Supporting Information of

“ Highly Concentrated Electrolyte Solutions for 4 V Class Potassium-Ion Batteries”

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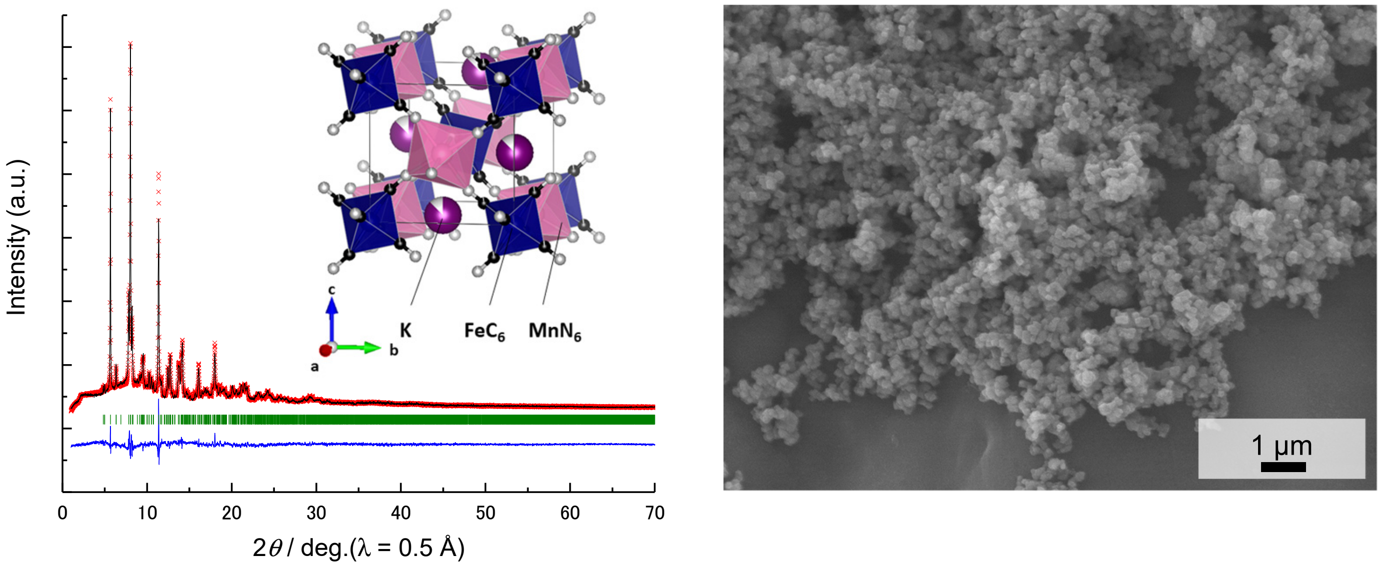

Fig. S1 Structural characterization of as-synthesized $K_xMn[Fe(CN)_6]$: (a) XRD patterns, where red plots, a black line, and green bars show the observed diffraction plots, the refined pattern, the difference between the observed and calculated plots, and the positions of Bragg reflections. The inset is crystal structure scheme of the sample. (b) The SEM image of $K_xMn[Fe(CN)_6]$. $K_xMn[Fe(CN)_6]$ was synthesized by chelate-assisted precipitation method. Firstly, 4 mmol $K_4Fe(CN)_6 \cdot 3H_2O$ and 4 mmol $MnCl_2 \cdot 4H_2O$ or $FeCl_2 \cdot 4H_2O$ were dissolved into 100 ml 0.2 mol dm^{-3} potassium citrate solution at 25 °C. Then, these two solutions were slowly dropped together with magnetic stirring under N_2 atmosphere at room temperature. 15 hours later, the precipitate was centrifuged and washed thoroughly with 400 ml deionized water. At last, the final product was obtained after vacuum drying under 100 °C for 24 hours.

Table S1 Structural parameters of $K_xMn[Fe(CN)_6]$ obtained from Rietveld analysis, which was conducted by RIETAN-FP [1].

Space group $P2_1/n$

a = 10.1131(6) Å, b = 7.3320(4) Å, c = 6.9692(4) Å, β = 90.303(7) °

	Site	*x*	*y*	*Z*	Occ.	B / Å^2
Mn	2d	0.000	0.500	0.500	1.000*	0.500*
Fe	2a	0.000	0.000	0.000	0.987(10)	0.500*
N1	4e	0.452(2)	0.259(3)	0.854(3)	= Occ. (Fe)	0.700*
N2	4e	0.066(2)	0.329(2)	0.742(3)	= Occ. (Fe)	0.700*
N3	4e	0.2003(19)	0.456(2)	0.395(2)	= Occ. (Fe)	0.700*
C1	4e	0.529(2)	0.638(3)	0.253(3)	= Occ. (Fe)	0.700*
C2	4e	0.965(2)	0.783(3)	0.171(3)	= Occ. (Fe)	0.700*
C3	4e	0.687(2)	0.490(3)	0.556(3)	= Occ. (Fe)	0.700*
K	4e	0.7529(9)	0.9352(4)	0.4746(6)	0.920(8)	2.000*

S = 1.09, R_{wp} = 6.67 %, R_B = 6.33 %, R_f = 8.13 %

Isotropic atomic displacement parameters were fixed.

