

# Supporting Information

## Potassium Difluorophosphate as an Electrolyte

### Additive for Potassium Ion Batteries

*Huan Yang,<sup>a</sup> Chih-Yao Chen,<sup>b</sup> Jinkwang Hwang,<sup>a</sup> Keigo Kubota,<sup>b</sup>*

*Kazuhiko Matsumoto,<sup>a, b, c,\*</sup> Rika Hagiwara<sup>a, b, c</sup>*

<sup>a</sup> Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

<sup>b</sup> AIST-Kyoto University Chemical Energy Materials Open Innovation Laboratory (ChEM-OIL), National Institute of Advanced Industrial Science and Technology (AIST), Sakyo-ku, Kyoto 606-8501, Japan

<sup>c</sup> Unit of Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Katsura, Kyoto 615-8510, Japan

\*Corresponding author:

E-mail: [k-matsumoto@energy.kyoto-u.ac.jp](mailto:k-matsumoto@energy.kyoto-u.ac.jp)

**Table S1.** Fitting results of the EIS data for the K/K symmetric cells with 0.5 M KPF<sub>6</sub>-EC/DEC electrolytes containing different amounts of KDFP or FEC.<sup>a</sup>

| Additives, EIS component |                             | 1 h                    | 12 h                   | 1 day                  | 3 day                  | 5 day                  |
|--------------------------|-----------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| 0 wt% KDFP               | $R_{\text{bulk}} / \Omega$  | 9.49                   | 36.65                  | 41.96                  | 63.24                  | 114.9                  |
|                          | $R_{\text{int}} / \Omega$   | 6175                   | 7331                   | 8061                   | 11853                  | 13914                  |
|                          | $C.F. / \text{Hz}$          | 7.99                   | 5.39                   | 5.56                   | 2.46                   | 2.60                   |
|                          | $Q / \text{F s}^{\alpha-1}$ | $6.01 \times 10^{-6}$  | $6.04 \times 10^{-6}$  | $5.94 \times 10^{-6}$  | $6.01 \times 10^{-6}$  | $6.51 \times 10^{-6}$  |
|                          | $\alpha$                    | 0.899                  | 0.907                  | 0.909                  | 0.910                  | 0.899                  |
| 0.1 wt% KDFP             | $R_{\text{bulk}} / \Omega$  | 10.48                  | 36.52                  | 44.55                  | 82.40                  | 102.2                  |
|                          | $R_{\text{int}} / \Omega$   | 2875                   | 4062                   | 5023                   | 7585                   | 8636                   |
|                          | $C.F. / \text{Hz}$          | 18.38                  | 11.83                  | 11.83                  | 5.69                   | 5.69                   |
|                          | $Q / \text{F s}^{\alpha-1}$ | $5.10 \times 10^{-6}$  | $5.52 \times 10^{-6}$  | $5.43 \times 10^{-6}$  | $5.24 \times 10^{-6}$  | $5.21 \times 10^{-6}$  |
|                          | $\alpha$                    | 0.840                  | 0.881                  | 0.883                  | 0.886                  | 0.886                  |
| 0.2 wt% KDFP             | $R_{\text{bulk}} / \Omega$  | 6.707                  | 22.31                  | 32.38                  | 67.00                  | 103.79                 |
|                          | $R_{\text{int}} / \Omega$   | 1 794                  | 3 077                  | 3 128                  | 4 831                  | 5 424                  |
|                          | $C.F. / \text{Hz}$          | 25.97                  | 11.84                  | 11.84                  | 7.99                   | 7.99                   |
|                          | $Q / \text{F s}^{\alpha-1}$ | $6.27 \times 10^{-6}$  | $7.445 \times 10^{-6}$ | $7.13 \times 10^{-6}$  | $7.976 \times 10^{-6}$ | $7.195 \times 10^{-6}$ |
|                          | $\alpha$                    | 0.904                  | 0.881                  | 0.887                  | 0.861                  | 0.881                  |
| 0.3 wt% FEC              | $R_{\text{bulk}} / \Omega$  | 23.63                  | 36.21                  | 82.34                  | 107.96                 | 145.64                 |
|                          | $R_{\text{int}} / \Omega$   | 17909                  | 40580                  | 77062                  | 181307                 | 203896                 |
|                          | $C.F. / \text{Hz}$          | 2.46                   | 0.76                   | 0.51                   | 0.17                   | 0.17                   |
|                          | $Q / \text{F s}^{\alpha-1}$ | $5.104 \times 10^{-6}$ | $5.242 \times 10^{-6}$ | $4.636 \times 10^{-6}$ | $4.581 \times 10^{-6}$ | $4.298 \times 10^{-6}$ |
|                          | $\alpha$                    | 0.880                  | 0.861                  | 0.869                  | 0.852                  | 0.864                  |
| 3 wt% FEC                | $R_{\text{bulk}} / \Omega$  | 19.01                  | 64.38                  | 79.69                  | 108.4                  | 208.6                  |
|                          | $R_{\text{int}} / \Omega$   | 16246                  | 40041                  | 66 449                 | 179735                 | 223455                 |
|                          | $C.F. / \text{Hz}$          | 2.60                   | 1.12                   | 0.51                   | 0.16                   | 0.11                   |
|                          | $Q / \text{F s}^{\alpha-1}$ | $4.994 \times 10^{-6}$ | $5.039 \times 10^{-6}$ | $4.722 \times 10^{-6}$ | $4.249 \times 10^{-6}$ | $4.028 \times 10^{-6}$ |
|                          | $\alpha$                    | 0.893                  | 0.842                  | 0.883                  | 0.840                  | 0.852                  |

<sup>a</sup>  $C.F.$ ,  $Q$ , and  $\alpha$  denote characteristic frequency, CPE parameter, and CPE exponent, respectively.

**Table S2.** The peak positions (unit: V) in the  $dQ/dV$  plots of the K/graphite cells in 0.5 M KPF<sub>6</sub>-EC/DEC with different additives during the first charge and discharge processes. See Figures 4 and S10 for the  $dQ/dV$  plots.

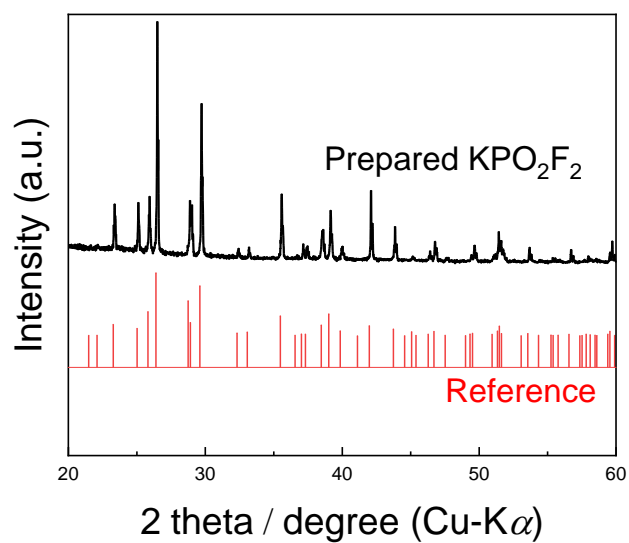
| Additive      | SEI formation | Charge           |                  |                 | Discharge       |                  |                  |
|---------------|---------------|------------------|------------------|-----------------|-----------------|------------------|------------------|
|               |               | Potassiation     |                  |                 | Depotassiation  |                  |                  |
|               |               | KC <sub>36</sub> | KC <sub>24</sub> | KC <sub>8</sub> | KC <sub>8</sub> | KC <sub>24</sub> | KC <sub>36</sub> |
| Additive-free | 0.295         | 0.264            | 0.201            | 0.151           | 0.279           | 0.367            | 0.485            |
| 0.1 wt% KDFP  | 0.351         | 0.263            | 0.228            | 0.172           | 0.265           | 0.352            | 0.464            |
| 0.2 wt% KDFP  | 0.358         | 0.280            | 0.241            | 0.184           | 0.261           | 0.350            | 0.462            |
| 0.3 wt% FEC   | 1.197         | 0.227            | 0.140            | 0.068           | 0.438           | 0.583            | 0.739            |
| 3 wt% FEC     | 1.245         | 0.035            | 0.079            | 0.136           | 0.410           | 0.518            | 0.680            |

**Table S3.** Coulombic efficiencies (%) of the K/graphite cells with 0.5 M KPF<sub>6</sub>-EC/DEC electrolytes containing different amounts of KDFP or FEC. The charge-discharge rate is C/20.

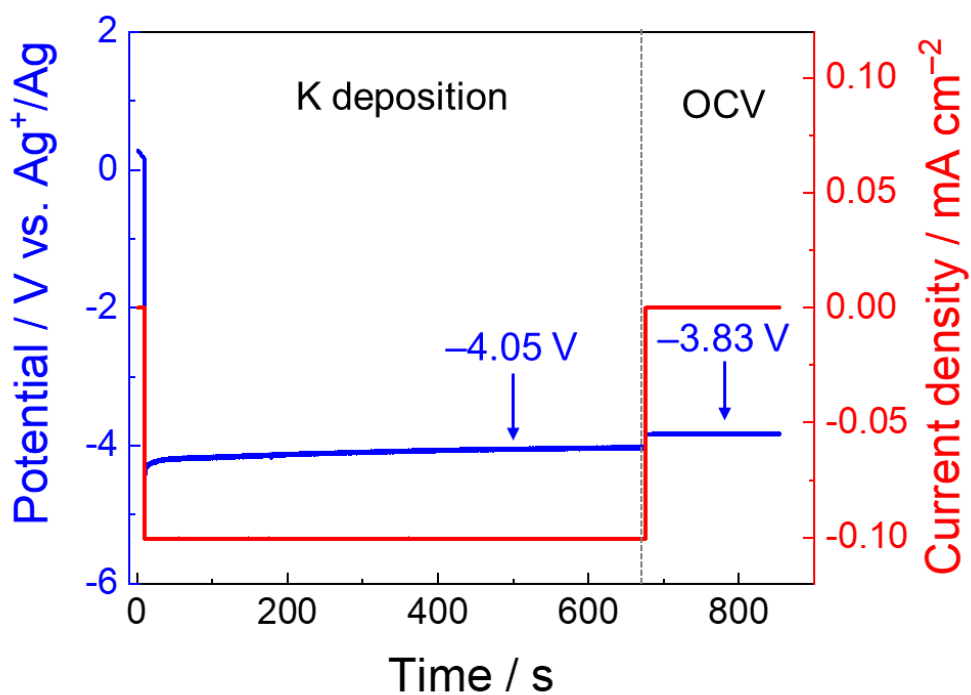
| Cycle number | KDFP  |         |         | FEC     |       |
|--------------|-------|---------|---------|---------|-------|
|              | 0 wt% | 0.1 wt% | 0.2 wt% | 0.3 wt% | 3 wt% |
| 1st          | 84.5  | 86.1    | 86.9    | 79.2    | 65.3  |
| 2nd          | 95.9  | 98.2    | 99.8    | 96.0    | 88.7  |
| 3rd          | 96.9  | 99.1    | 99.8    | 99.2    | 92.8  |

**Table S4.** Binding energy (eV) and assignments of the XPS data on the graphite and in 0.5 M KPF<sub>6</sub>-EC/DEC electrolytes containing different amounts of KDFP.

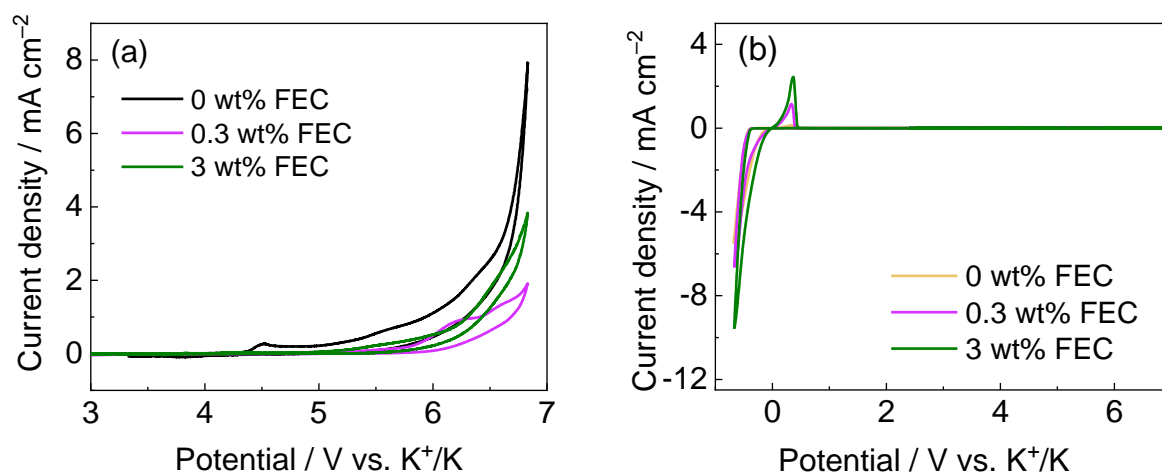
|                           | K2p                            | F1s                                  | C1s                                    | O1s         | P2p                                     |
|---------------------------|--------------------------------|--------------------------------------|----------------------------------------|-------------|-----------------------------------------|
| <b>Graphite electrode</b> |                                |                                      |                                        |             |                                         |
| 0 wt%                     | 295.2 (KF, 2p <sub>3/2</sub> ) | 687.5                                | 289.5 (CO <sub>3</sub> <sup>2-</sup> ) | 533.3 (C–O) | 137.6 (K <sub>x</sub> PF <sub>y</sub> ) |
| KDFP                      | 292.5 (KF, 2p <sub>1/2</sub> ) | (CF <sub>x</sub> , PF <sub>x</sub> ) | 288.1 (C=O)                            | 531.4 (C=O) |                                         |
|                           |                                | 683.6 (KF)                           | 286.4 (C–O)                            | 529.4 (K–O) |                                         |
|                           |                                |                                      | 284.7 (C–C)                            |             |                                         |
|                           |                                |                                      | 282.6 (K–C)                            |             |                                         |
| 0.2 wt%                   | 295.4 (KF, 2p <sub>3/2</sub> ) | 687.6                                | 289.5 (CO <sub>3</sub> <sup>2-</sup> ) | 533.6 (C–O) | 137.7 (K <sub>x</sub> PF <sub>y</sub> ) |
| KDFP                      | 292.6 (KF, 2p <sub>1/2</sub> ) | (CF <sub>x</sub> , PF <sub>x</sub> ) | 288.0 (C=O)                            | 531.7 (C=O) | 133.7                                   |
|                           |                                | 683.6 (KF)                           | 286.4 (C–O)                            | 528.8 (K–O) | (PO <sub>x</sub> ,                      |
|                           |                                |                                      | 284.6 (C–C)                            |             | Phosphate)                              |
|                           |                                |                                      | 282.9 (K–C)                            |             |                                         |
| Pristine                  |                                |                                      | 290.9                                  | 533.6 (C–O) |                                         |
|                           |                                |                                      | (CF <sub>x</sub> , PVDF)               | 532.1 (C=O) |                                         |
|                           |                                |                                      | 287.2 (C=O)                            |             |                                         |
|                           |                                |                                      | 286.1 (C–O)                            |             |                                         |
|                           |                                |                                      | 285.3 (C, <i>sp</i> <sup>3</sup> )     |             |                                         |
|                           |                                |                                      | 284.4 (C, <i>sp</i> <sup>2</sup> )     |             |                                         |
| <b>K metal</b>            |                                |                                      |                                        |             |                                         |
| 0 wt%                     |                                | 687.5                                |                                        |             |                                         |
| KDFP                      |                                | (CF <sub>x</sub> , PF <sub>x</sub> ) |                                        |             |                                         |
| 2 wt%                     |                                | 687.4                                |                                        |             |                                         |
| KDFP                      |                                | (CF <sub>x</sub> , PF <sub>x</sub> ) |                                        |             |                                         |
|                           |                                | 683.2 (KF)                           |                                        |             |                                         |



**Figure S1.** X-ray diffraction pattern of the prepared KDFP. The reference pattern of K[PO<sub>2</sub>F<sub>2</sub>] created from the single crystal X-ray diffraction data[1] is also shown for comparison.

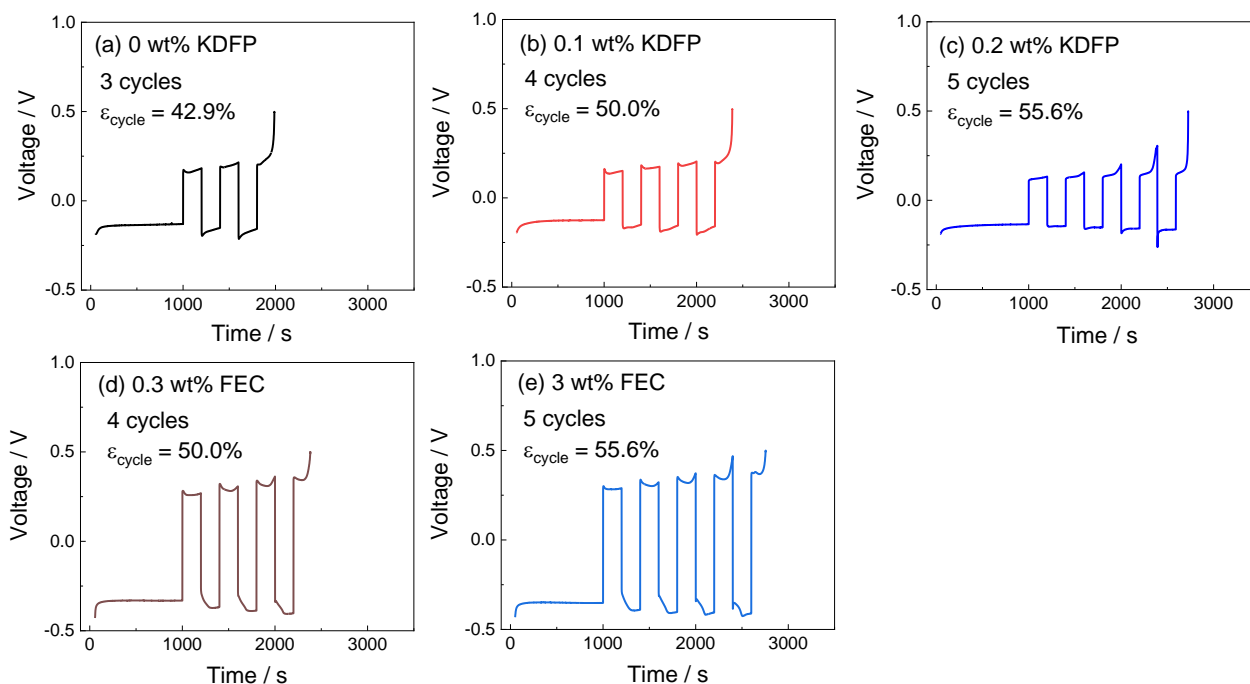


**Figure S2.** The voltage profile of K deposition/dissolution in 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  on the Al working electrode (area:  $0.25 \text{ cm}^2$ ) with the  $\text{Ag}^+/\text{Ag}$  reference electrode and Pt counter electrode in a three-electrode cell. The  $\text{K}^+/\text{K}$  equilibrium potential in 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  is determined to be  $-3.83 \text{ V}$  vs.  $\text{Ag}^+/\text{Ag}$  by an open circuit potential (OCP) measurement after galvanostatic K metal deposition at  $0.1 \text{ mA cm}^{-2}$  in a three-electrode cell.

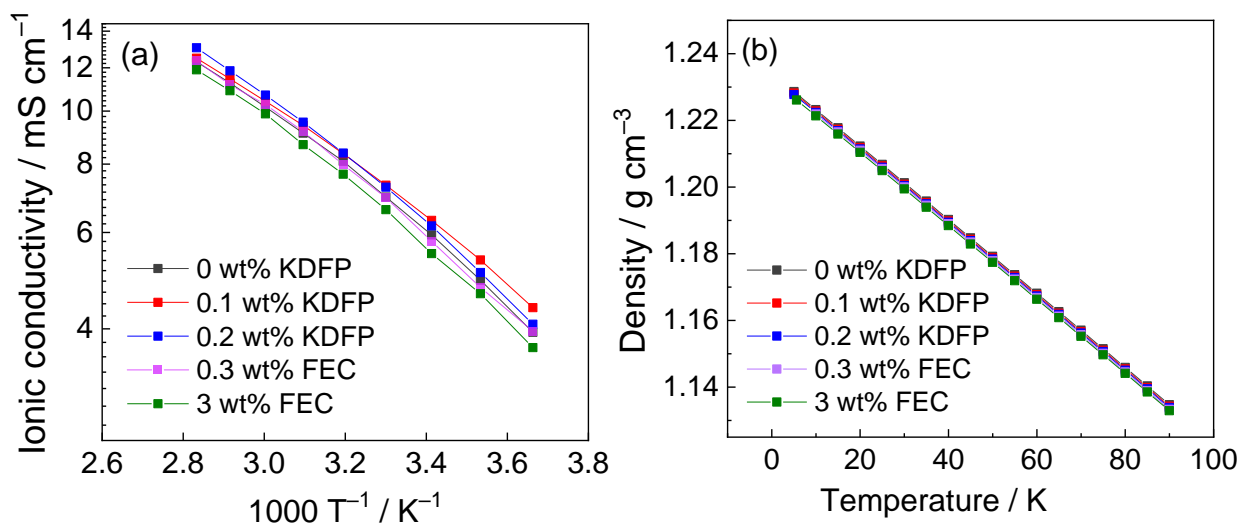


**Figure S3.** Cyclic voltammograms of (a) Pt (at anodic side) and (b) Al (at anodic and cathodic sides) plate electrodes in 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  with 0.3 wt% KDFP, 0.3 wt% and 3 wt% FEC. Scan rate: 5  $\text{mV s}^{-1}$ .

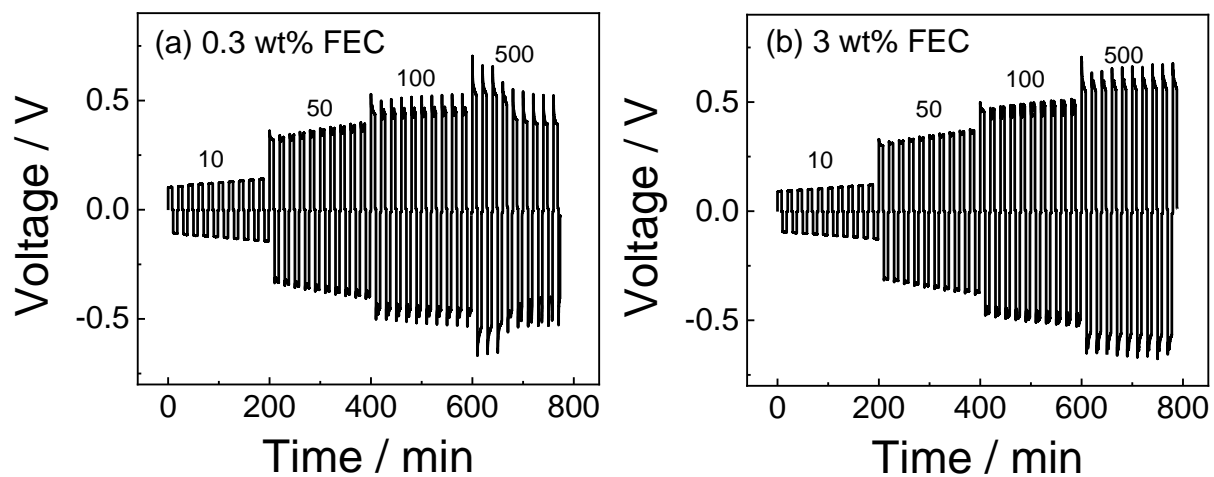




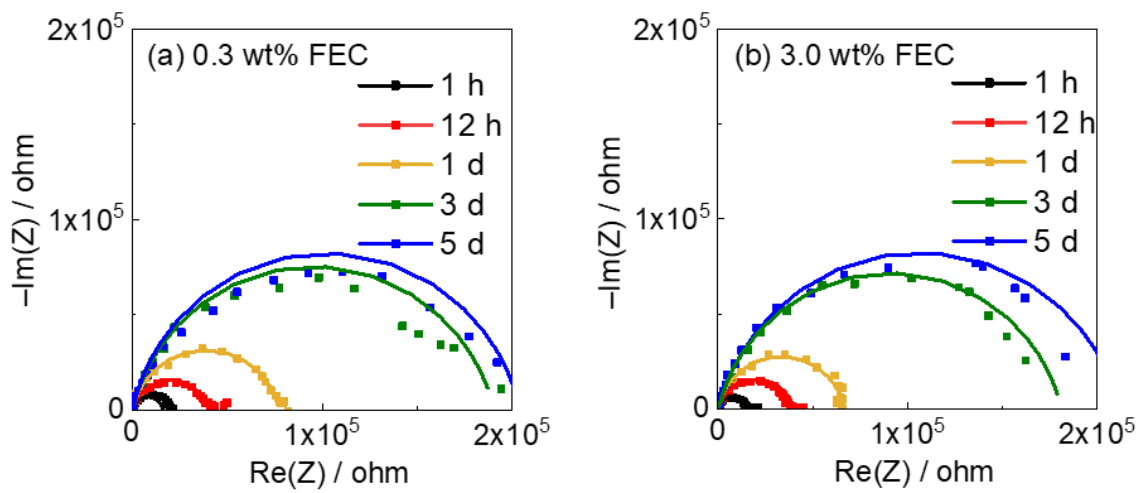
**Figure S4.** Voltage profiles during K deposition/dissolution in 0.5 M KPF<sub>6</sub>-EC/DEC with (a) 0 wt% KDFP, (b) 0.1 wt% KDFP, (c) 0.2 wt% KDFP, (d) 0.3 wt% FEC, and (e) 3 wt% FEC at 25 °C. The working and counter electrodes were Cu and K metal plates, respectively. K metal (0.1 C cm<sup>-2</sup>) was pre-deposited on the Cu plate, followed by repeated dissolution and deposition at a capacity of 0.02 C cm<sup>-2</sup> until the electrode potential reached 0.5 V vs. K<sup>+</sup>/K during dissolution. The current density was  $\pm 0.1$  mA cm<sup>-2</sup> for all the tests.



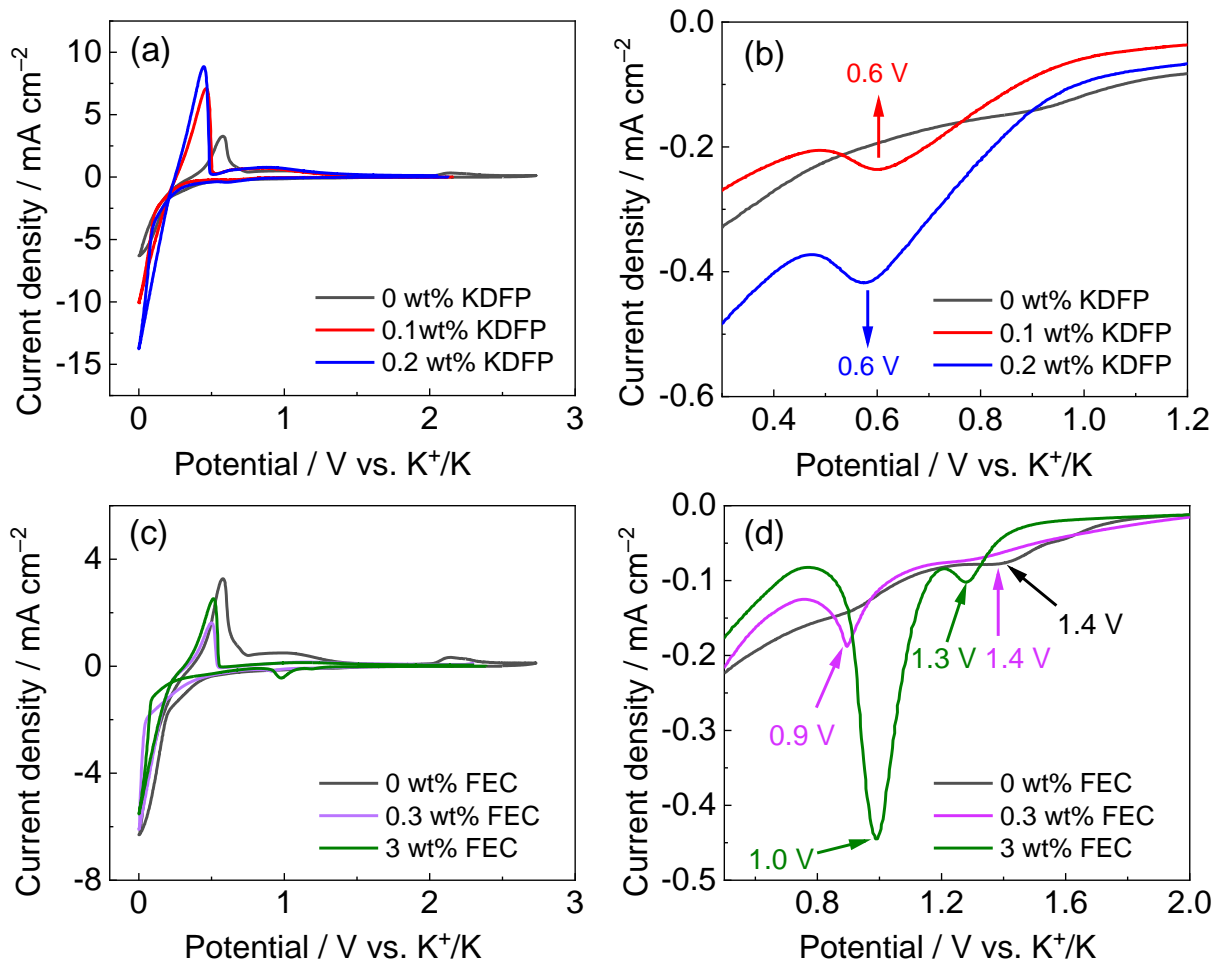
**Figure S5.** (a) Arrhenius plots of ionic conductivities and (b) densities of 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  (1:1, v:v) without and with KDFP or FEC additives in the temperature range between 0 and 90 °C.



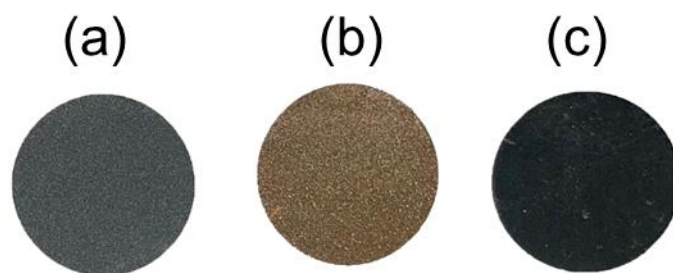
**Figure S6.** Voltage profiles of the K/K symmetrical cells during galvanostatic K metal deposition/dissolution in 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  with (a) 0.3 wt% and (b) 3 wt% FEC additives at 25 °C. The numbers shown in each panel denote current densities in  $\mu\text{A}\cdot\text{cm}^{-2}$ .



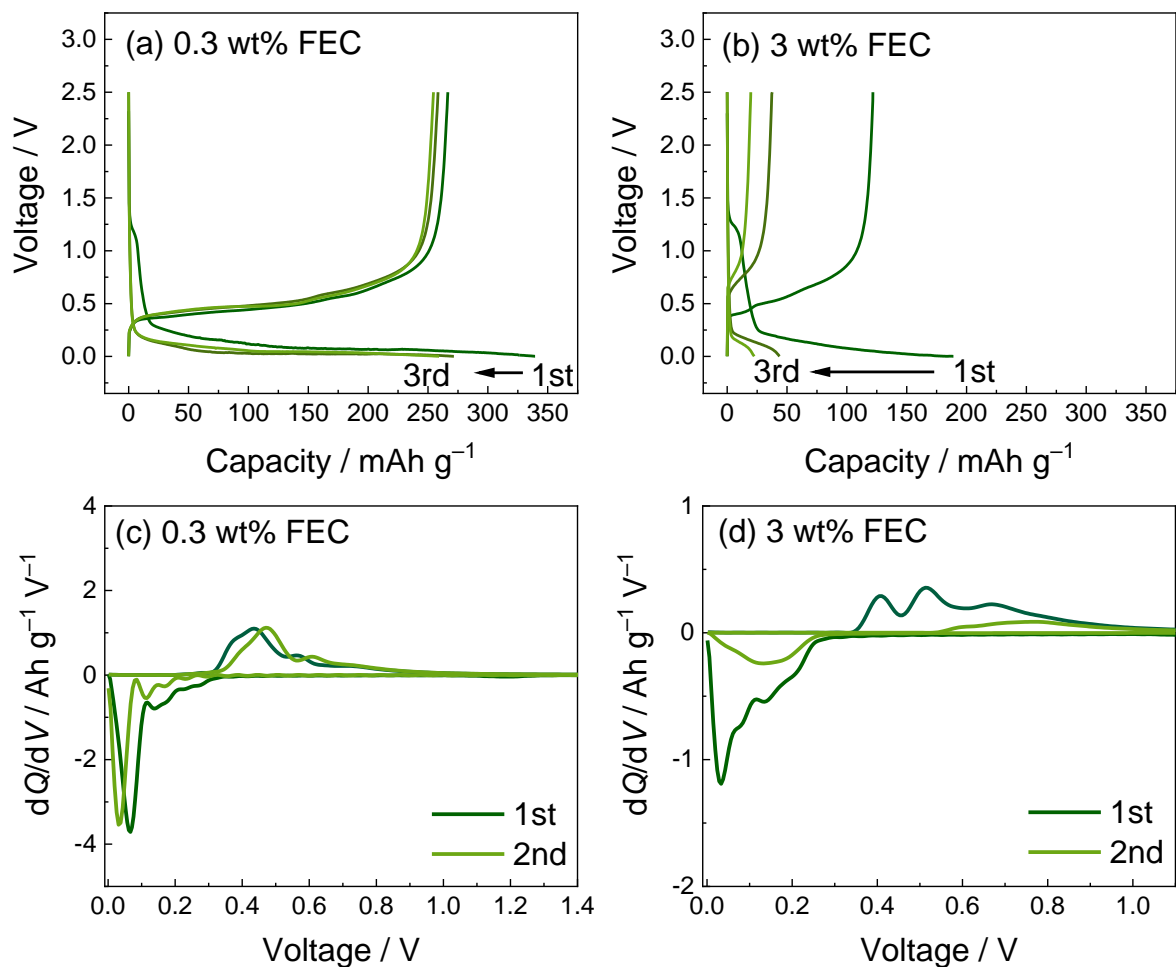
**Figure S7.** Nyquist plots and fitting lines of the K/K symmetric cells with  $0.5 \text{ M KPF}_6\text{-EC/DEC}$  with (a)  $0.3 \text{ wt\%}$  and (c)  $3 \text{ wt\%}$  FEC additives at  $25^\circ \text{C}$  in the frequency range of  $100 \text{ kHz}$ – $10 \text{ mHz}$ . AC amplitude:  $10 \text{ mV}$ .



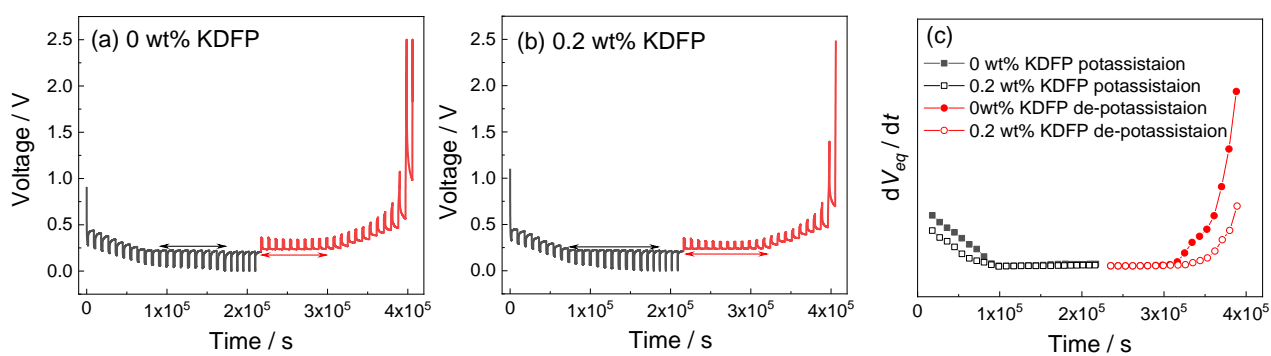
**Figure S8.** Cyclic voltammograms of graphite electrodes in 0.5 M KPF<sub>6</sub>-EC/DEC with (a) 0 wt%, 0.1 wt%, and 0.2 wt% KDFP, (c) 0 wt% FEC, 0.3 wt% FEC and 3 wt% FEC additives at 25 °C. (b, d) Magnified figures of (a) and (c). Scan rate: 5 mV s<sup>-1</sup>. Pt counter and Ag<sup>+</sup>/Ag reference electrodes were used. The potential was converted to that against the K<sup>+</sup>/K reference.



**Figure S9.** Photos of (a) as-prepared, (b) fully potassiated, and (c) fully depotassiated graphite electrodes obtained in 0.5 M  $\text{KPF}_6\text{-EC/DEC}$  by galvanostatic charge-discharge tests. C-rate: C/20 ( $1\text{C} = 279 \text{ mA g}^{-1}$ ).

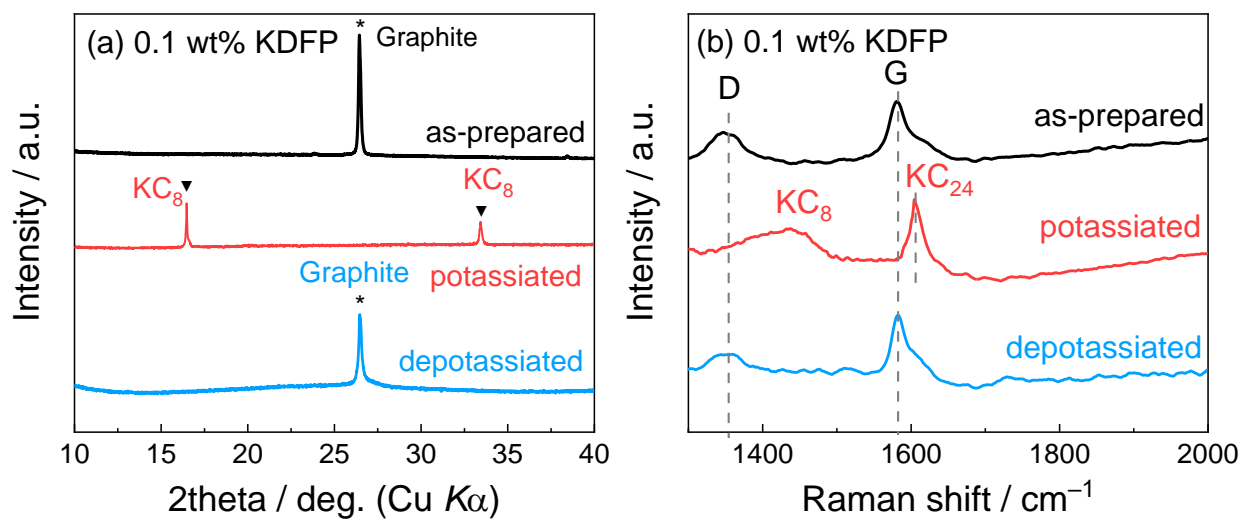


**Figure. S10.** Charge-discharge curves of the K/graphite cells in 0.5 M KPF<sub>6</sub>-EC/DEC electrolytes with (a) 0.3 wt% and (b) 3 wt% FEC. C-rate: C/20 (1C = 279 mA g<sup>-1</sup>). The corresponding differential capacity vs. voltage (dQ/dV) plots of the first two charge-discharge cycles are shown in (c) and (d).

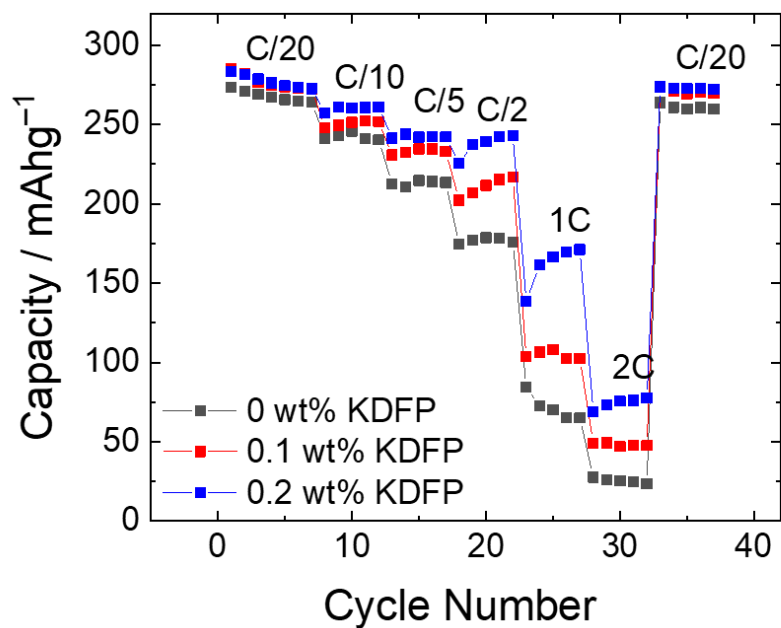


**Figure S11.** Galvanostatic intermittent titration technique (GITT) curves of graphite electrodes in 0.5 M KPF<sub>6</sub>-EC/DEC with (a) 0 wt% and (b) 0.2 wt% KDFP. (c) Quasi-equilibrium voltage variation depends on the time change during charge-discharge process. GITT was measured by applying a constant rate of C/20 for 30 min followed by voltage relaxation for 2 h.

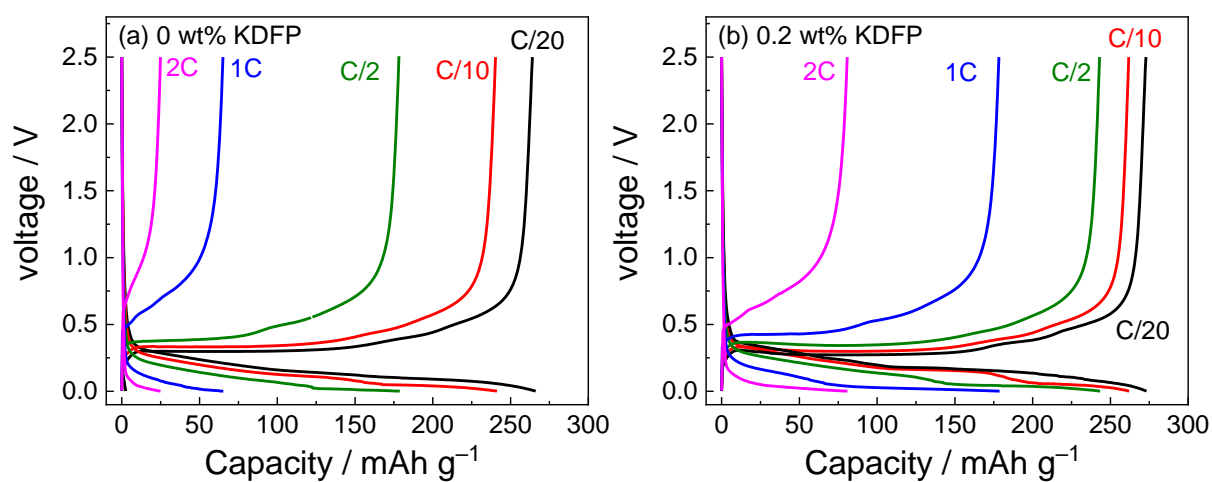




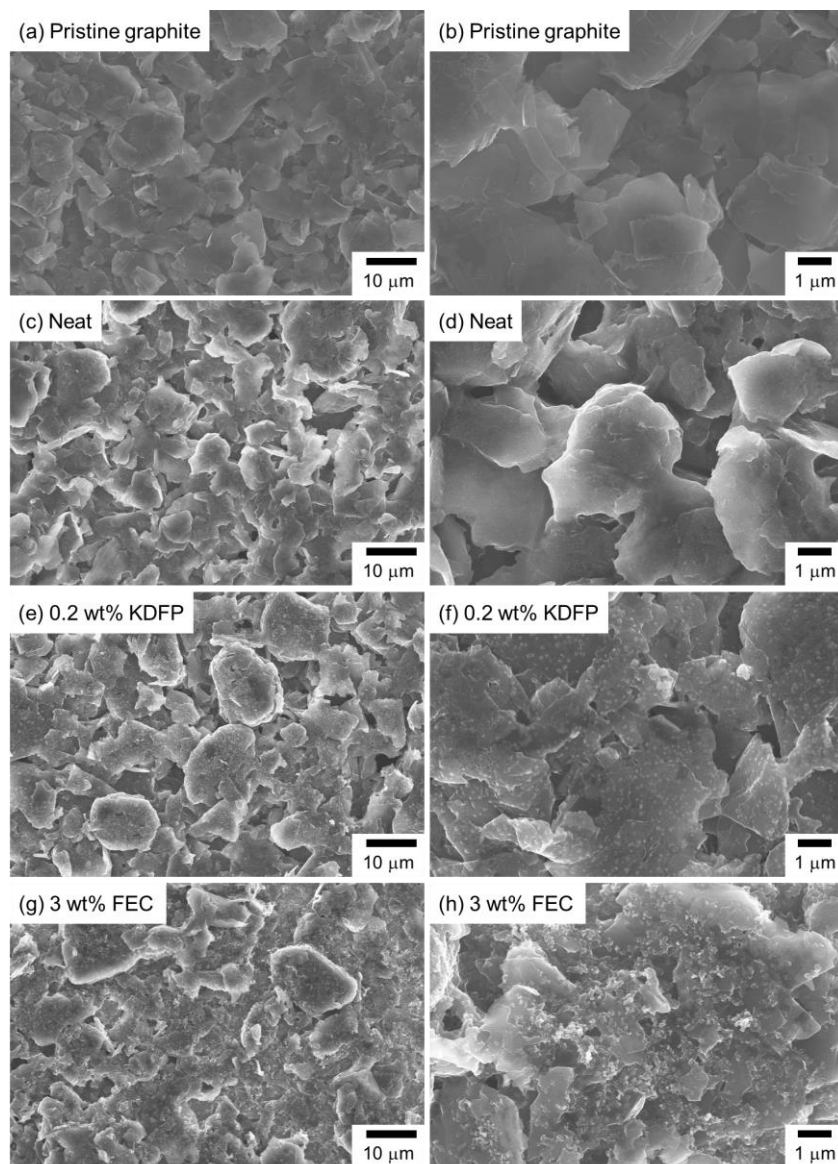
**Figure S12.** (a) *Ex-situ* XRD patterns and (b) Raman spectra of graphite electrodes at the pristine (black), fully potassiated (red), and fully depotassiated (blue) states recovered from 0.5 M  $\text{KPF}_6$ -EC/DEC with 0.1 wt% KDFP.



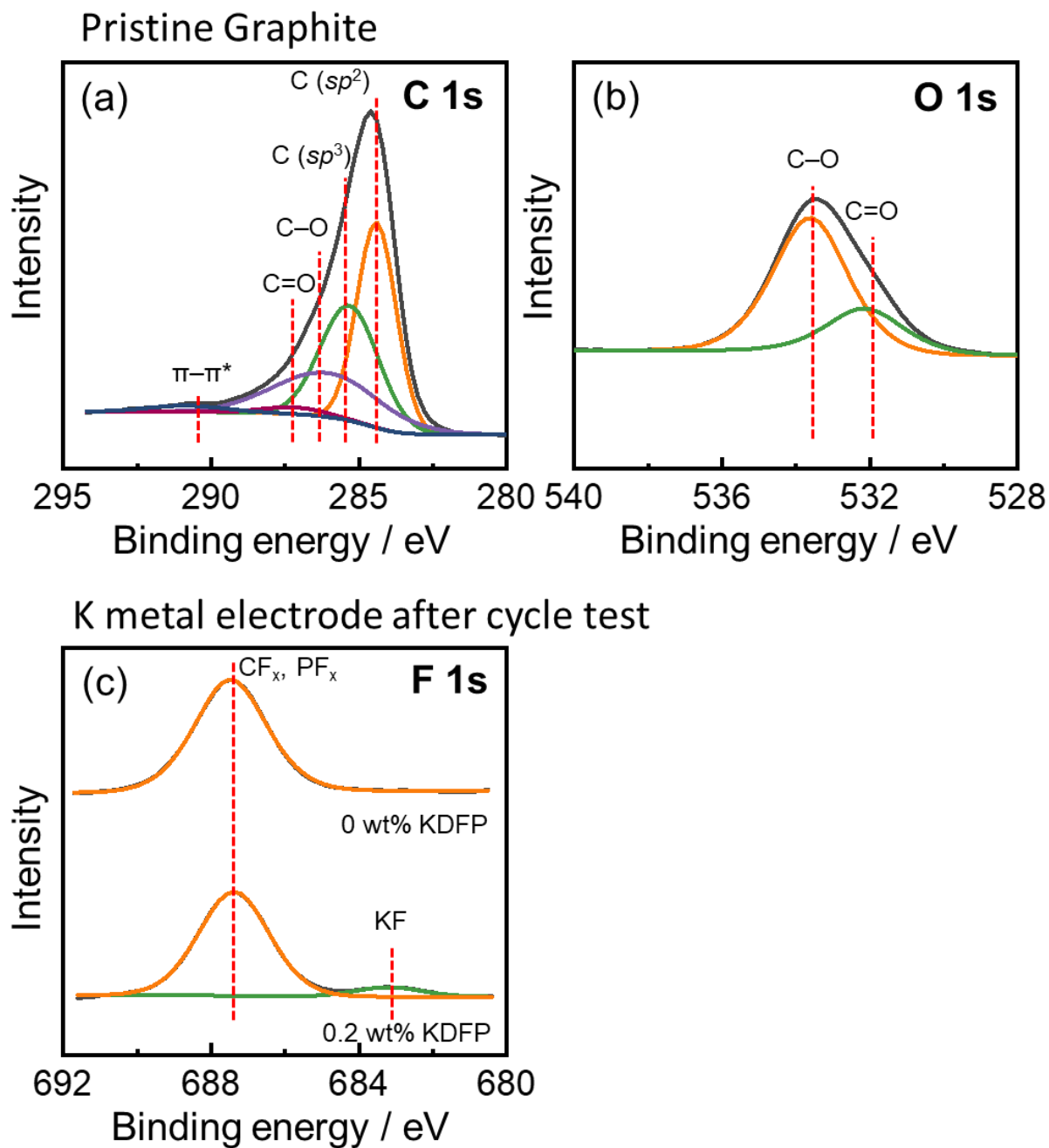
**Figure S13.** Rate capability of the K/graphite cells with 0.5 M KPF<sub>6</sub>-EC/DEC electrolytes containing different amounts of KDFP at 25 °C. Rate: C/20 to 2C. Cut-off voltages: 0.001–2.5 V



**Figure S14.** Charge-discharge curves of the K/graphite cells in 0.5 M KPF<sub>6</sub>-EC/DEC with (a) 0 wt% and (b) 0.2 wt% KDFP during rate capability tests from C/20 to 2C at 25 °C. Cut-off voltages: 0.001–2.5 V.



**Figure S15.** SEM images of (a, b) the pristine graphite electrode and the graphite electrodes after cycling in (c, d) 0 wt% additive (neat) (400 cycles), (e, f) 0.2 wt% KDFP (400 cycles), and (g, h) 3 wt% FEC (3 cycles). C-rate: C/3. Cut-off voltage: 0.001–2.5 V.



**Figure S16.** X-ray photoelectron spectra of the pristine graphite electrode ((a) C 1s and (b) O 1s) and (c) K metal counter electrode (F 1s) after 400 cycles using 0.5 M  $KPF_6$  EC/DEC with and without KDFP additive.

## References

- [1] R. Harrison, R. