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Supporting Information for

KFSA/Glyme Electrolytes for 4 V-Class K-Ion Batteries

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Electrolyte Preparation

KFSA (Solvionic) was dried at 100 °C and 24 h under vacuum before electrolyte preparation. Battery grade reagents of G1, G2, G3 solvents (Kishida Chemical) were used as received. The KFSA/glyme electrolyte solutions were prepared by dissolving KFSA powders in an Ar-filled glovebox where the dew point is lower than −80 °C . The concentration was fixed by the mol ratio of K and O in the solutions, and we prepared three different concentrations of K:O = 1:10 (ca. 2.2 mol kg^{-1}), K:O = 1:6 (ca. 3.7 mol kg^{-1}), and K:O = 1:4 (ca. 5.6 mol kg^{-1}) for each solvent.

Physical Characterization

Ionic conductivity measurements of the electrolyte solutions were performed with an ionic conductivity meter (Eutech CON2700, Eutech Instruments) at 25 °C . The viscosity of the electrolyte solutions was measured with an electromagnetically spinning viscometer (EMS-1000, Kyoto Electronics Manufacturing) at 25 °C . Raman spectra of the solutions were recorded with a 532 nm laser Raman spectrometer (Raman 11i, Nanophoton) at room temperature. The samples were sealed in a crystal tube in the Ar-filled glovebox. The obtained spectra were analyzed using the Origin Pro program. All the intensity was normalized with respect to the Raman band at 780–900 cm^{-1} (assigned to mixed modes of CH_2 rocking vibrations and C−O−C stretching vibrations in glymes). The normalized spectra were deconvoluted using a Gaussian–Lorentzian function for spectroscopic analysis.

Electrode Material and Electrode Preparation

$K_2Mn[Fe(CN)_6]$ was synthesized via a chelate-assisted precipitation method as previously reported.[1] The $K_2Mn[Fe(CN)_6]$ electrodes consisting of a mixture of 70 wt % $K_2Mn[Fe(CN)_6]$, 20 wt % Ketjen black (KB, Carbon ECP, Lion), and 10 wt % poly(vinylidene fluoride) (PVdF, #9100, Kureha) were prepared, and graphite electrodes were prepared by mixing 90 wt % graphite (SNO3, SEC Carbon) and 10 wt % sodium polyacrylate (PANa, Kishida Chemical). Both electrodes were prepared by coating mixture slurry on Al foil by doctor blade method and drying the coat at 150 °C under vacuum. The mass loading of $K_2Mn[Fe(CN)_6]$ in the electrodes was ca. 0.8 mg cm^{-2}. This small mass loading was utilized to minimize the effect of the polarization of the K-metal counter electrode by reducing the current density per area. The mass loading ratio of negative and positive electrodes for full cells was fixed to N/P = 1.0:2.0, corresponding to the discharge capacity ratio of N/P = 1.0–1.1, which is based on the half cell tests. Activated carbon electrodes consisting of 80 wt % activated carbon (YP50F, Kuraray), 10 wt % KB, and 10 wt % polytetrafluoroethylene (PTFE, Daikin) were formed on Al expanded metal and dried at 200 °C under vacuum.

Electrochemical Characterization

Cyclic voltammetry and linear sweep voltammetry were conducted with a three-electrode cell (SB1A, EC FRONTIER) with Al foil as a working electrode, the activated carbon counter electrode, and a K-metal (Sigma-Aldrich) reference electrode, which is separated from the working and counter electrode by a ceramic filter. The surfaces of Al working electrodes after the electrochemical tests were observed with a three-dimensional (3D) laser scanning microscope (VK-X200, Keyence). Galvanostatic charge/discharge tests of $K_2Mn[Fe(CN)_6]$ and graphite electrodes were conducted in an R2032 coin-type cell assembled with a K metal counter electrode and a glass fiber separator (GB-100R, Advantec). Al-clad caps (Hohsen) were used for the coin cell to avoid corrosion of stainless steel.[2] For the full cells, 0.5 wt % vinylene carbonate was added to the electrolytes to suppress initial undesirable side reactions.

Surface Analysis

Hard X-ray photoelectron spectroscopy (HAXPES) spectra of the tested graphite electrodes were acquired by high excitation energy of hard X-ray, 7939 eV, and a photoelectron energy analyzer of R-4000 (Scienta Omicron) at BL46XU at SPring-8, Japan. The photoelectron detection angle and pass energy of the analyzer were 80° and 200 eV, respectively. Electrochemically tested graphite electrodes were carefully taken out from cycled coin cells, rinsed with G1, dried at room temperature in an Ar-filled glovebox under ambient pressure, and transferred using a transfer vessel to avoid air exposure. The detailed setup and condition of the HAXPES measurement are described in our previous paper.[3] The binding energy of the obtained spectrum was calibrated with the binding energy of sp^2 carbon of graphite being 284.3 eV. Photoelectron peaks were deconvoluted with the peak-fit program, Fityk, with Pseudo-Voigt functions. The photoelectron intensity of every spectrum was corrected by relative sensitivity factors [4] and normalized by the integrated intensity of sp^2 C peak at 284.3 eV to conduct a semi-quantitative analysis of chemical species.

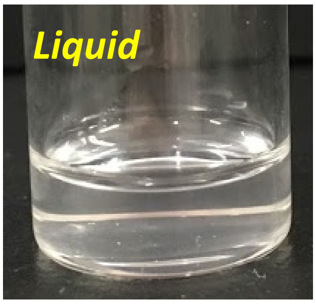
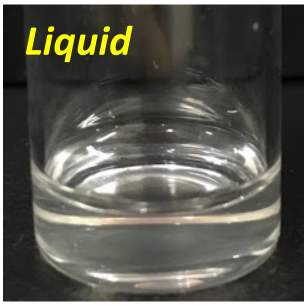
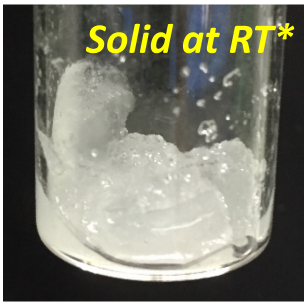
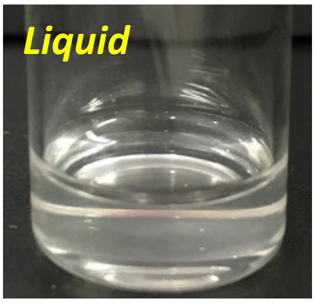
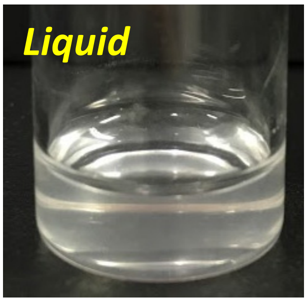
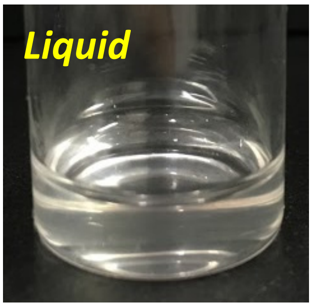
K : ether ratio	KFSA in G1	KFSA in G2	KFSA in G3
1 : 10	2.2 mol kg^{-1}  *Liquid*	2.2 mol kg^{-1}  *Liquid*	2.2 mol kg^{-1}  *Solid at RT**
1 : 4	5.5 mol kg^{-1}  *Liquid*	5.6 mol kg^{-1}  *Liquid*	5.6 mol kg^{-1}  *Liquid*