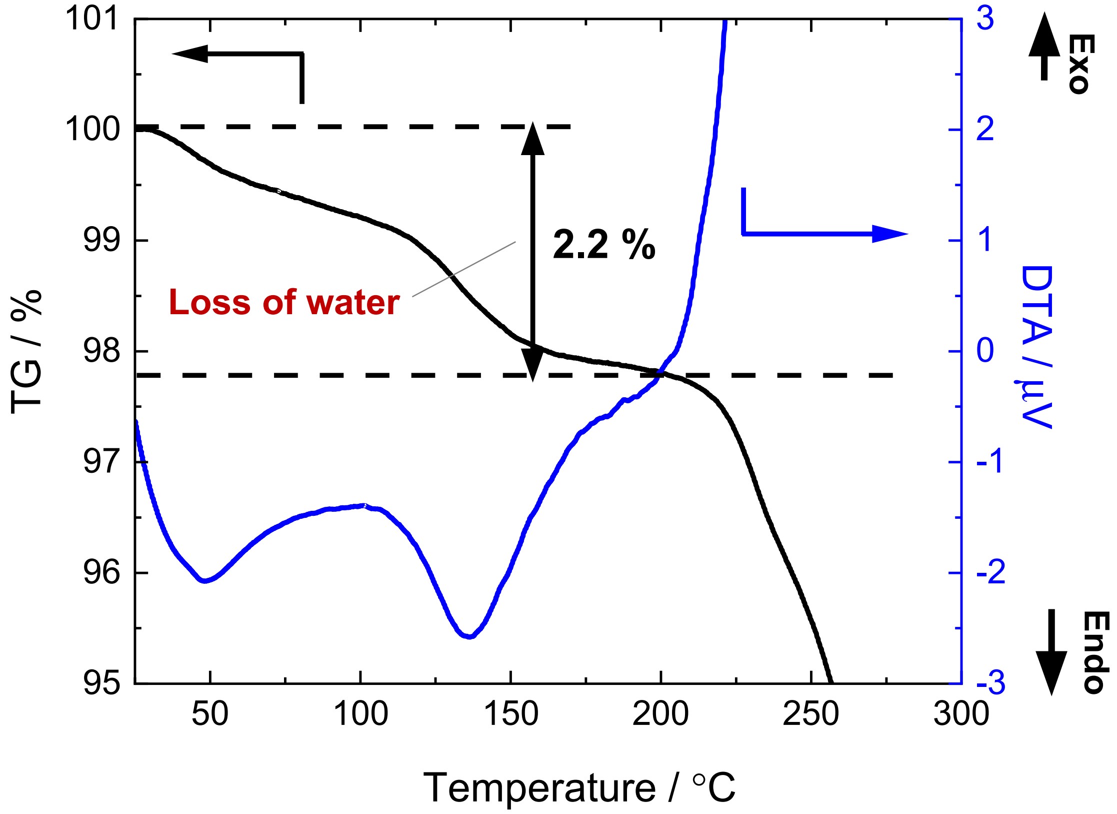

Fig. S2 TG-DTA curve of $K_xMn[Fe(CN)_6]$, where black line and blue line are TGA curve and DTA curve, respectively. The TGA test was conducted at a heating rate of 5 °C min^{-1} under Ar gas flow. Two endothermic peaks located at 49 °C and 135 °C can originate from loss of crystal water and following exothermic peak above 200 °C indicates the compound decomposition. TGA curve indicates that $K_xMn[Fe(CN)_6]$ contains 2.2 % of crystal water. From ICP-AES and TGA, the chemical formula of $K_xMn[Fe(CN)_6]$ was calculated as $K_{1.94}Mn[Fe(CN)_6]_{1.01}\cdot 0.49H_2O$.

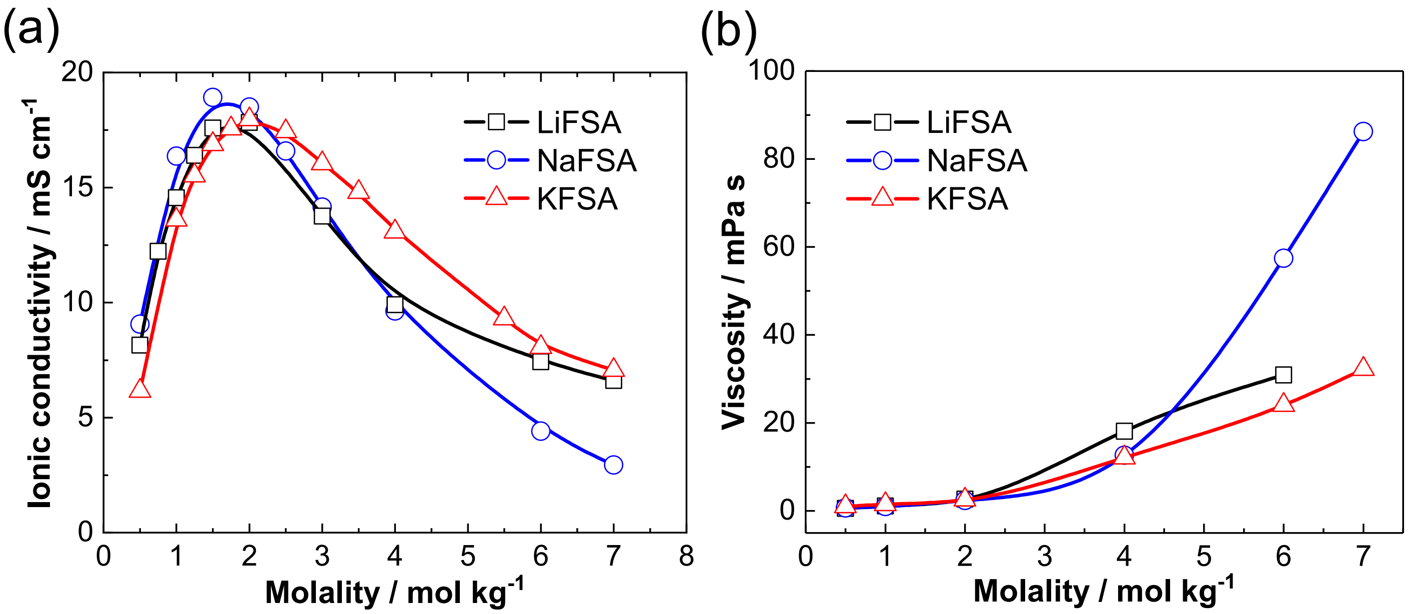

Fig. S3 Physical properties of LiFSA, NaFSA and KFSA in DME solutions: (a) ionic conductivity at room temperature and (b) viscosity at various molality at 25 °C.

