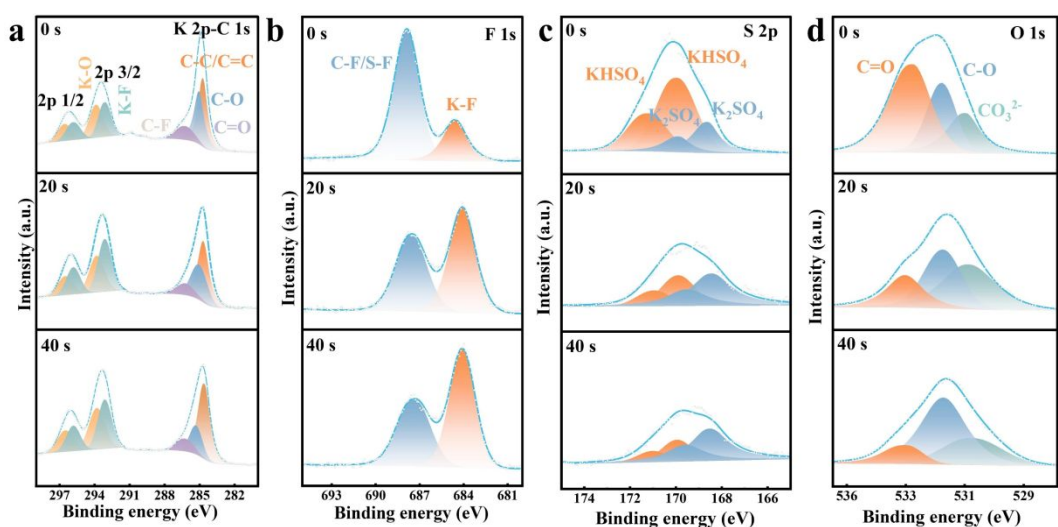


Figure S9. a-d) XPS depth profiles of KMO electrodes in 3 M KFSI EC/DEC electrolyte after sputtering for 0, 20 and 40 seconds. a) K 2p-C 1s, b) F 1s, c) S 2p, and d) O 1s.

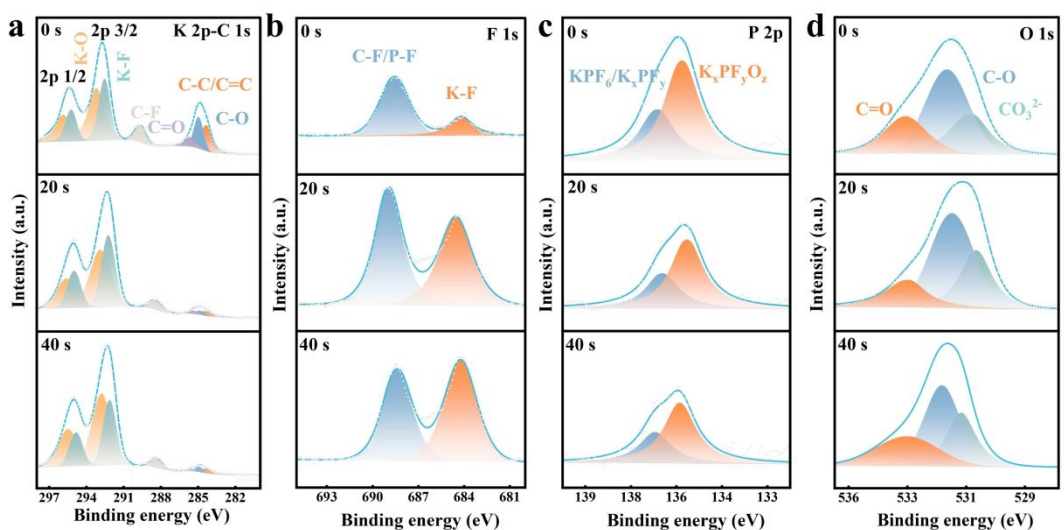


Figure S10. a-d) XPS depth profiles of KMO electrodes in 0.8 M KPF₆ EC/PC electrolyte after sputtering for 0, 20 and 40 seconds. a) K 2p-C 1s, b) F 1s, c) P 2p, and d) O 1s.

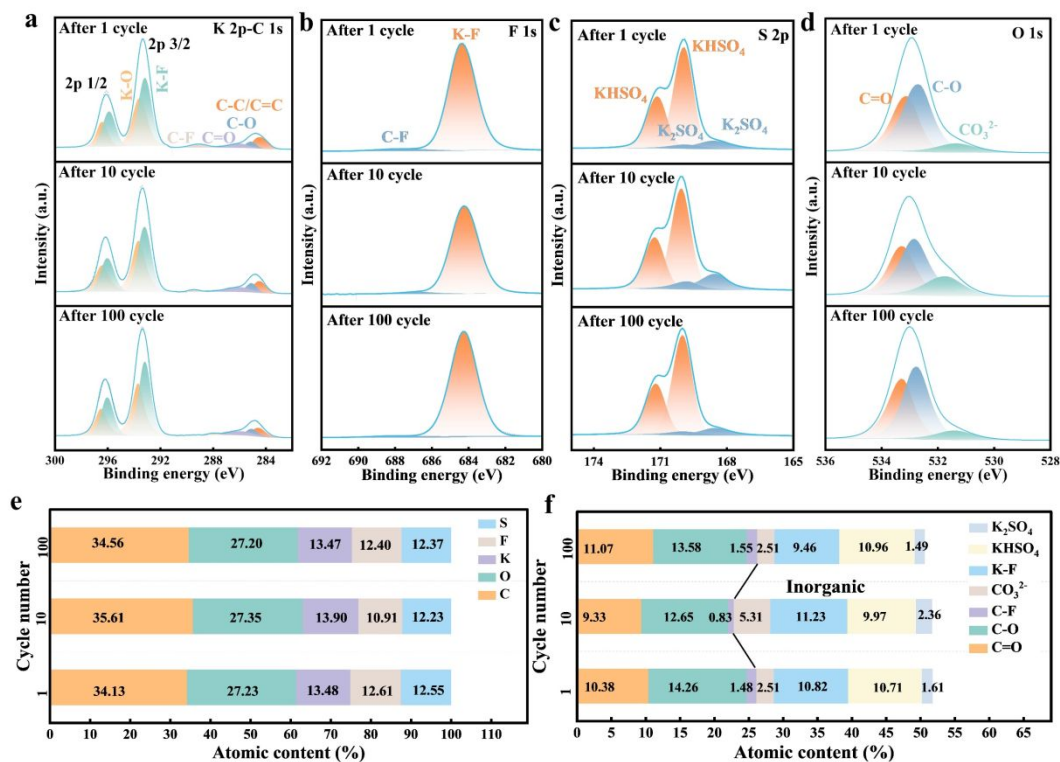


Figure S11. a-e) XPS of KMO electrodes with 3 M KFSI EMC as electrolyte after 1, 10 and 100 cycles at a current density of 50 mA g⁻¹. a) K 2p-C 1s, b) F 1s, c) S 2p, and d) O 1s. The calculated percent compositions of e) elements and f) inorganic salts in the KMO electrodes.

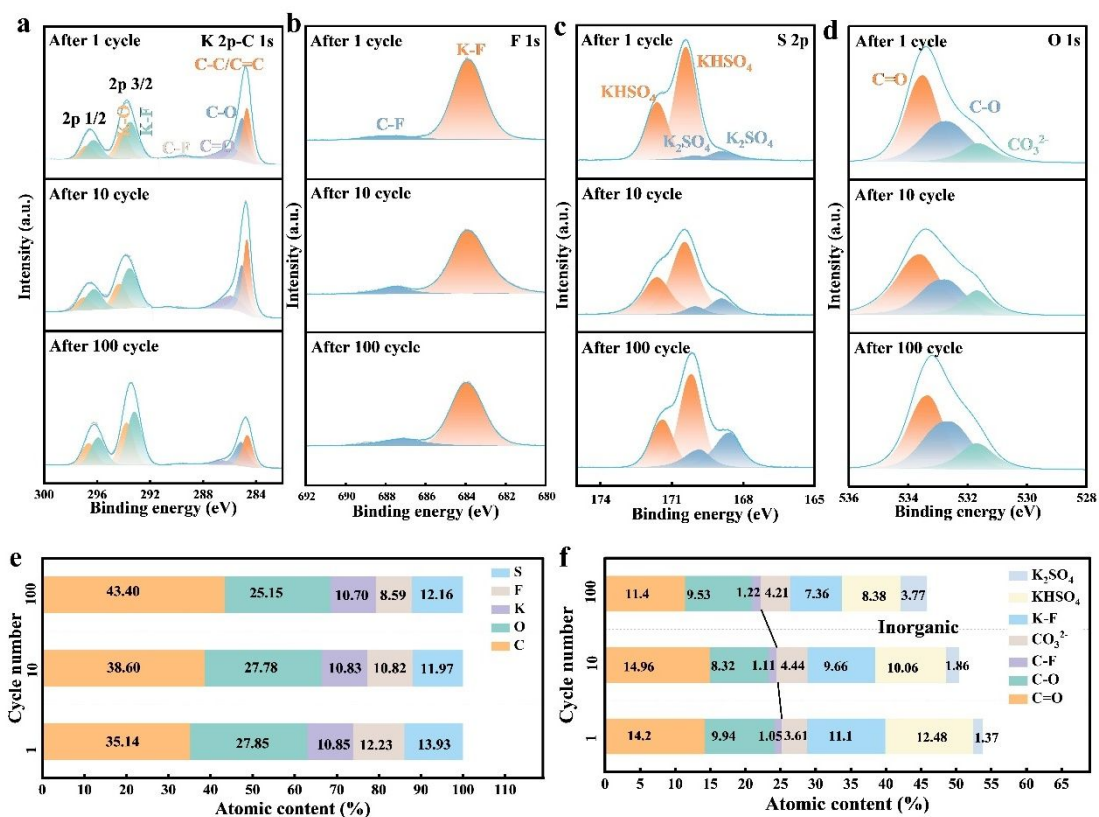


Figure S12. a-e) XPS of KMO electrodes with 3 M KFSI EC/DEC as electrolyte after 1, 10 and 100 cycles at a current density of 50 mA g⁻¹. a) K 2p-C 1s, b) F 1s, c) S 2p, and d) O 1s. The calculated percent compositions of e) elements and f) inorganic salts in the KMO electrodes.