Figure S1. Photographs of prepared electrolytes at 25 °C.

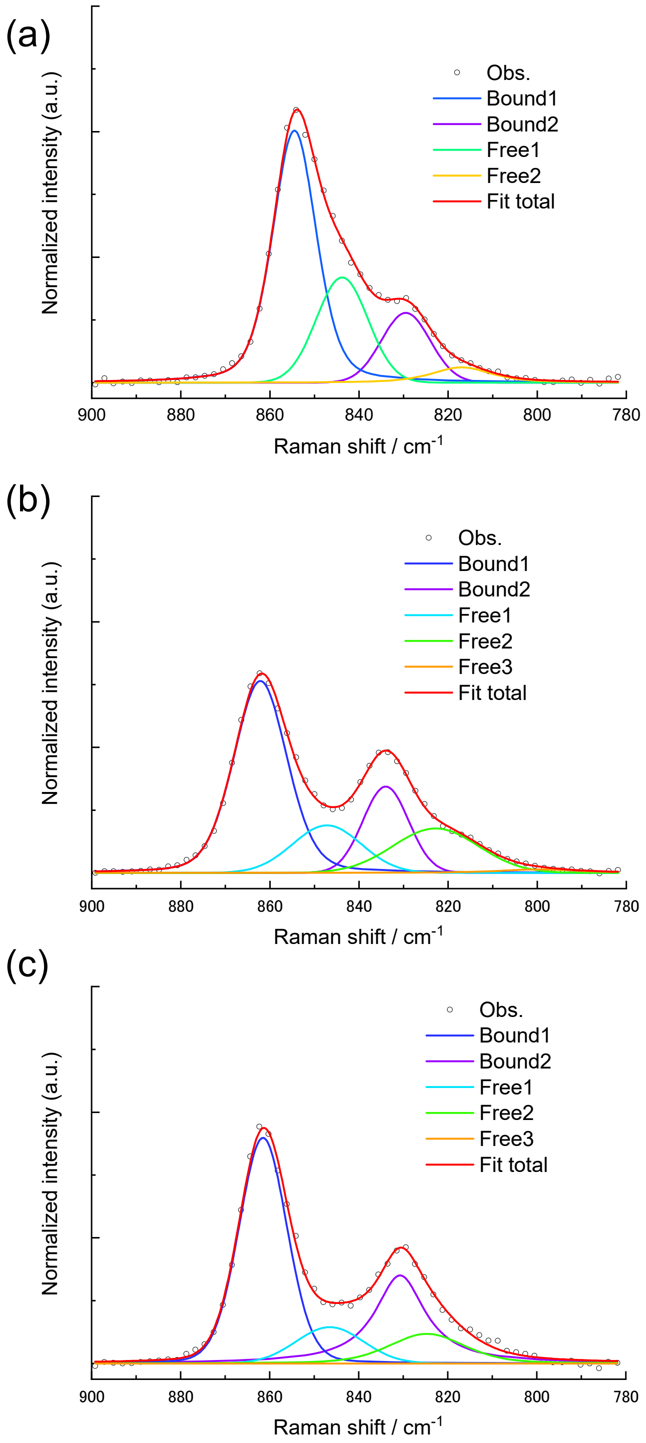


Figure S2. Deconvoluted Raman spectra of (a) 5.5 mol kg^{-1} KFSA/G1, (b) 5.6 mol kg^{-1} KFSA/G2, and (c) 5.6 mol kg^{-1} KFSA/G3. All the R^2 values for deconvolution are higher than 0.995.