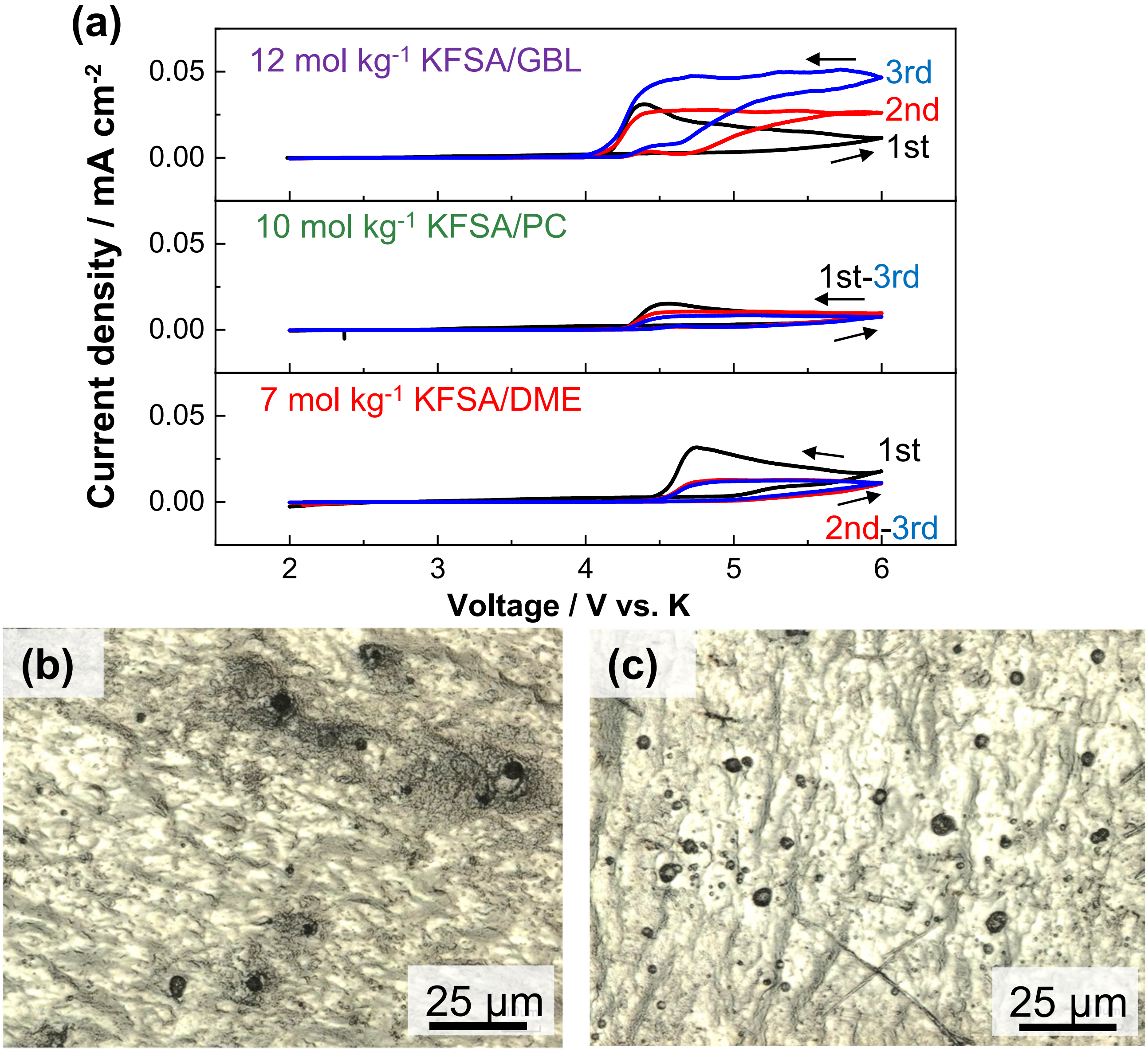

Fig. S4 (a) Cyclic voltammograms of Al foil in 12 mol kg^{-1} KFSA/GBL, 10 mol kg^{-1} KFSA/PC, and 7 mol kg^{-1} KFSA/DME at a scanning speed of 0.5 mV s^{-1} in voltage range of 2 – 6 V in K//Al foil cell. Microscopic images of Al working electrodes tested in (b) 10 mol kg^{-1} KFSA/PC and (c) 12 mol kg^{-1} KFSA/GBL after 3 cycles of CV measurement in voltage range of 2 – 6 V.

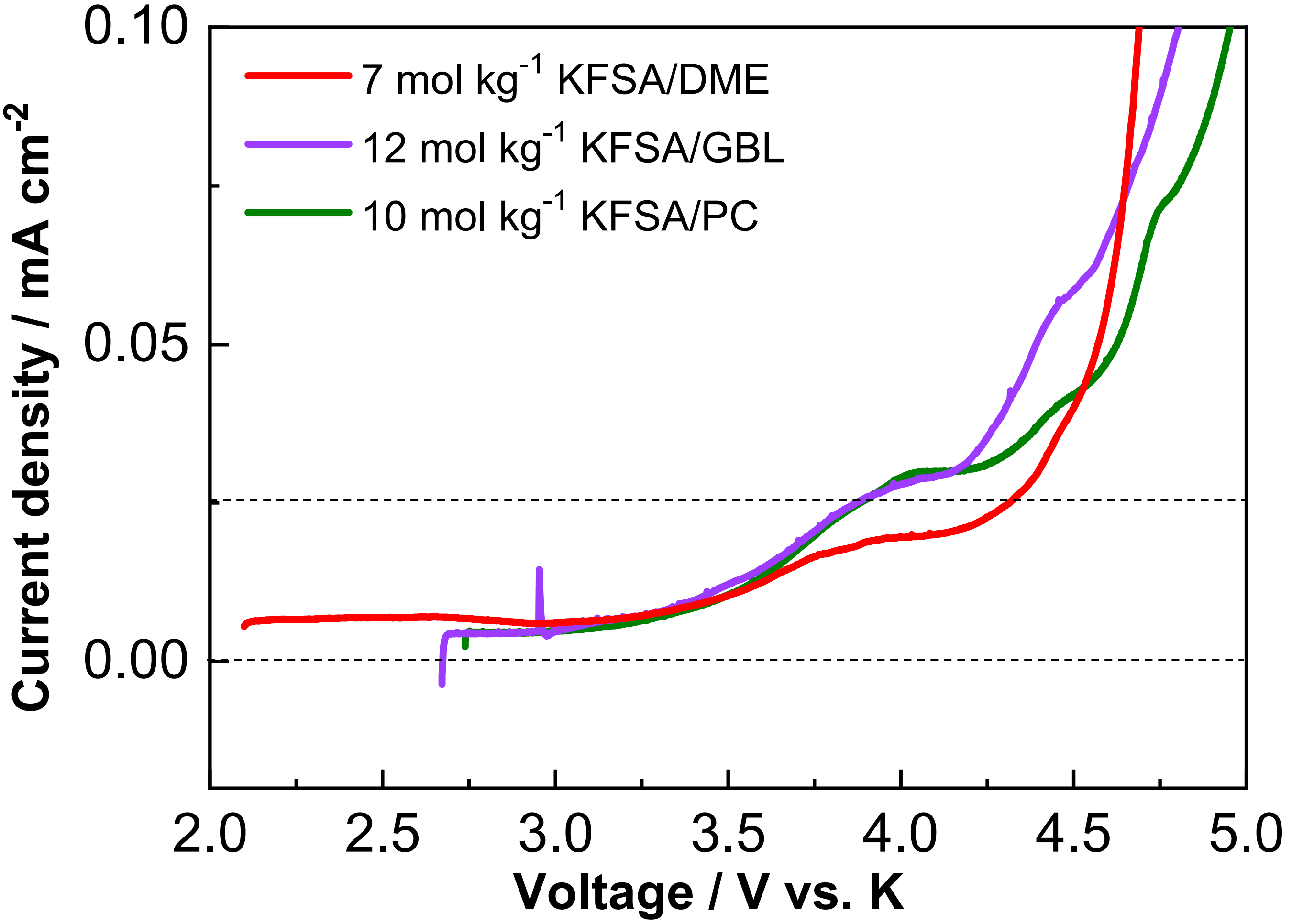

Fig. S5 Linear sweep voltammograms of KB:PVdF = 60:40 (wt%) composite electrodes formed on Al foil in 7 mol kg^{-1} KFSA/DME, 12 mol kg^{-1} KFSA/GBL, and 10 mol kg^{-1} KFSA/PC at a scanning speed of 0.5 mV s^{-1} .

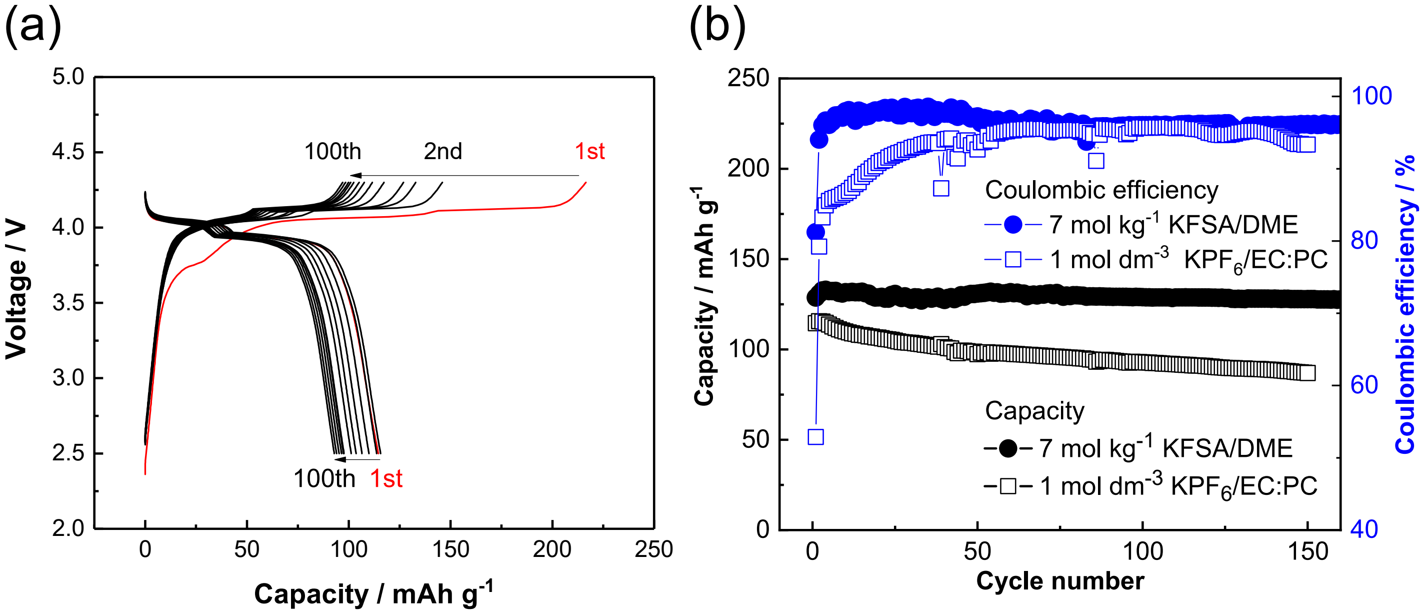

Fig. S6 Charge/discharge curves of $K_2Mn[Fe(CN)_6]$ electrode at current density of 16 mA g^{-1} in K cell filled with (a) 1 mol dm^{-3} KPF$_6$/EC:PC electrolyte and (b) comparison of coulombic efficiency and cyclability between 7 mol kg^{-1} KFSA/DME and 1 mol dm^{-3} KPF$_6$/EC:PC.