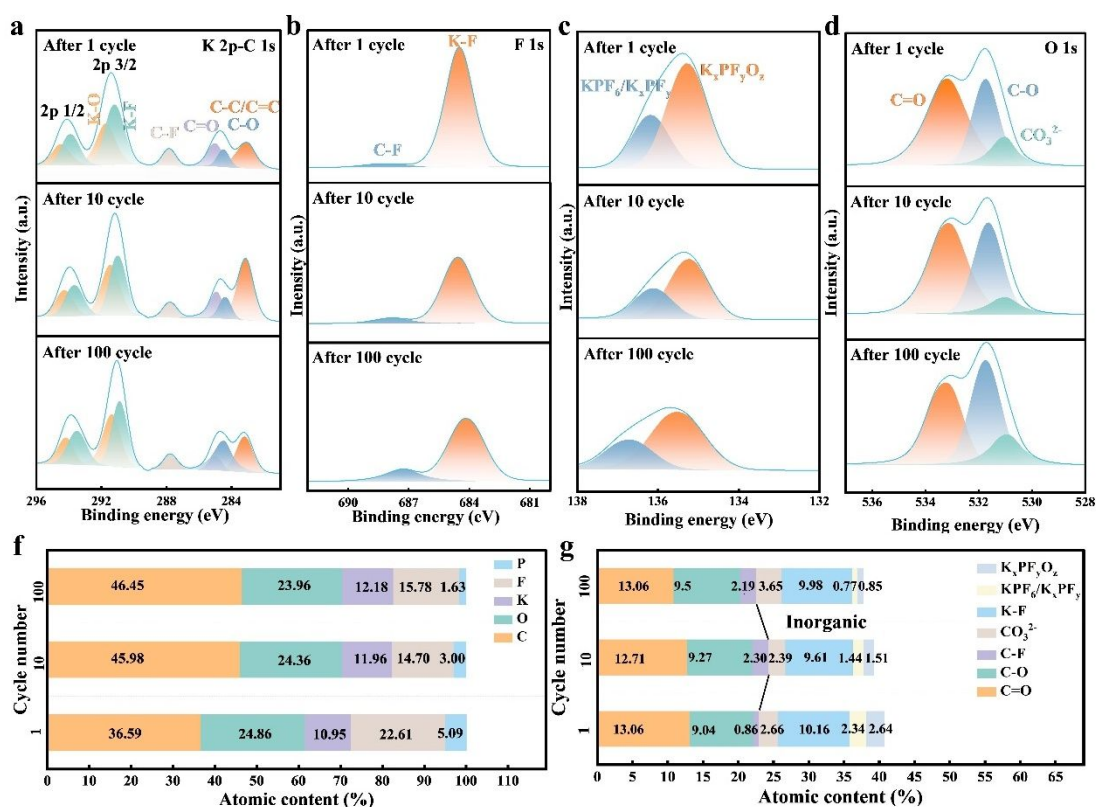


Figure S13. a-e) XPS of KMO electrodes with 0.8 M KPF_6 EC/PC as electrolyte after 1, 10 and 100 cycles at a current density of 50 mA g^{-1} . a) K 2p-C 1s, b) F 1s, c) S 2p, and d) O 1s. The calculated percent compositions of e) elements and f) inorganic salts in the KMO electrodes.

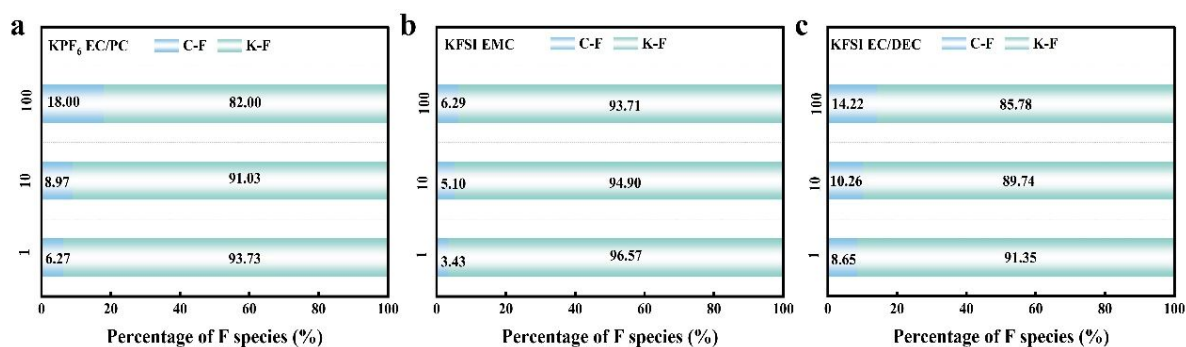


Figure S14. Evolution of percentage of the different F species in a) 0.8 M KPF_6 EC/PC, b) 3 M KFSI EMC, and c) 3 M KFSI EC/DEC electrolytes.

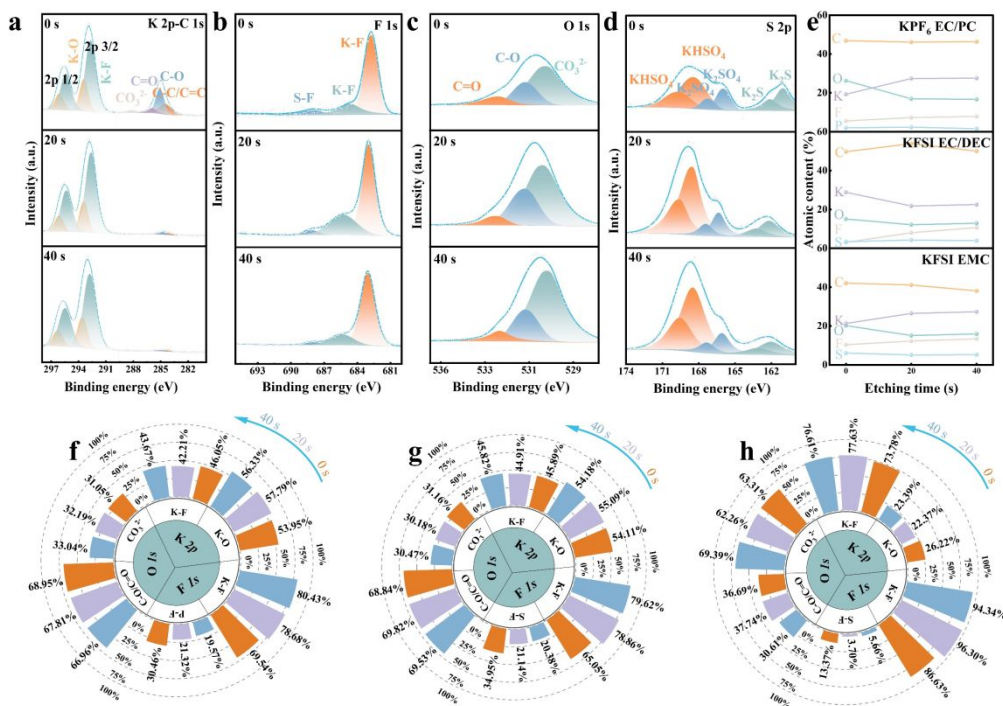


Figure S15. a-d) XPS depth profiles of Bare K electrodes in 3 M KFSI EMC electrolyte after sputtering for 0, 20 and 40 seconds. a) K 2*p*-C 1*s*, b) F 1*s*, c) S 2*p*, and d) O 1*s*. e) Atom concentration on the cycled Bare K electrode with varied sputtering depth in 0.8 M KPF₆ EC/PC, 3 M KFSI EC/DEC and 3 M KFSI EMC. As the etching time increases, the ratio of individual chemical bonds. f) 0.8 M KPF₆ EC/PC, g) 3 M KFSI EC/DEC, h) 3 M KFSI EMC.

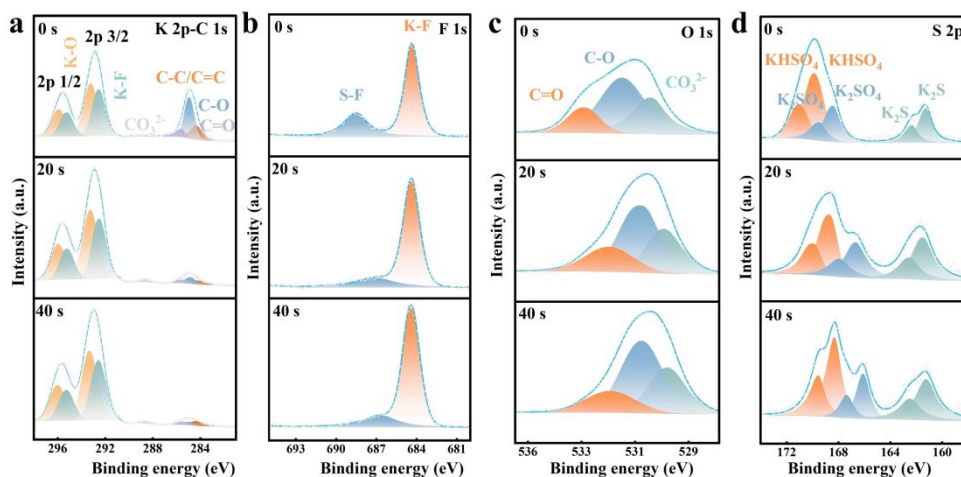


Figure S16. a-d) XPS depth profiles of Bare K electrodes in 3 M KFSI EC/DEC electrolyte after sputtering for 0, 20 and 40 seconds. a) K 2*p*-C 1*s*, b) F 1*s*, c) S 2*p*, and d) O 1*s*.