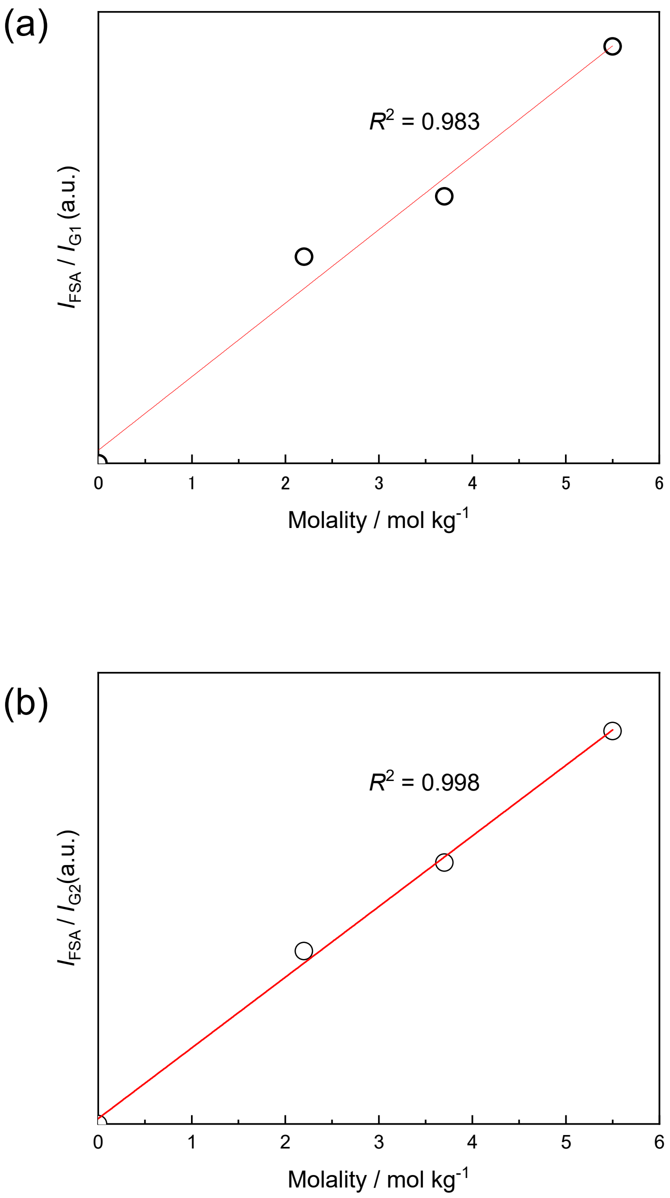


Figure S3. Sum of normalized integral intensity of Raman peak of S-N stretching mode of FSA$^-$ anion at 680–780 cm^{-1} as a function of molality of the solutions: (a) KFSA/G1 solutions and (b) KFSA/G2 solutions.

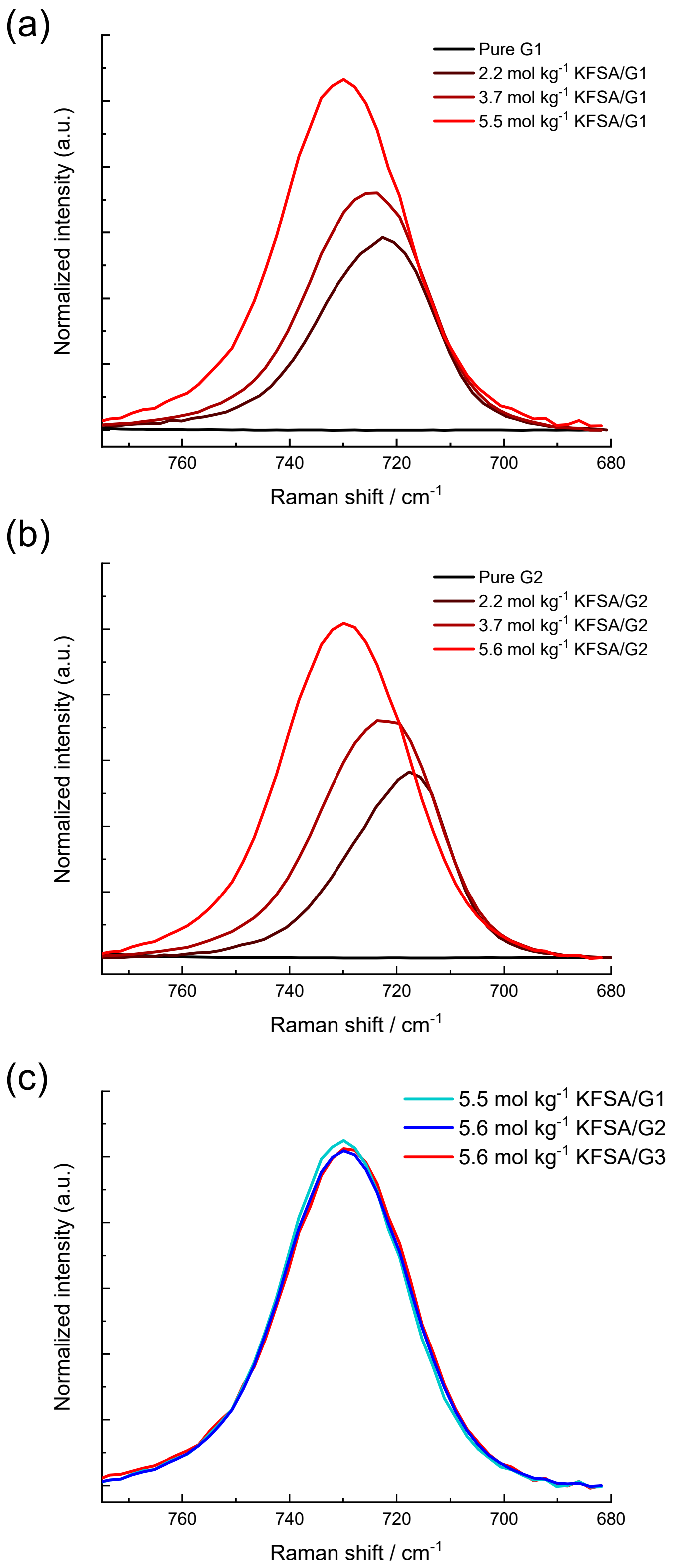


Figure S4. Normalized Raman spectra of (a) KFSA/G1, (b) KFSA/G2, and (c) KFSA/G3 solutions in the range of 680–900 cm^{-1}, which can be attributed to the S−N symmetric stretching vibration. Raman spectra of 5.5 mol kg^{-1} KFSA/G1 and 5.6 mol kg^{-1} KFSA/G2 are also shown in (c) for comparison.

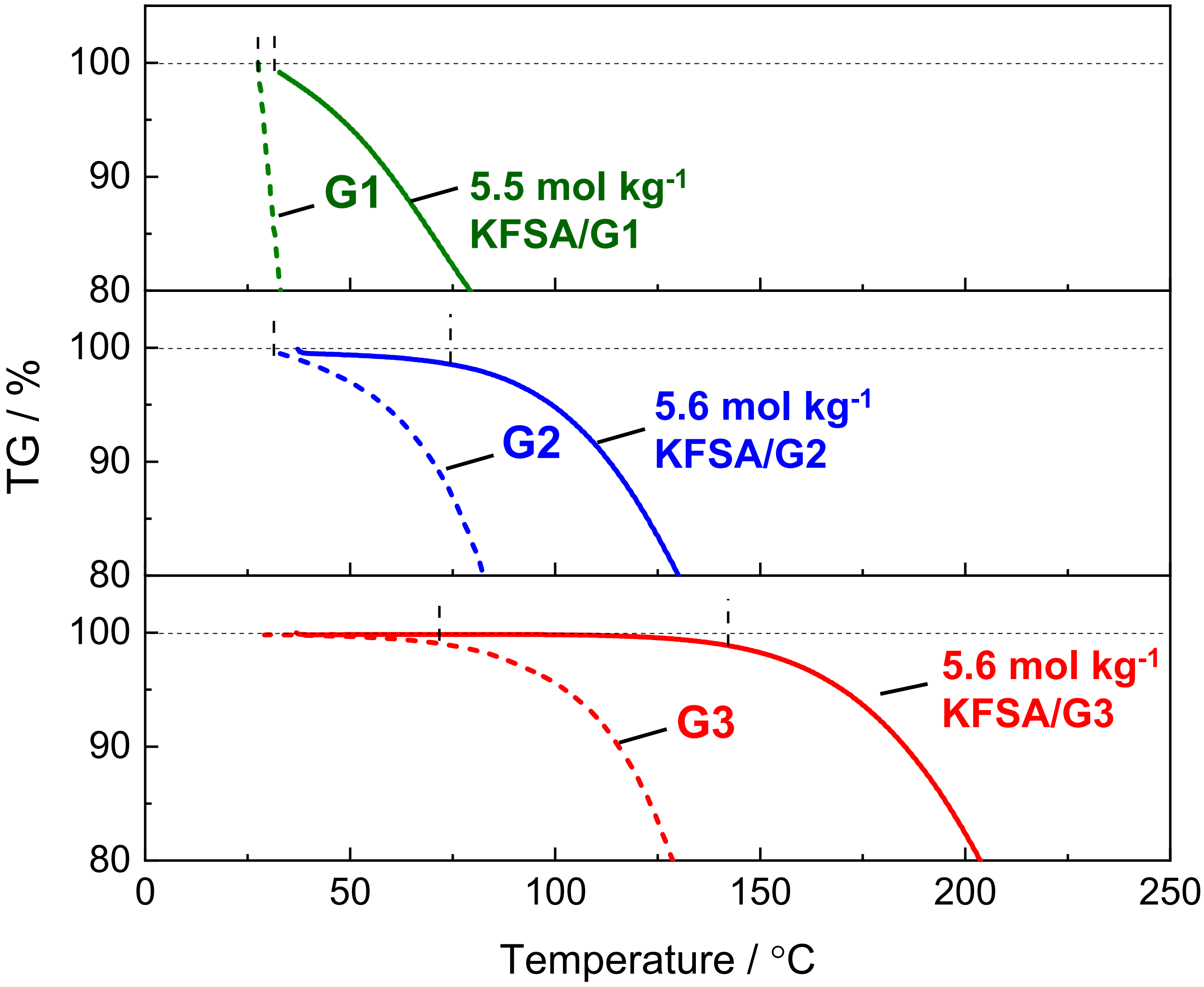


Figure S5. Thermogravimetric (TG) curves of pure solvents and highly concentrated KFSA/glyme solutions. The heating rate was 10 °C min^{-1}.

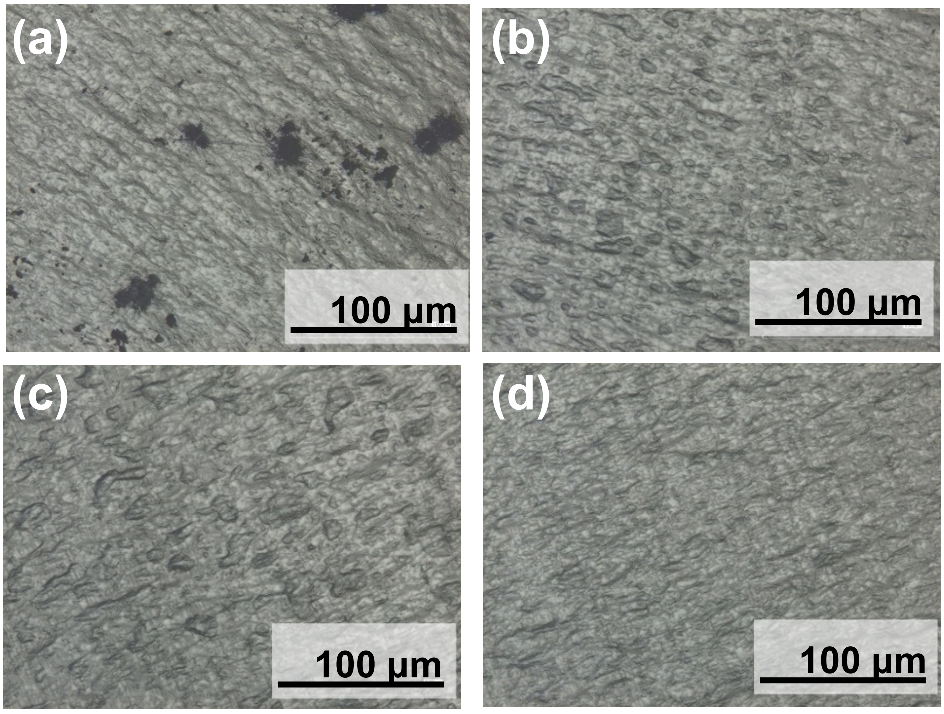


Figure S6. Microscopic images of surface morphology of Al foil electrodes tested in (a) 2.2 mol kg^{-1} KFSA/G1, (b) 5.5 mol kg^{-1} KFSA/G1, (c) 5.6 mol kg^{-1} KFSA/G2, and (d) 5.6 mol kg^{-1} KFSA/G3 after the CV in **Figure 2a**.

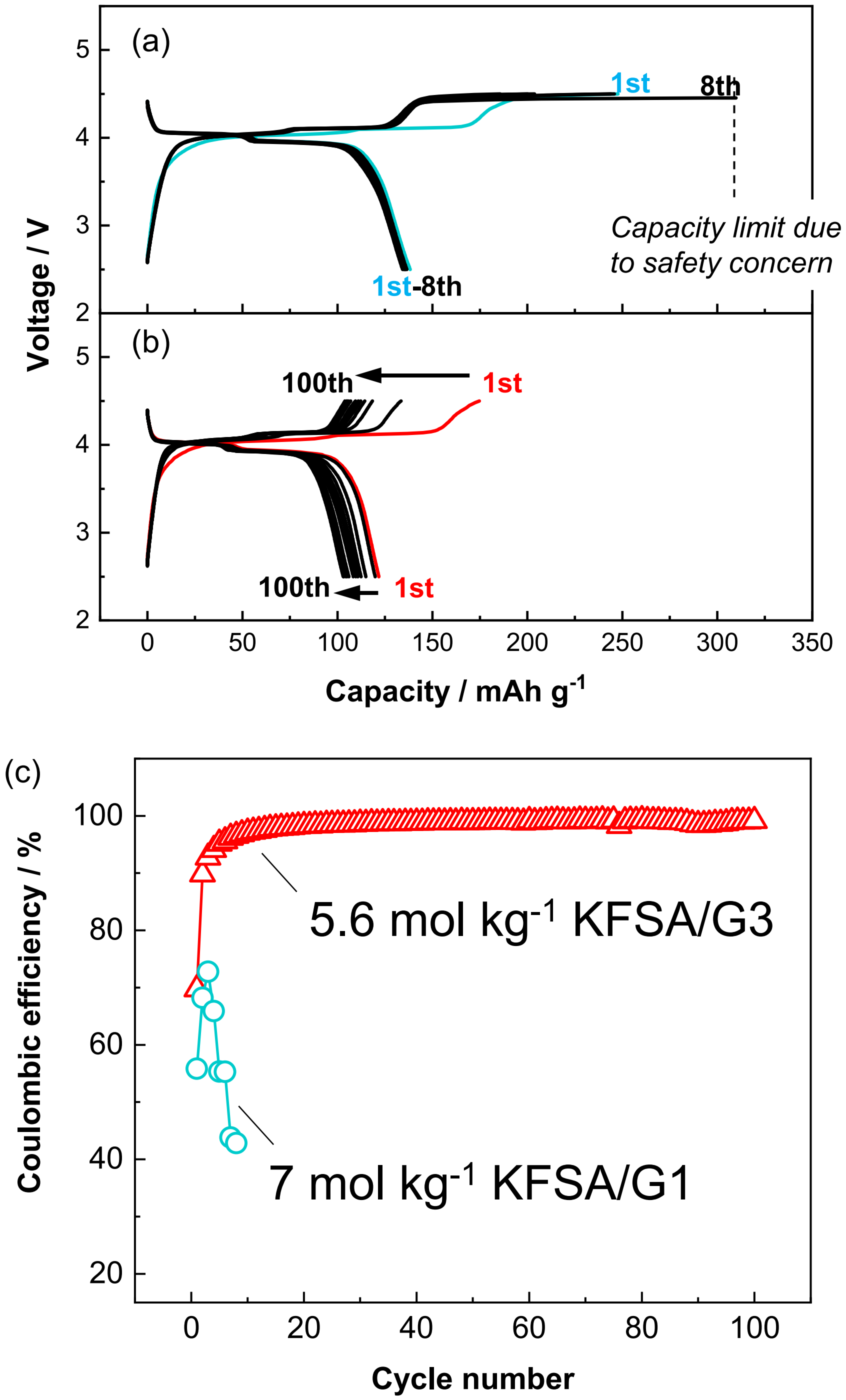


Figure S7. Charge/discharge curves of K||$K_2Mn[Fe(CN)_6]$ cells at cut-off voltage of 4.5 V. The electrolytes of (a) 7 mol kg^{-1} KFSA/G1 and (b) 5.6 mol kg^{-1} KFSA/G3, and (c) their Coulombic efficiencies.

Even when a higher concentration of 7 mol kg^{-1} KFSA/G1 solution is used instead of the 5.5 mol kg^{-1} solution, a large irreversible capacity was observed for the G1 cell around 4.4 V. In contrast, the G3 electrolyte cell showed good cycle performance and high Coulombic efficiency.