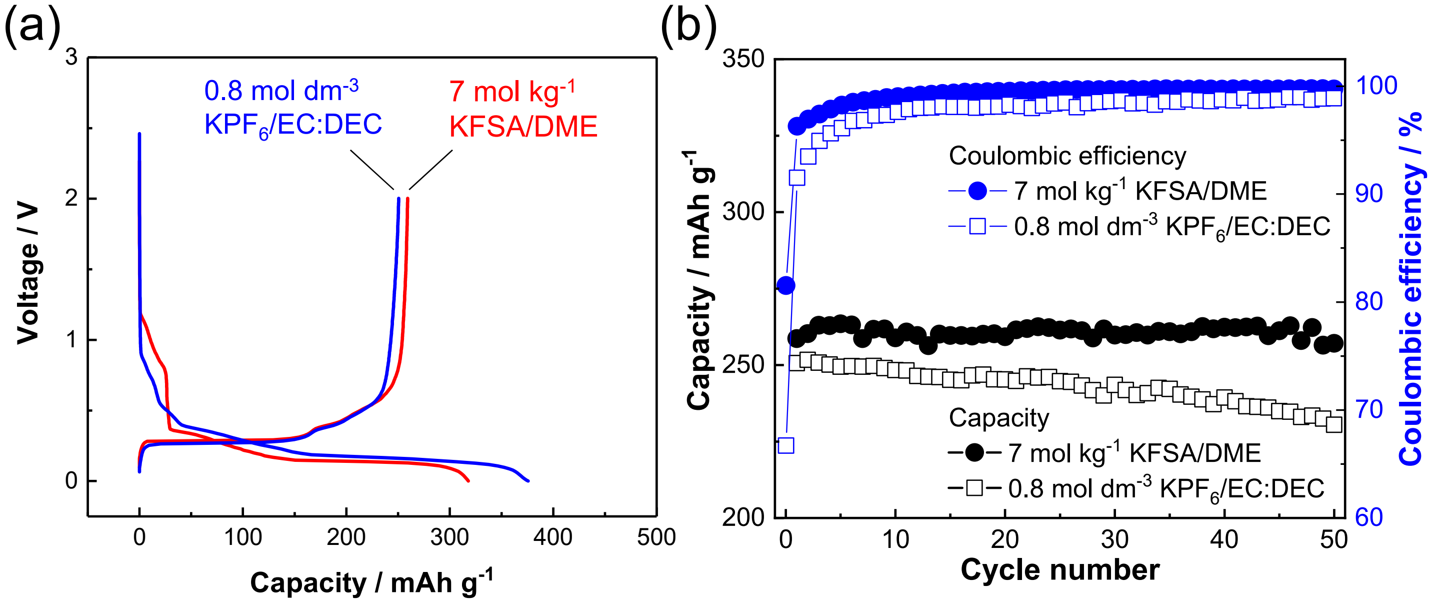

Fig. S7 Charge/discharge curves of graphite electrode at current density of 25 mA g^{-1} in K cell filled with (a) 0.8 mol dm^{-3} KPF$_6$/EC:DEC electrolyte and (b) comparison of coulombic efficiency and cyclability between 7 mol kg^{-1} KFSA/DME and 0.8 mol dm^{-3} KPF$_6$/EC:DEC.