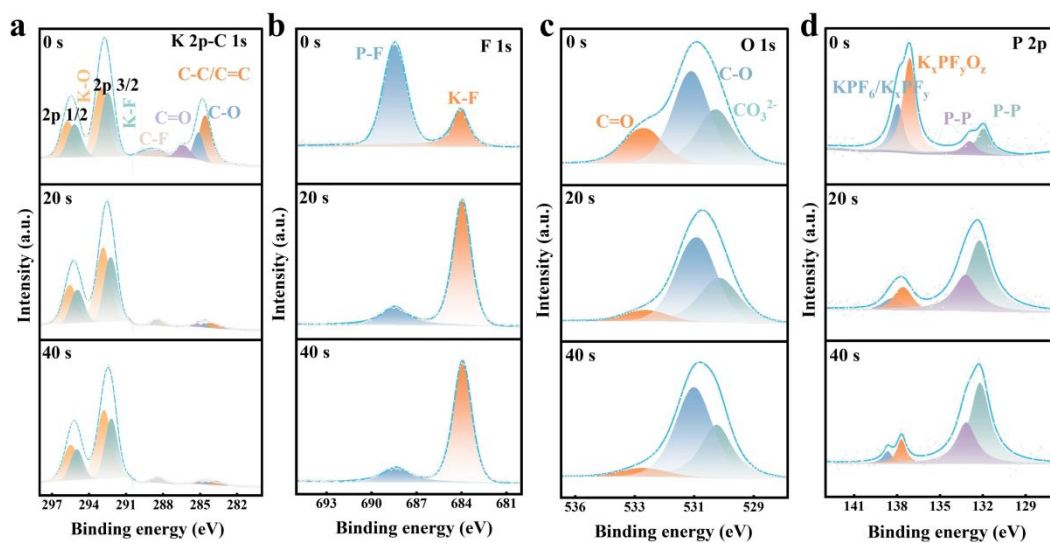


Figure S17. a-d) XPS depth profiles of Bare K electrodes in 0.8 M KPF_6 EC/PC electrolyte after sputtering for 0, 20 and 40 seconds. a) K 2p-C 1s, b) F 1s, c) P 2p, and d) O 1s.

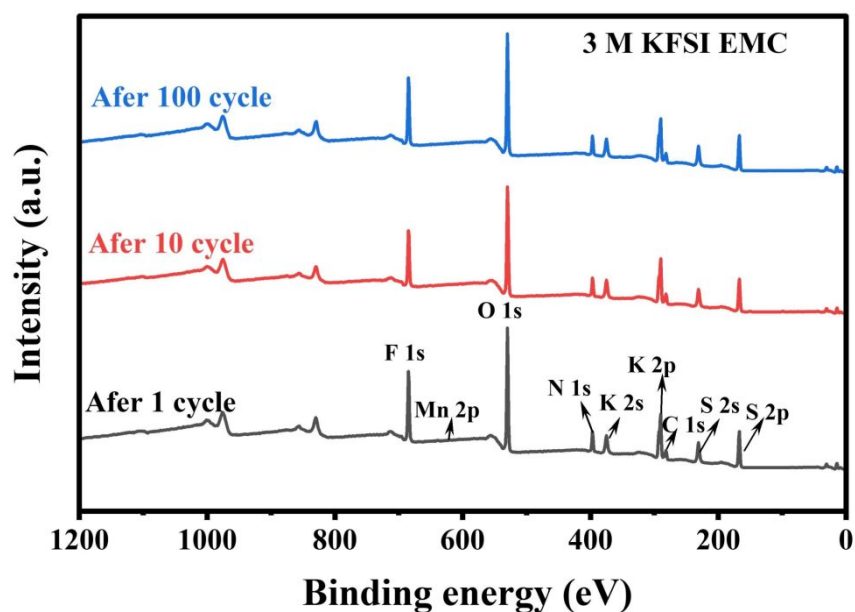


Figure S18. XPS full spectrum of KMO electrodes in 3 M KFSI EMC electrolyte after 1, 10 and 100 cycles, respectively.

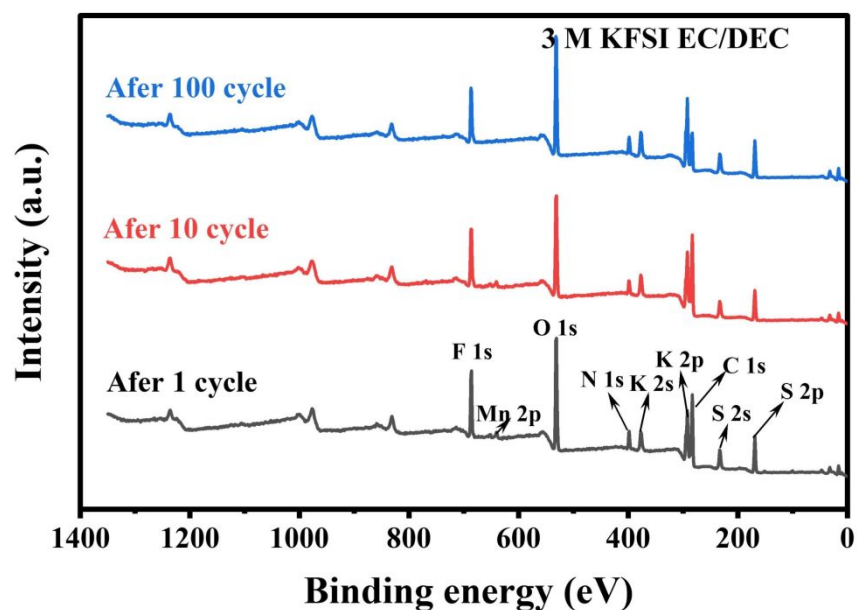


Figure S19. XPS full spectrum of KMO electrodes in 3 M KFSI EC/DEC electrolyte after 1, 10 and 100 cycles, respectively.

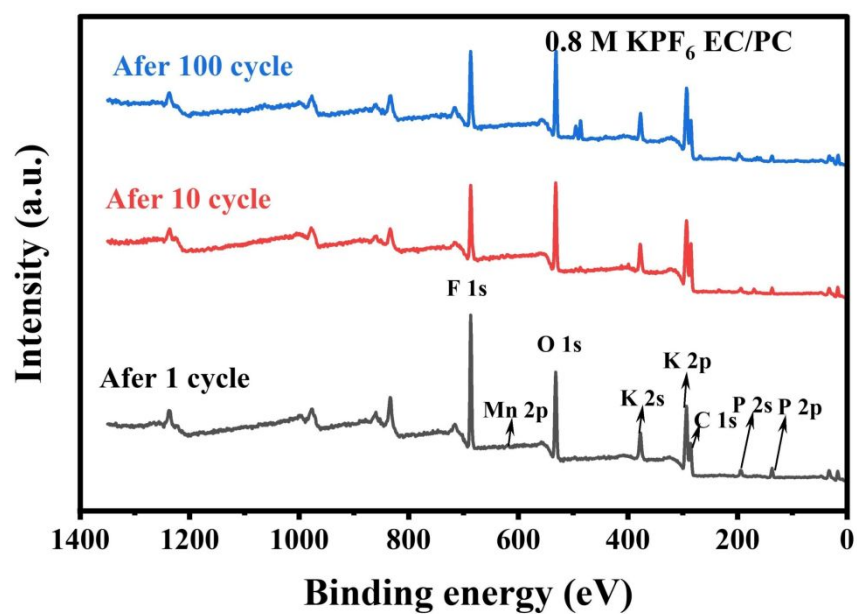


Figure S20. XPS full spectrum of KMO electrodes in 0.8 M KPF₆ EC/PC electrolyte after 1, 10 and 100 cycles, respectively.

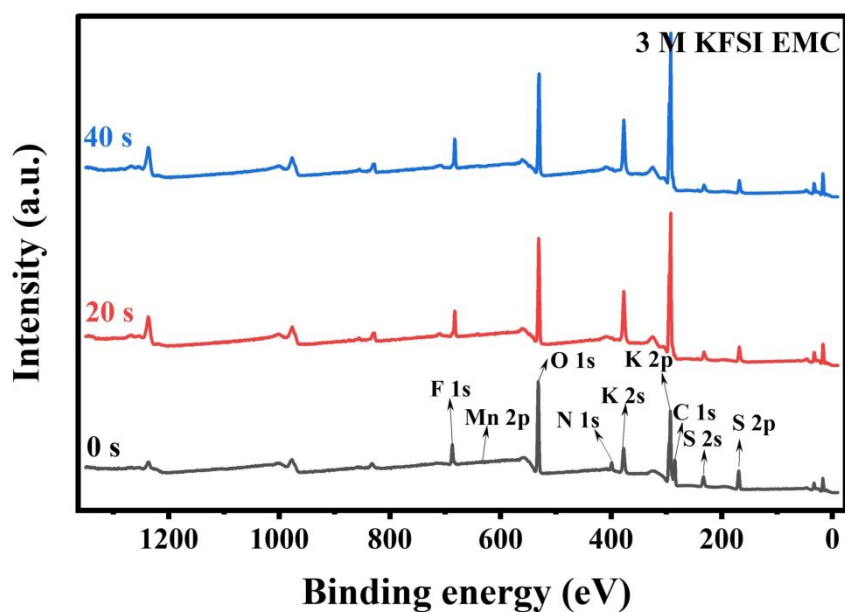


Figure S21. XPS full spectrum of KMO electrodes in 3 M KFSI EMC electrolyte after sputtering for 0, 20 and 40 seconds.