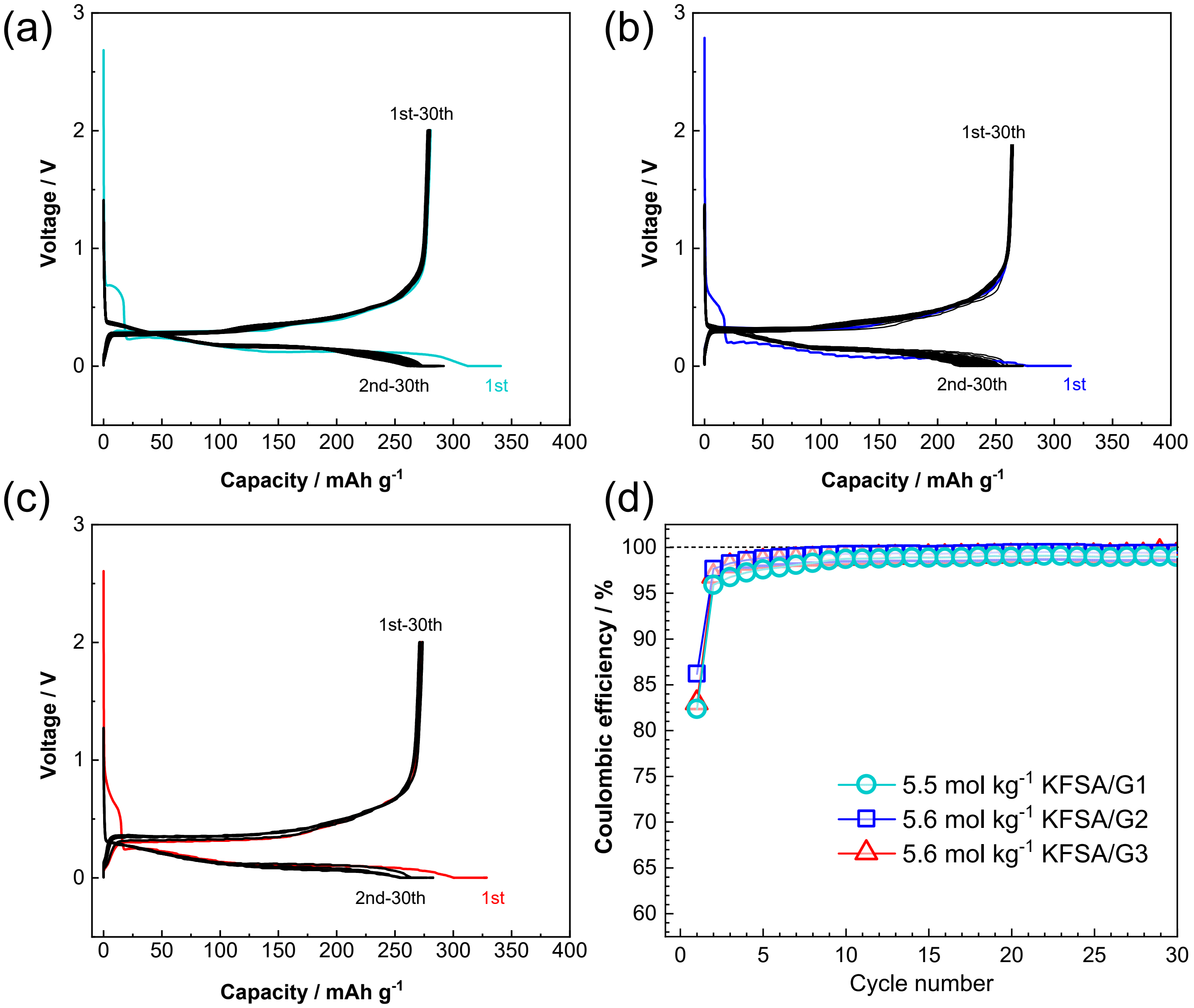


Figure S8. Charge/discharge curves of the K||graphite cells filled with (a) 5.5 mol kg^{-1} KFSA/G1, (b) 5.6 mol kg^{-1} KFSA/G2, and (c) 5.6 mol kg^{-1} KFSA/G3. (b) Variations in Coulombic efficiency of the cells. The current density was 25 mA g^{-1}.

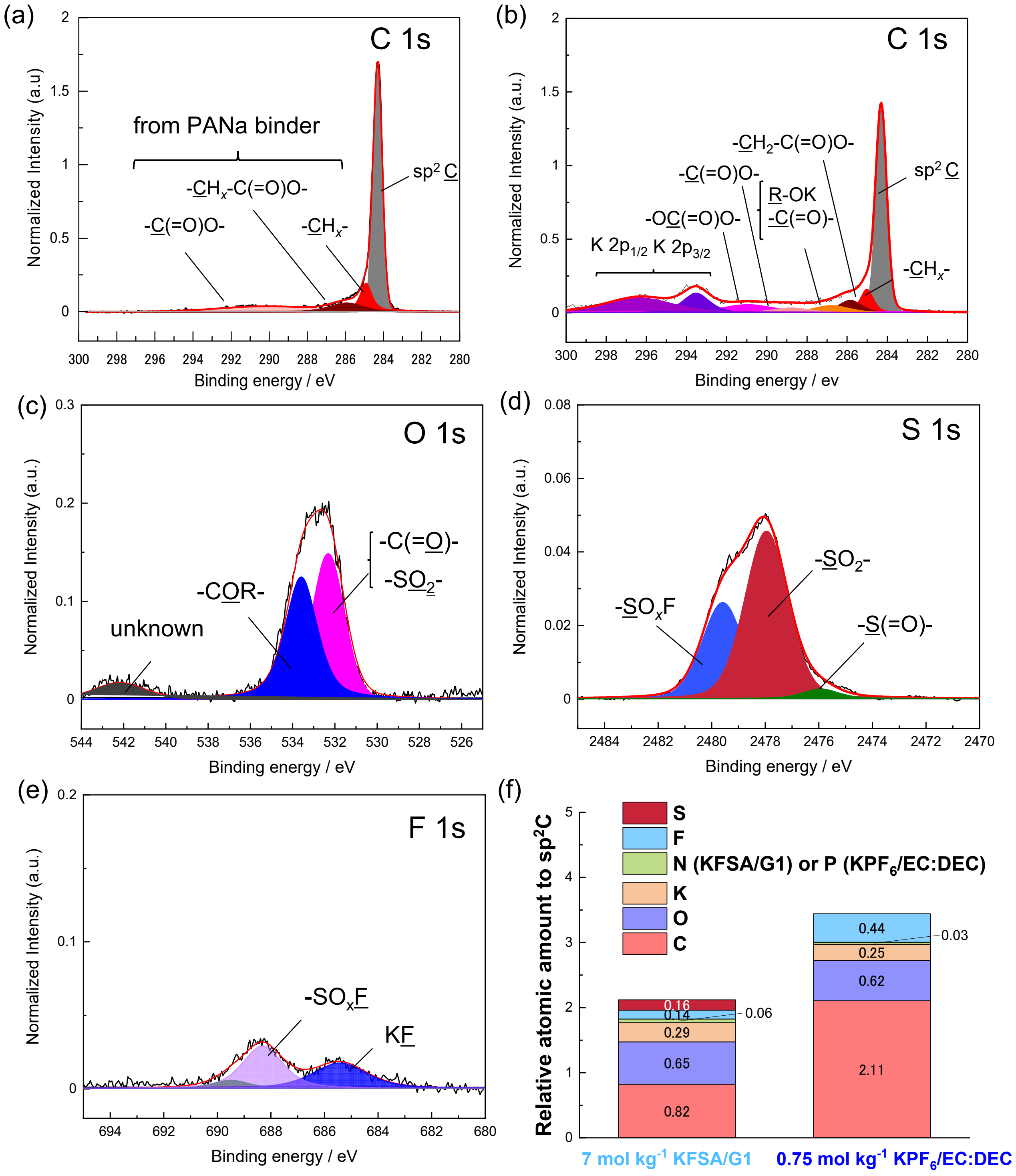


Figure S9. Hard X-ray photoelectron spectroscopy (HAXPES) spectra of pristine graphite electrode and that tested in K half cell filled with highly concentrated (7 mol kg^{-1}) KFSA/G1 electrolyte for 10 cycles: C 1s and K 2p of (a) pristine electrode and (b) cycled electrode, (c) O 1s, (d) P 1s, (e) F 1s spectra. (f) Relative atomic amount to sp^2 C of graphite electrodes cycled in 7 mol kg^{-1} KFSA/G1 electrolyte in comparison with that in 0.75 mol kg^{-1} KPF_6/EC:DEC which was reported our previous study [3] and was obtained by the same experimental procedures and conditions.

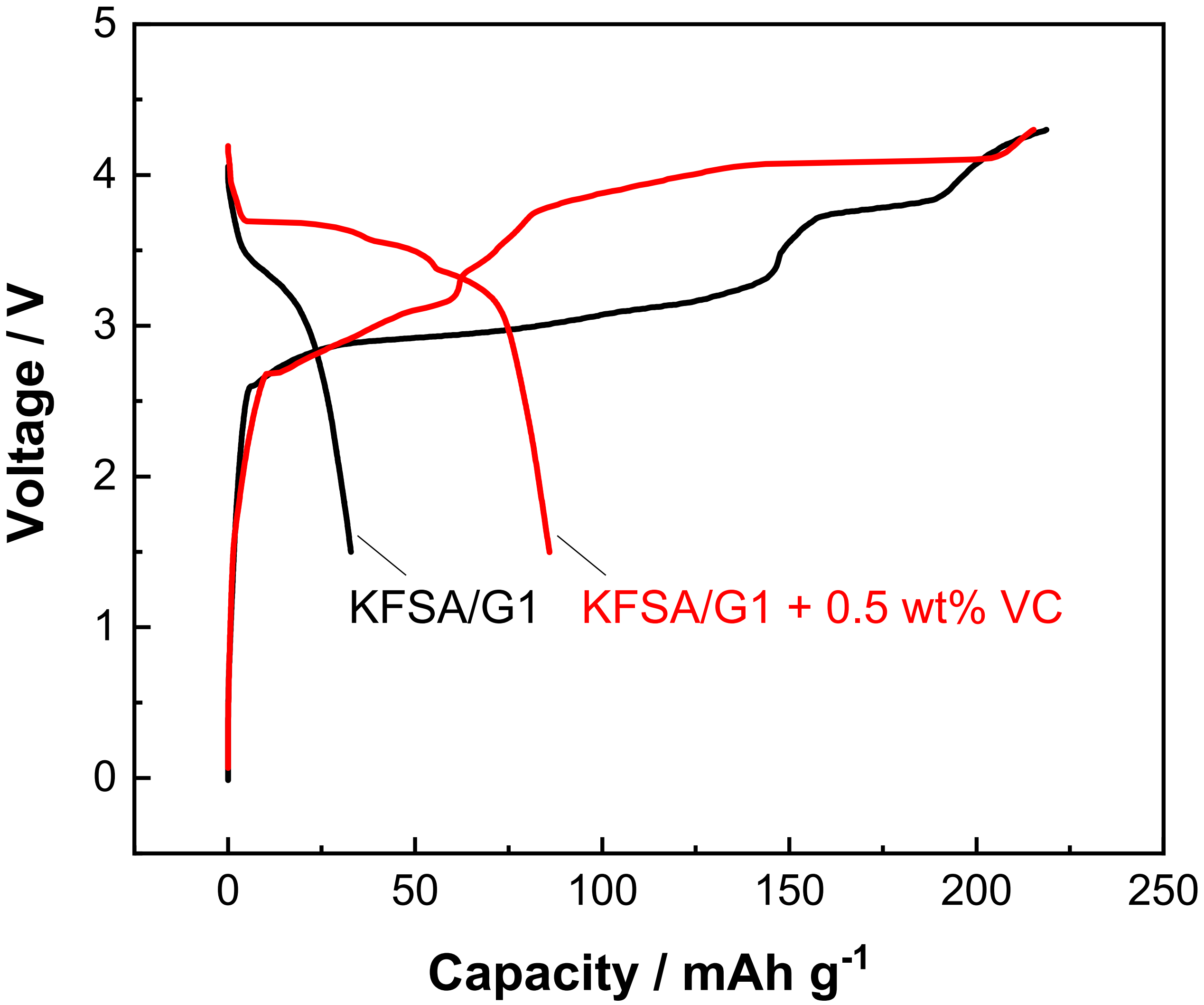


Figure S10. Initial charge/discharge curves of graphite||$K_2Mn[Fe(CN)_6]$ full cell filled with 5.5 mol kg^{-1} KFSA/G1 with/without 0.5 wt% vinylene carbonate as an additive..

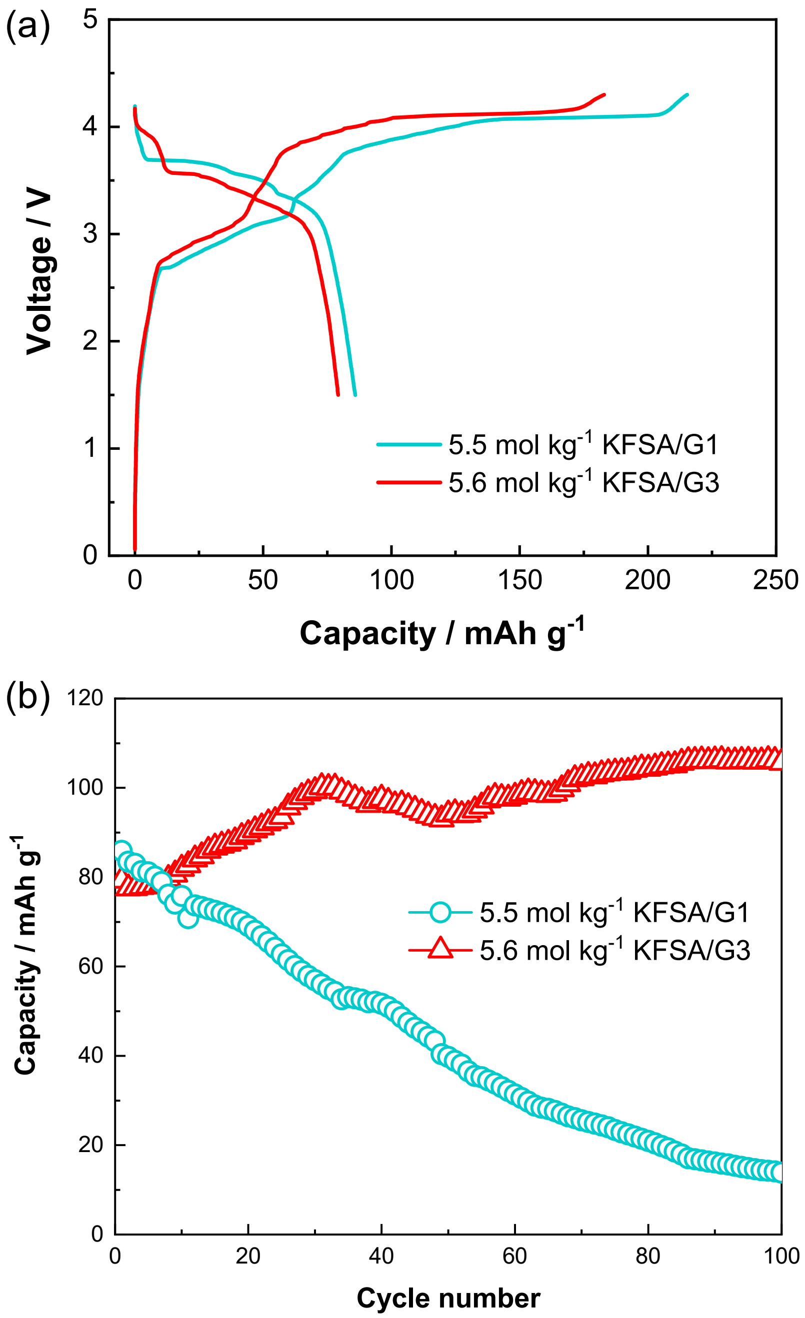


Figure S11. (a) Initial charge/discharge curves of graphite||$K_2Mn[Fe(CN)_6]$ full cell filled with 5.5 mol kg^{-1} KFSA/G1 and 5.6 mol kg^{-1} KFSA/G3 and (b) their cycle performance.

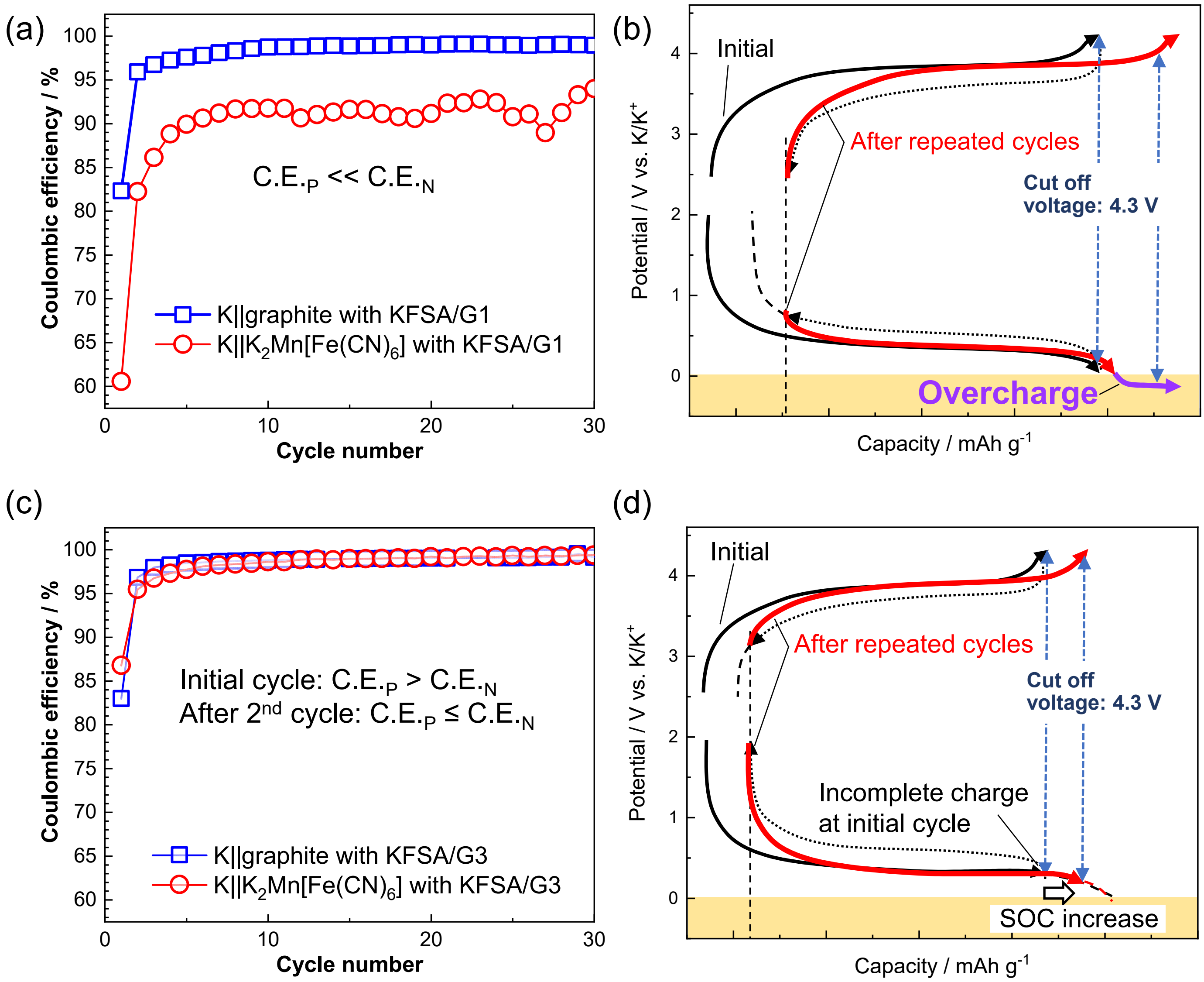


Figure S12 (a) Variations in Coulombic efficiency of K||graphite and K||$K_2Mn[Fe(CN)_6]$ cells filled with 5.5 mol kg^{-1} KFSA/G1 and schematic diagrams for capacity slippage between graphite negative and $K_2Mn[Fe(CN)_6]$ positive electrodes of the cell, where Coulombic efficiency of the negative electrode is always higher than those of the positive electrode. The unbalanced Coulombic efficiency induces the overcharge of the negative electrode during cycling. (c) Variations in Coulombic efficiency of K||graphite and K||$K_2Mn[Fe(CN)_6]$ cells filled with 5.6 mol kg^{-1} KFSA/G3 electrolytes and schematic diagrams for capacity slippage between graphite negative and $K_2Mn[Fe(CN)_6]$ positive electrodes of the cell, where the positive electrode shows higher Coulombic efficiency than the negative electrode at the initial cycle, but they are reversed after the second cycle. The negative electrode is not fully charged at the initial cycle due to its lower Coulombic efficiency. The state of charge (SOC) of the negative electrode continuously increases after the second cycle due to its higher Coulombic efficiency than that of the positive electrode. The SOC increase induces capacity increase during cycling.

References

1. Hosaka, T.; Kubota, K.; Kojima, H.; Komaba, S., *Chem. Commun.* 2018, **54** (60), 8387-8390.
2. Kim, H. J.; Yashiro, H.; Kim, H.; Lee, S.; Myung, S.-T., *J. Mater. Chem. A* 2019, **7** (46), 26250-26260.
3. T. Hosaka, T. Matsuyama, K. Kubota, S. Yasuno and S. Komaba, *ACS Appl. Mater. Interfaces*, 2020, **12**, 34873-34881.
4. S. Yasuno, S. Ishimaru and N. Ikeno, *Surf. Interface Anal.*, 2018, **50**, 1191-1194.