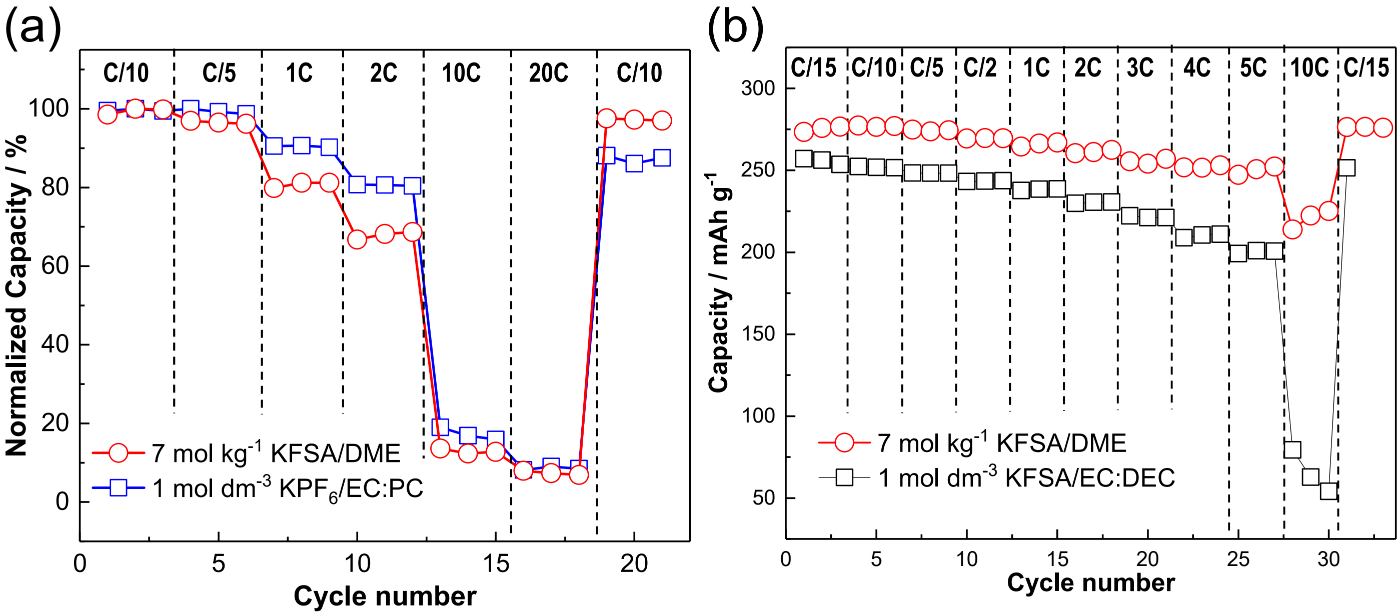

Fig. S8 Rate capability of (a) K//K$_2$Mn[Fe(CN)$_6$] coin-type cells and (b) K//graphite three electrode cells with a K metal reference electrode to avoid the influence of K-metal polarization [2]. K//K$_2$Mn[Fe(CN)$_6$] cells were charged at C/10 (15 mA g^{-1}) and discharged at different current densities. K//graphite three electrode cells were charged and discharged at different current densities. Mass loading of K$_2$Mn[Fe(CN)$_6$] electrode was ~0.6 mg cm^{-2} and that of graphite electrode was ~1.2 mg cm^{-2}.

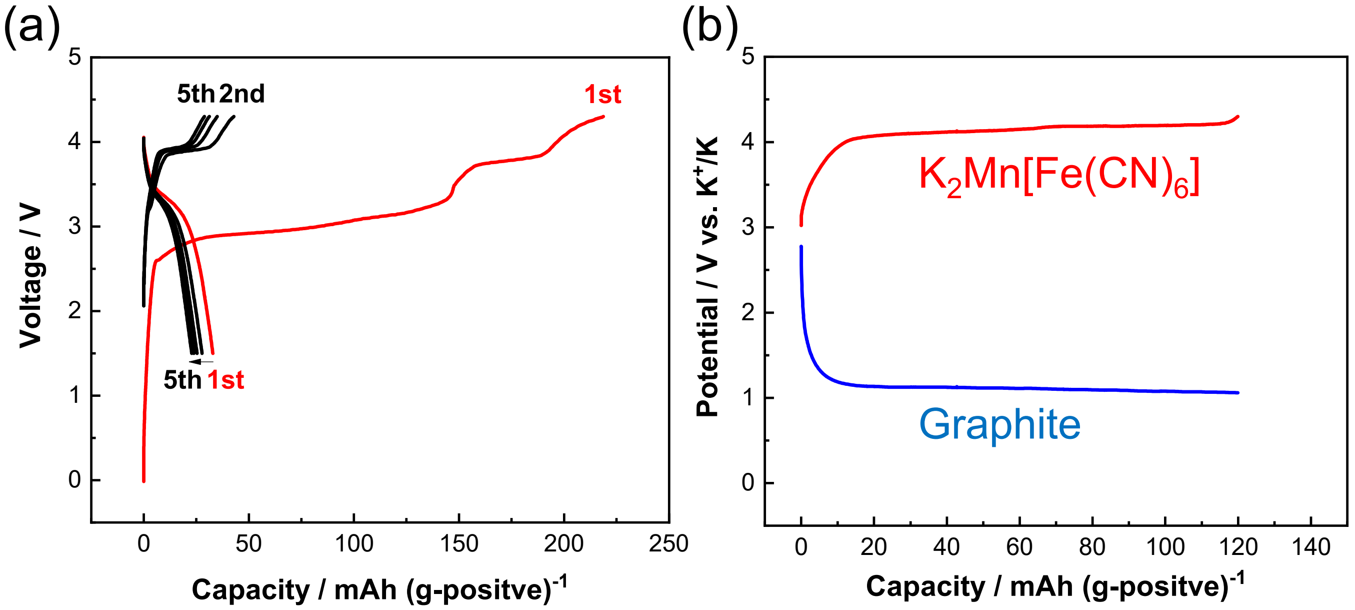

Fig. S9 Charge/discharge curves of graphite//$K_2Mn[Fe(CN)_6]$ full-cell filled with non-pretreated 7 mol kg^{-1} KFSA/DME electrolyte in (a) a coin cell and (b) three electrode cell (EC Frontier) with K metal wire as a reference electrode. The weight ratio of $K_2Mn[Fe(CN)_6]$/graphite was 2.1:1, corresponding to 1.1:1 of their reversible capacity ratio.

Table S2 H_2O content of the 7 mol kg^{-1} KFSA/DME solutions with/without pretreatment by K metal.

n	As-prepared electrolyte / ppm	K metal soaked electrolyte / ppm
1st	42.79	9.74
2nd	43.13	12.9
Average	42.96	11.3

The H_2O content was measured by Karl Fischer coulometric titration (MKC-610, Kyoto Electronics Manufacturing).

To prepare the pretreated samples, 3 pieces of K metal of 15 mm in diameter were soaked in 2 ml of 7 mol kg^{-1} KFSA/DME solution for 2 days. Both non-pretreated and pretreated samples for the 1st measurement were prepared from the same solution at the same time. Both samples for 2nd measurement were also prepared from a solution, though the original solution was different from the 1st samples.

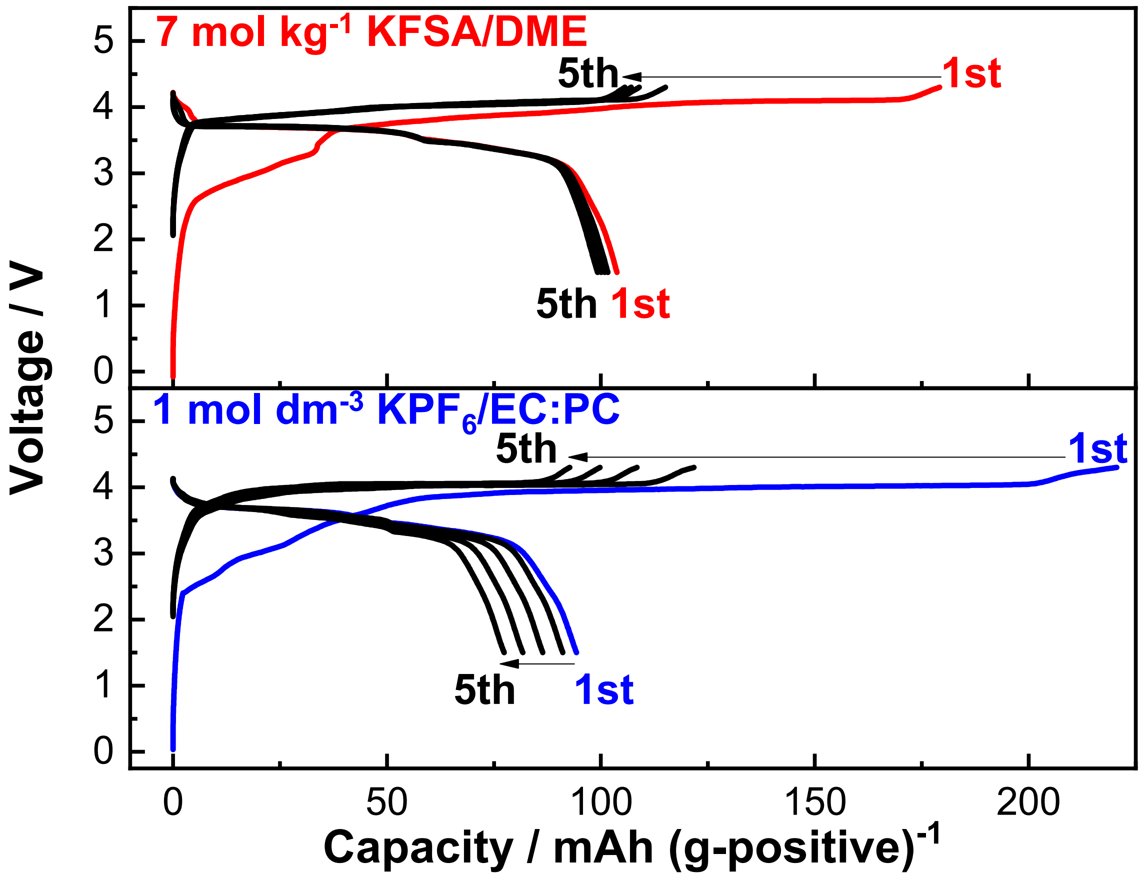

Fig. S10 Charge/discharge curves of graphite//$K_2Mn[Fe(CN)_6]$ full-cell filled with 7 mol kg^{-1} KFSA/DME electrolytes with K-metal pretreatment (top) and 1 mol dm^{-3} KPF_6/EC:PC (1:1 v/v) electrolyte with K-metal pretreatment (bottom) at current density of 15 mA g^{-1}. K-metal pretreatment was conducted by soaking K metal foil of 15 mm in diameter in the 500 μL of the electrolyte for two days. In both full cells, the weight ratio of $K_2Mn[Fe(CN)_6]$/graphite were 2.1:1, corresponding to 1.1:1 of their reversible capacity ratio.

Reference:

1. F. Izumi and K. Momma, *Solid State Phenom.*, 2007, **130**,15-20.
2. K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura and S. Komaba, *Chem. Rec.*, 2018, **18**, 459-479.