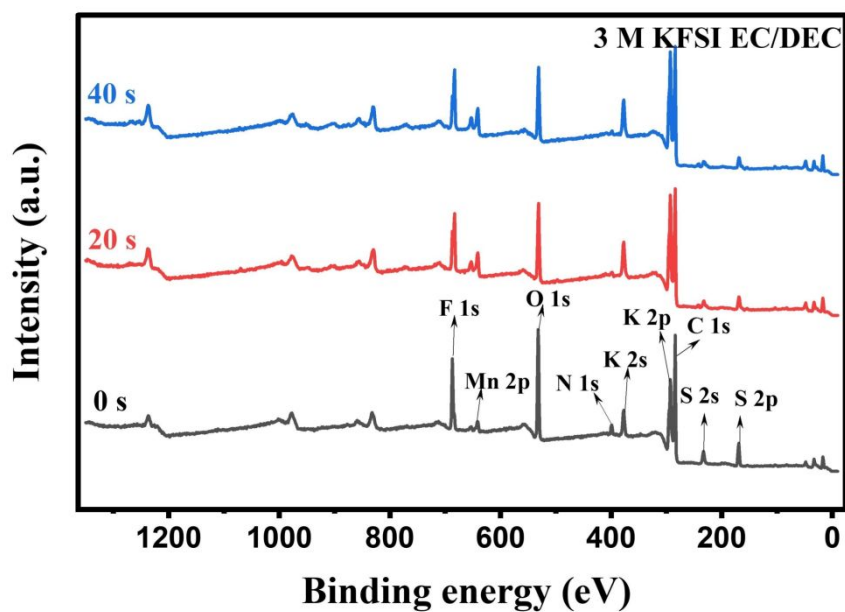


Figure S22. XPS full spectrum of KMO electrodes in 3 M KFSI EC/DEC electrolyte after sputtering for 0, 20 and 40 seconds.

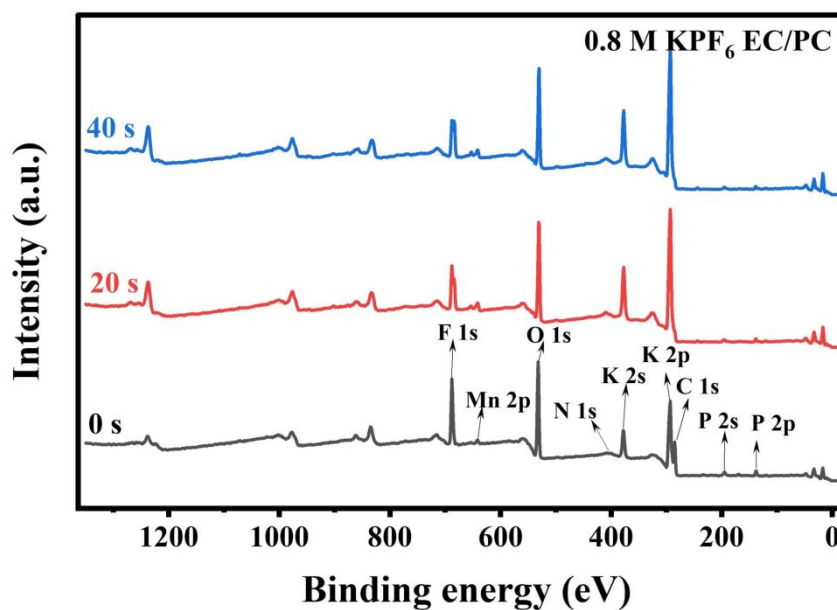


Figure S23. XPS full spectrum of KMO electrodes in 0.8 M KPF₆ EC/PC electrolyte after sputtering for 0, 20 and 40 seconds.

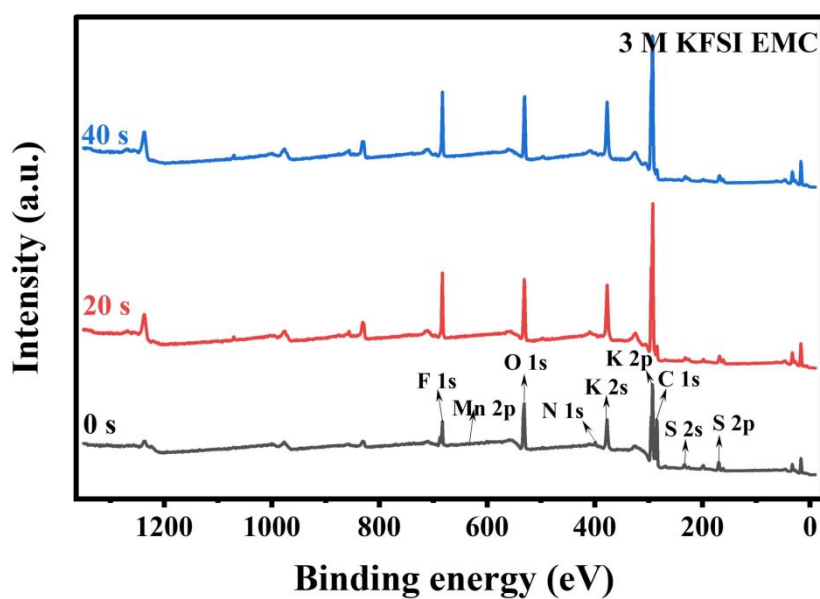


Figure S24. XPS full spectrum of Bare K electrodes in 3 M KFSI EMC electrolyte after sputtering for 0, 20 and 40 seconds.

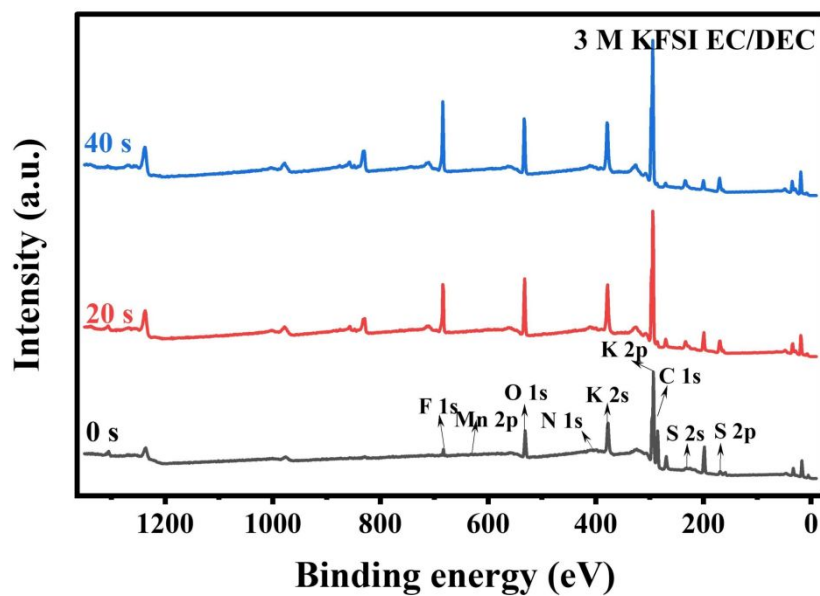


Figure S25. XPS full spectrum of Bare K electrodes in 3 M KFSI EC/DEC electrolyte after sputtering for 0, 20 and 40 seconds.

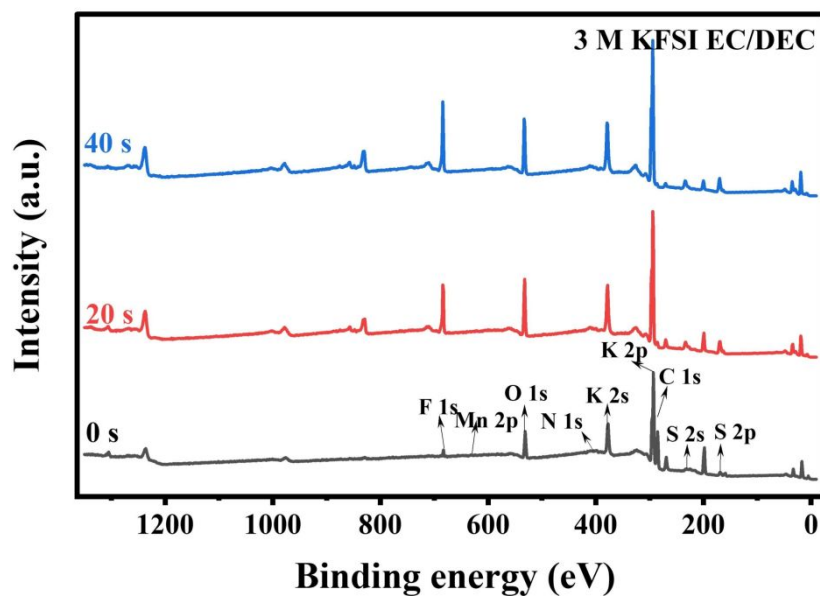


Figure S26. XPS full spectrum of Bare K electrodes in 0.8 M KPF₆ EC/PC electrolyte after sputtering for 0, 20 and 40 seconds.

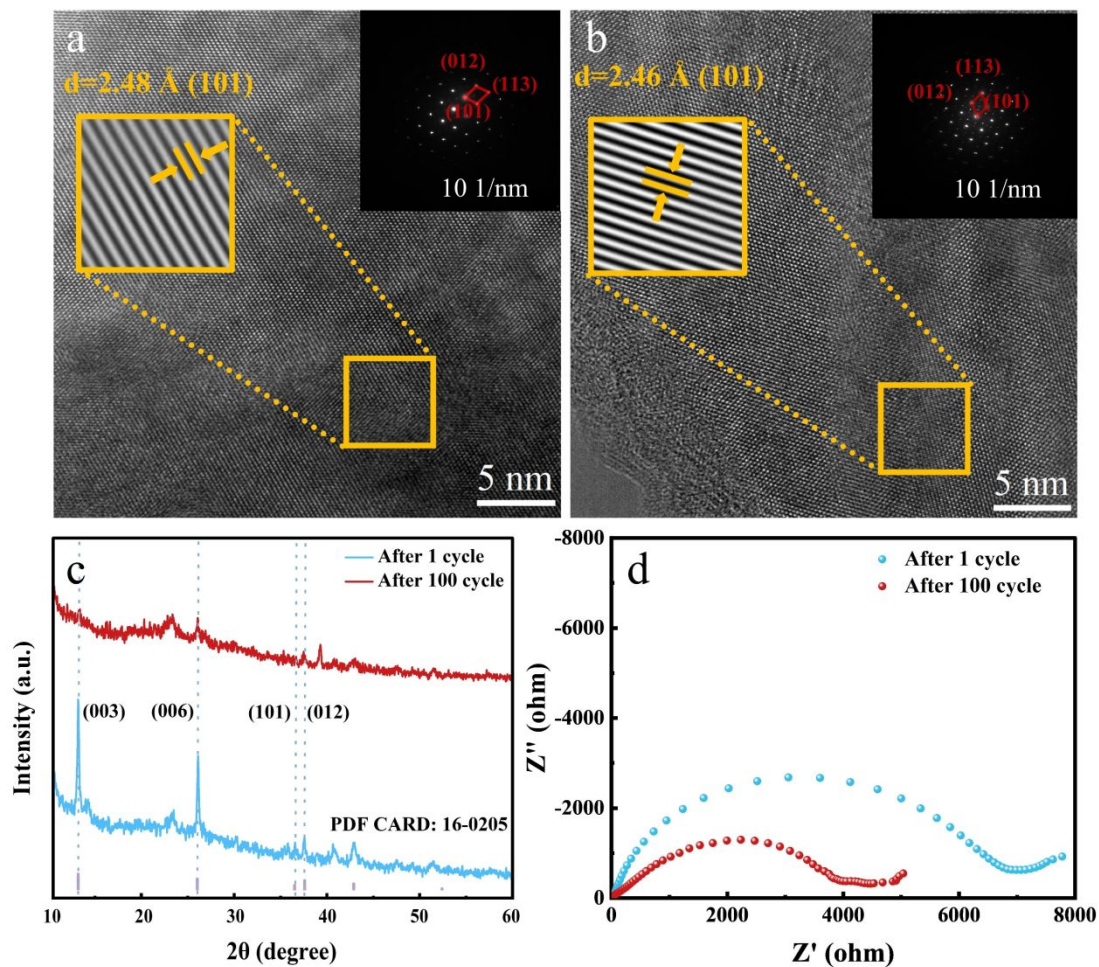


Figure S27. TEM images of different cycles at a current density of 50 mA g^{-1} . a) after 1 cycle, b) after 100 cycle. c) XRD of the electrode sheet after 1 cycle and 100 cycles. d) EIS mapping after 1 cycle and 100 cycles.

The results indicate that the R_{CEI} value after one cycle is 430.6Ω , while after 100 cycles, the R_{CEI} value increases to 479.2Ω , showing only a minor increase in resistance. This slight change in resistance suggests that the KFSI-EMC electrolyte can effectively maintain a stable Cathode Electrolyte Interface (CEI) during the cycling process of the battery.

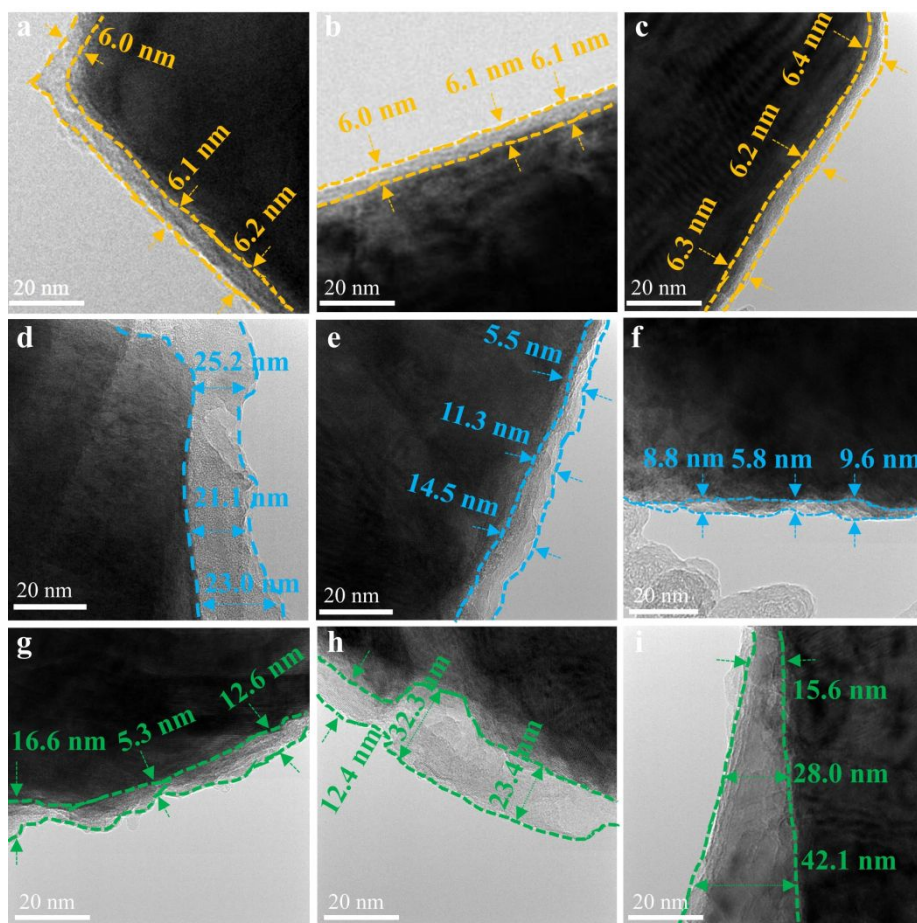


Figure S28. TEM images of CEI in different electrolytes a-c) 3 M KFSI EMC, d-f) 3 M KFSI EC/DEC, g-h) 0.8 M KPF₆ EC/DEC. (a, d, g) are taken after 1 cycle of the cycle. (b, e, h) are taken after 10 cycles of the cycle. (c, f, i) are taken after 100 cycles of the cycle.

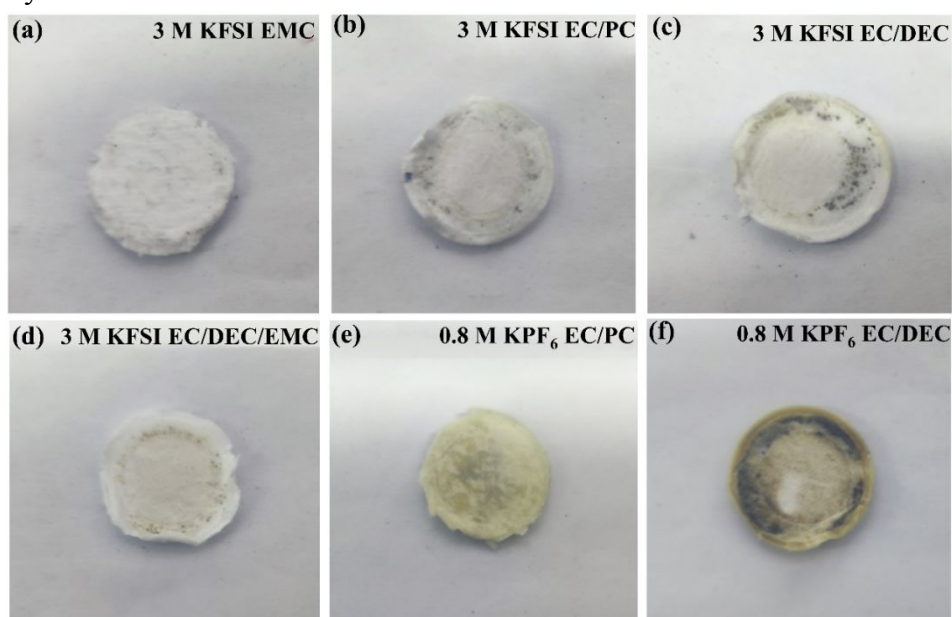


Figure S29. Optical photograph of the separators in KMO//K cells after 100 cycles at a current density of 50 mA g⁻¹ a) 3 M KFSI EMC, b) 3 M KFSI EC/PC, c) 3 M KFSI

EC/DEC, d) 3 M KFSI EC/DEC/EMC, e) 0.8 M KPF₆ EC/PC, and f) 0.8 M KPF₆ EC/DEC.

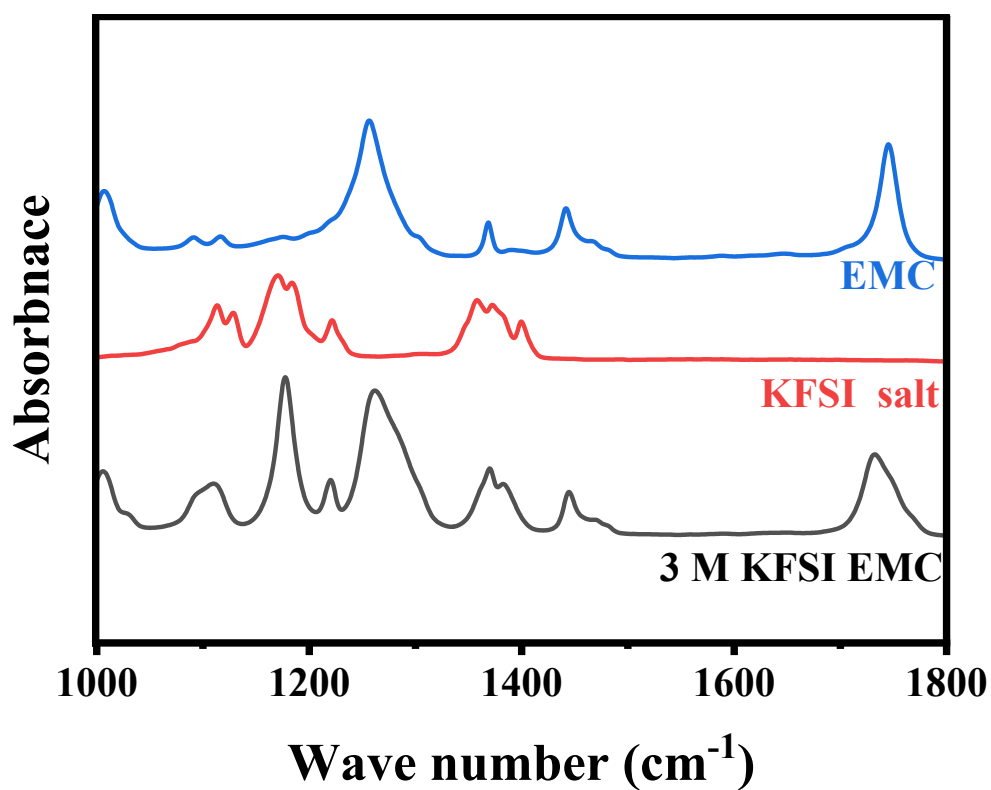


Figure S30. FT-IR spectra for EMC, electrolyte potassium salts and electrolytes.

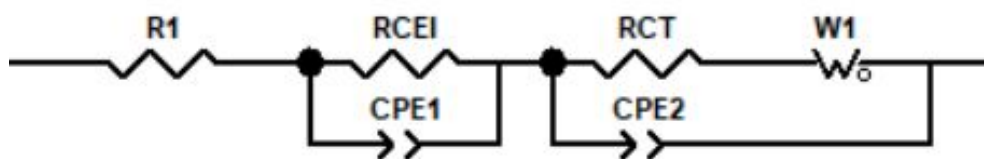


Figure S31. EIS equivalent circuit.

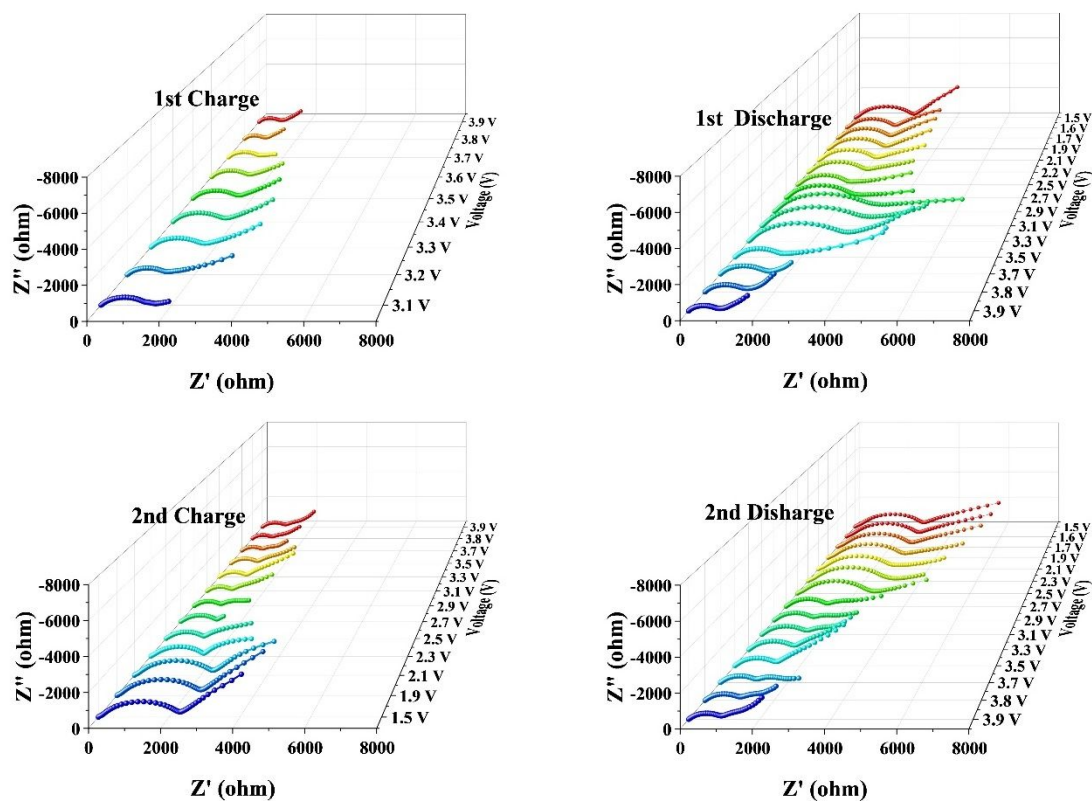


Figure S32. *Ex-situ* EIS spectra of KMO electrodes with 3 M KFSI EMC.

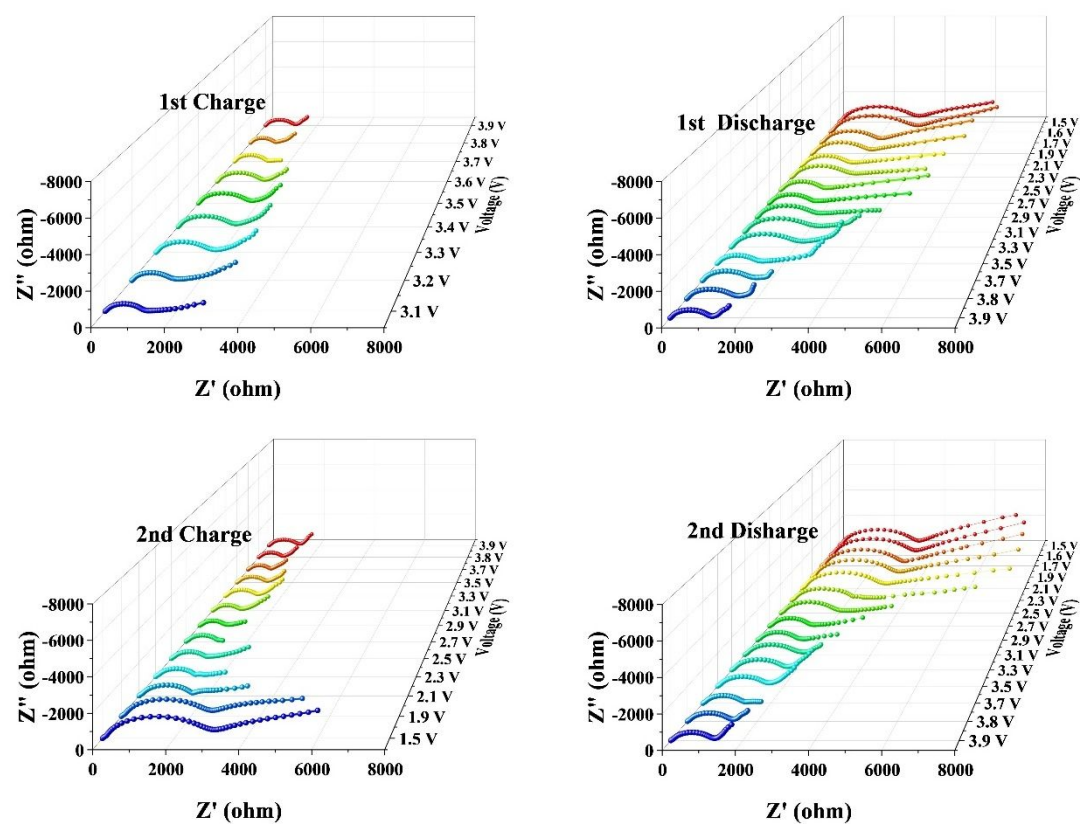


Figure S33. *Ex-situ* EIS spectra of KMO electrodes with 3 M KFSI EC/DEC/EMC.

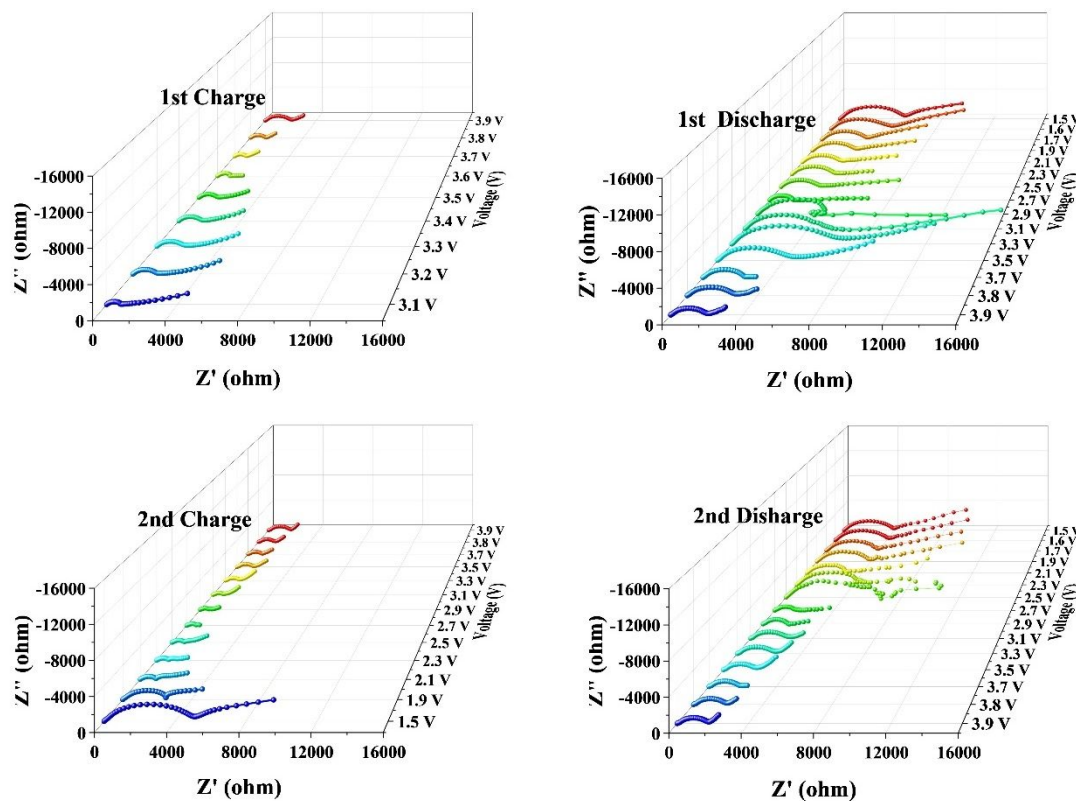


Figure S34. *Ex-situ* EIS spectra of KMO electrodes with 3 M KFSI EC/PC.

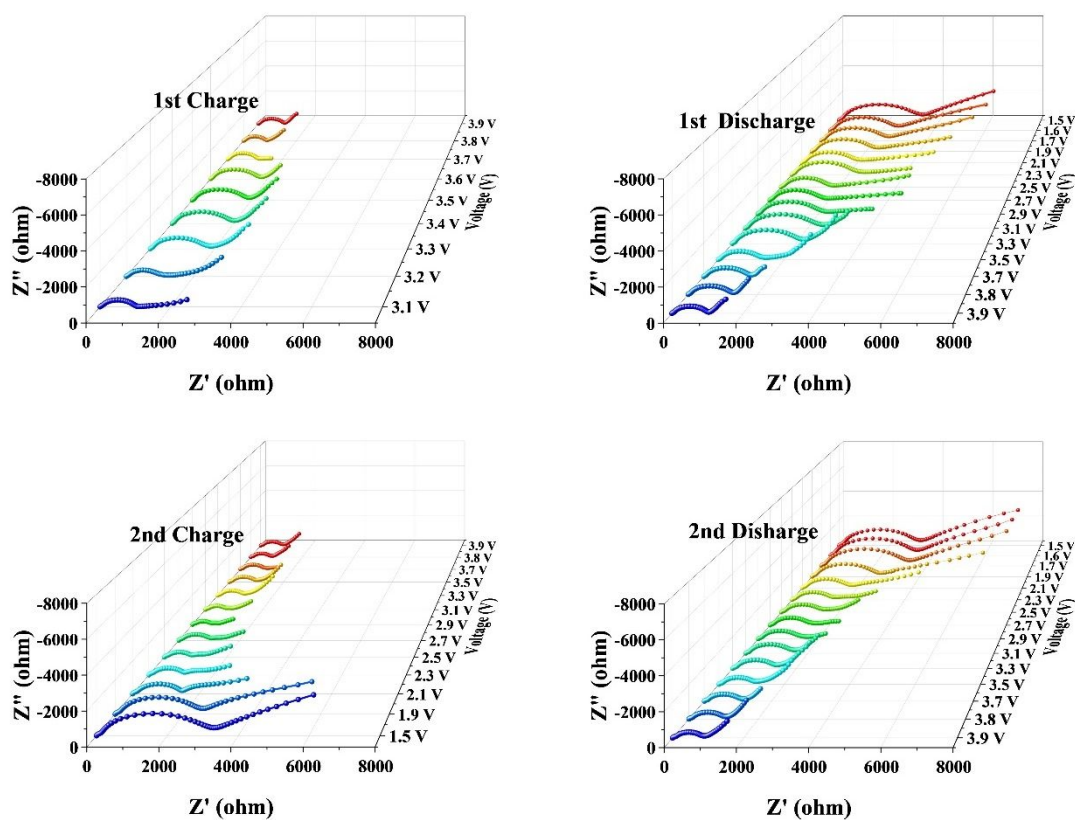


Figure S35. *Ex-situ* EIS spectra of KMO electrodes with 3 M KFSI EC/DEC.

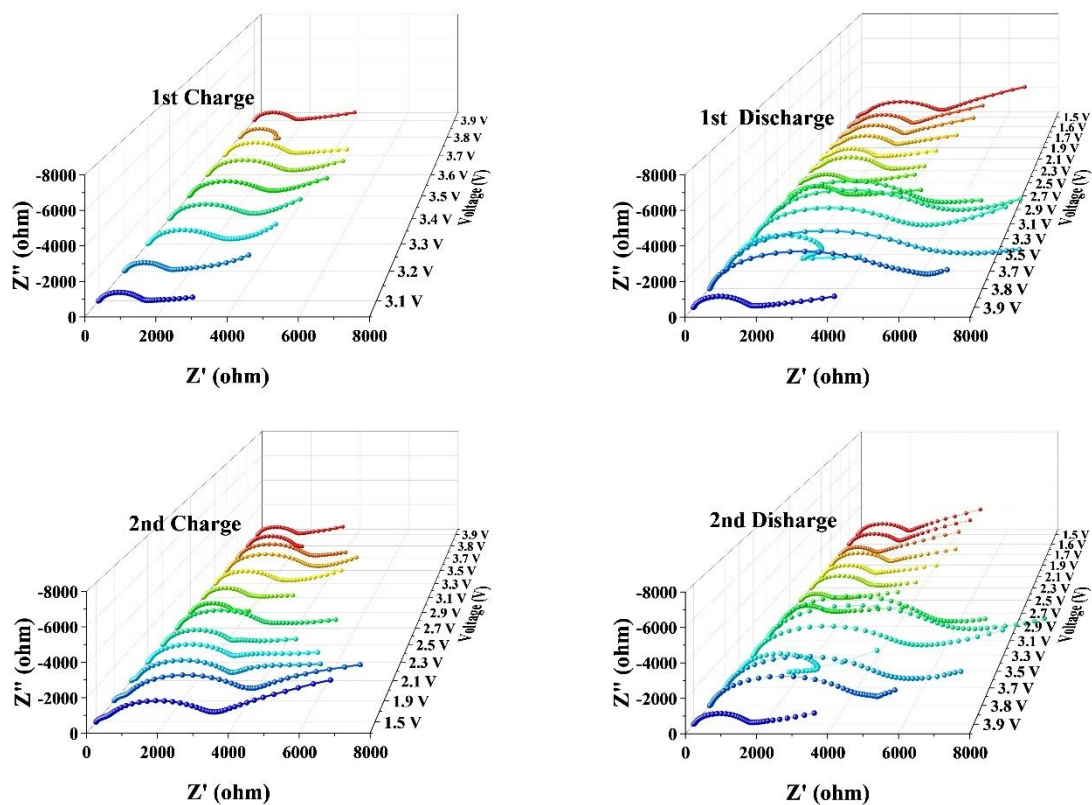


Figure S36. *Ex-situ* EIS spectra of KMO electrodes with 0.8 M KPF₆ EC/PC.

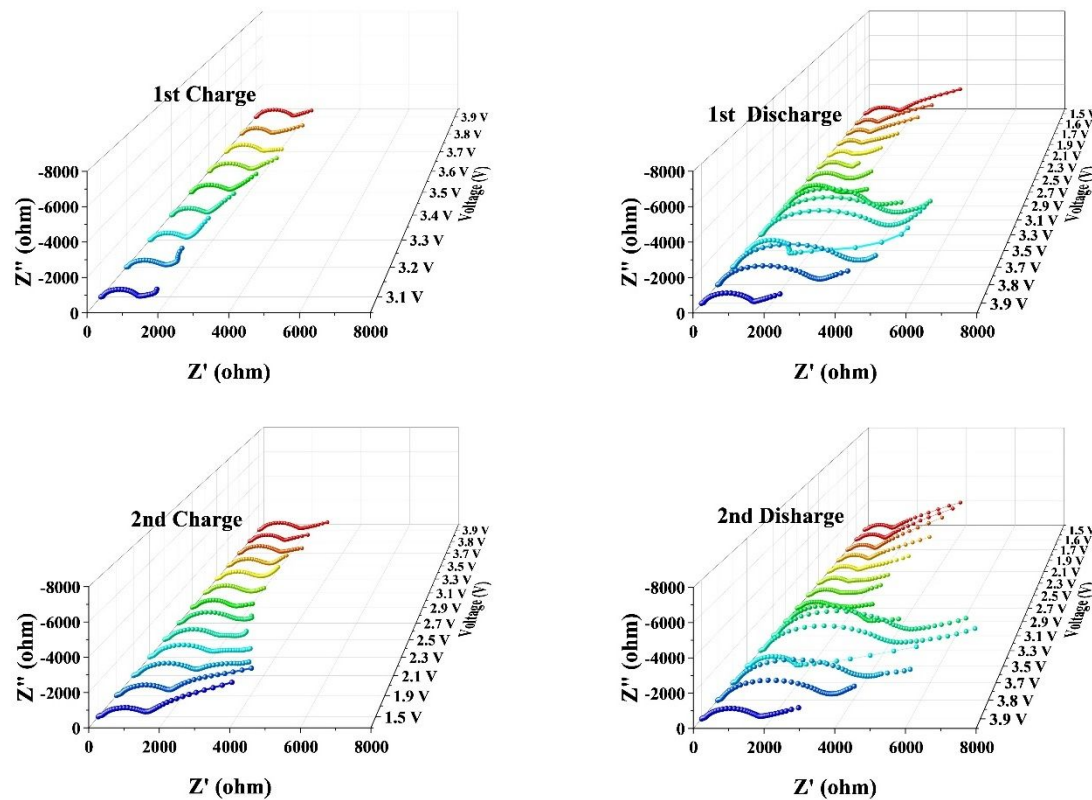


Figure S37. *Ex-situ* EIS spectra of KMO electrodes with 0.8 M KPF₆ EC/DEC.

Table S1. Desolvation energy of solvated K⁺ ions ([K-EMC₂]⁺, [K-EC/DEC]⁺, [K-EC/PC]⁺, [K-EC₂]⁺, [K-PC₂]⁺, [K-DEC₂]⁺)

Desolvation process	Desolvation energy (kJ mol ⁻¹)
[K-EMC ₂] ⁺ →[K-EMC] ⁺ +EMC	26.96
[K-EMC] ⁺ →K ⁺ +EMC	35.45
[K-EC/DEC] ⁺ →[K-EC] ⁺ +DEC	45.62
[K-EC] ⁺ →K ⁺ +EC	50.02
[K-EC/DEC] ⁺ →[K-DEC] ⁺ +EC	45.72
[K-DEC] ⁺ →K ⁺ +DEC	49.02
[K-EC/PC] ⁺ →[K-EC] ⁺ +PC	46.53
[K-EC] ⁺ →K ⁺ +EC	48.25
[K-EC/PC] ⁺ →[K-PC] ⁺ +EC	44.62
[K-PC] ⁺ →K ⁺ +PC	50.16
[K-PC ₂] ⁺ →[K-PC] ⁺ +PC	46.22
[K-PC] ⁺ →K ⁺ +PC	50.28
[K-EC ₂] ⁺ →[K-EC] ⁺ +EC	37.63
[K-EC] ⁺ →K ⁺ +EC	39.80
[K-DEC ₂] ⁺ →[K-DEC] ⁺ +DEC	44.50
[K-DEC] ⁺ →K ⁺ +DEC	56.59

Table S2. Deconvoluted XPS peaks position and content (% area) for KMO anode using 3 M KFSI EMC as electrolyte

		After 1 cycle		After 10 cycle		After 100 cycle	
		BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
C 1s	C-C/C=C	284.41	40.50	284.44	36.75	284.53	45.03
	C-O	285.13	13.52	285.08	20.74	285.05	15.93
	C=O	285.85	29.35	285.90	36.18	285.90	33.51
	C-F	290.89	16.63	289.45	6.33	288.80	5.54
K 2p	K-F	293.17	28.60	293.20	27.86	293.17	27.85
		295.89	28.81	296.02	26.66	296.01	28.02
	K-O	293.56	21.86	293.64	23.76	293.69	22.40
		296.41	20.73	296.39	21.72	296.49	21.72
O 1s	CO ₃ ²⁻	531.35	9.23	531.52	12.68	531.41	9.23
	C-O	532.67	52.53	532.68	52.56	532.75	50.00
	C=O	533.10	38.24	533.29	34.76	533.27	40.77
F 1s	K-F	684.17	96.57	685.30	94.90	684.34	93.71
	C-F	687.97	3.43	687.85	5.10	688.84	6.29
S 2p	KHSO ₄	169.93	43.69	170.05	39.85	169.99	43.97
		171.13	43.18	171.25	40.79	171.20	44.16
	K ₂ SO ₄	168.60	6.67	168.48	9.96	168.53	5.57
		169.85	6.46	169.74	9.40	169.90	6.30

Table S3. Deconvoluted XPS peaks position and content (% area) for KMO anode using 3 M KFSI EC/DEC as electrolyte

		After 1 cycle		After 10 cycle		After 100 cycle	
		BE (eV)	Area	BE (eV)	Area	BE (eV)	Area
			(%)		(%)		(%)
C 1s	C-C/C=C	284.65	50.21	284.70	44.26	284.58	43.63
	C-O	285.19	27.50	285.05	36.82	285.11	31.47
	C=O	285.89	19.73	286.01	16.89	286.12	23.15
	C-F	289.52	2.56	290.37	1.99	289.39	1.75
K 2p	K-F	293.47	31.12	293.47	28.34	293.15	33.44
		296.22	32.11	296.23	32.04	295.96	32.19
	K-O	294.09	18.68	294.33	19.43	293.80	17.99
		296.84	18.09	296.99	20.20	296.58	16.38
O 1s	CO ₃ ²⁻	531.62	13.11	531.68	16.02	531.66	16.75
	C-O	532.71	35.78	532.75	30.02	532.63	37.90
	C=O	533.50	51.12	533.60	53.96	533.34	45.35
F 1s	K-F	684.90	91.35	684.43	89.74	684.63	85.78
	C-F	689.01	8.65	688.02	10.26	688.89	14.22
S 2p	KHSO ₄	170.41	45.22	170.40	41.31	170.13	33.42
		171.65	44.87	171.51	43.08	171.34	35.56
	K ₂ SO ₄	168.89	4.62	168.87	8.56	168.60	17.54
		170.00	5.29	169.98	7.04	169.96	13.47

Table S4. Deconvoluted XPS peaks position and content (% area) for KMO anode using 0.8 M KPF₆ EC/PC as electrolyte

		After 1 cycle		After 10 cycle		After 100 cycle	
		BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
C 1s	C-C/C=C	283.05	39.13	283.13	53.62	283.18	36.66
	C-O	284.49	16.08	284.36	14.44	284.44	38.64
	C=O	284.99	16.81	284.89	20.75	284.98	11.11
	C-F	287.84	27.98	287.78	11.19	287.75	13.59
K 2p	K-F	291.17	30.15	290.97	25.59	290.87	25.37
		293.89	28.24	293.64	27.70	293.49	30.11
	K-O	291.72	24.16	291.44	24.33	291.33	23.55
		294.48	20.14	294.27	22.38	294.16	20.97
O 1s	CO ₃ ²⁻	529.00	10.74	528.98	9.82	528.91	15.23
	C-O	529.74	36.51	529.64	38.15	529.74	45.11
	C=O	531.16	52.75	531.11	52.03	531.19	39.66
F 1s	K-F	684.31	93.73	684.82	91.03	684.78	82.00
	C-F	688.01	6.27	687.92	8.97	687.93	18.00
P 2p	K _x PF _y O _z	135.31	53.00	135.24	51.35	135.54	52.38
	KPF ₆ /K _x PF _y	136.21	47.00	136.11	48.65	136.57	47.62

Table S5. The *in-situ* FT-IR peak information of KMO electrodes with 3 M KFSI EMC as electrolyte

Products	Wavenumber (cm ⁻¹)	Band Assignment Vibration Mode	Species of origin	References
	1036	S=O stretching mode	K ₂ SO ₄	5
	1190	C-F symmetric stretching mode	CF _x	6
	1230	S=O stretching mode	KHSO ₄	7
Products	1320	CO ₂ symmetric stretching mode	ROCO ₂ K	8
	1388	CO ₃ ²⁻ stretching vibration	K ₂ CO ₃	9
	1755	CO ₂ symmetric stretching mode	ROCO ₂ K	8

Table S6. Fitted results of *ex-situ* EIS spectra for KMO/K cells with different electrolytes.

Potential/V		3 M KFSI	3 M KFSI	3 M KFSI	3 M KFSI	0.8 M KPF ₆	0.8 M KPF ₆
		EMC	EC/PC	EC/DEC	EC/DEC/EMC	EC/PC	EC/DEC
		R _{CEI} /(Ω)	R _{CEI} /(Ω)	R _{CEI} /(Ω)	R _{CEI} /(Ω)	R _{CEI} /(Ω)	R _{CEI} /(Ω)
1st Charge	3.1	185	468.2	288.9	376.1	306.2	369.9
	3.2	187.1	372.9	285.5	377.7	303.6	378.8
	3.3	187.6	377	312.8	374.2	304.7	389.4
	3.4	187.4	380.1	317.1	374.8	304.2	387.7
	3.5	188.5	383	315	376.2	308.9	378.8
	3.6	189.7	280.9	310.6	376.8	303	360.4
	3.7	168.6	282	206.3	286.4	234	372.2
	3.8	167.3	277.2	207.2	294.1	206.9	349
	3.9	165.3	282	206.2	286.9	222.8	382.6
1st Discharge	3.8	166.9	281.4	253	281.7	236.9	392.4
	3.7	227.9	453.7	256.9	381.6	390.6	399.3
	3.5	222	459.9	269.1	369.5	358.2	413.8
	3.3	223.2	463.3	294	384.3	357.6	376.9
	3.1	218	454.5	304.6	379.6	332.7	385.9
	2.9	220.2	442.1	313.4	378	349.4	396.9
	2.7	227.2	451.7	335.9	388.9	343.3	377.4
	2.5	220.7	450.8	340.9	373.9	366.3	399.8
	2.3	221.7	452	341.9	372.9	365.9	346.6
	2.1	223	449.4	343.2	372.2	367.9	321.6
	1.9	220.9	452.4	350.6	374.9	422.4	359.9
	1.7	225.4	459.9	357.1	376.5	338.6	360.1
	1.6	228.5	461.6	362.5	385.1	381.7	388.3
	1.5	227.4	462.4	374.7	386.7	335.3	408.1
2nd Charge	1.9	219.1	476	368.2	384.2	390	423
	2.1	226.4	310.3	307.9	315.4	220.7	383.6

	2.3	230.6	290.8	290.9	310.6	235.3	405.1
	2.5	229.8	291.4	292	273.9	271.1	386.4
	2.7	230.2	279.3	291.7	267.6	311.8	391.4
	2.9	231.2	270.2	281.9	271.3	252.3	410.9
	3.1	234.4	264.7	293.3	275.3	284.5	392.7
	3.3	224	284.6	292.6	283.1	293.3	392.5
	3.5	226.7	287.6	291.7	283.1	239.7	414.3
	3.7	235.9	279.4	285.7	274.6	285.9	439.8
	3.8	230.3	276.7	307.4	268.2	267.2	382.3
	3.9	221.2	286.5	310	276	228.8	396.5
2nd Discharge	3.8	222.7	292	319.3	281.5	400.8	397.3
	3.7	231.5	298.7	325.7	288.2	376	402.1
	3.5	229.4	296.5	336.8	290.2	339.8	387.3
	3.3	229.5	295.5	303.9	299	329.1	387.8
	3.1	236.6	286.2	317.6	304	294.7	388.2
	2.9	225.1	282.6	321.7	304	315.6	384.4
	2.7	236.8	290.7	330.2	305.9	343	373.4
	2.5	264.9	316	351	342.8	370.4	366.8
	2.3	261.3	486.2	329.1	375.8	386.3	361.1
	2.1	233.8	488.9	340	378.3	290.8	352.7
	1.9	233.4	495.5	334.8	376.6	326.1	348.5
	1.7	238.8	496.6	358	374.3	338.4	349.8
	1.6	240.8	497.9	362.2	380	337.7	351.8
	1.5	241.9	496.5	367.1	383.6	329.9	353.6

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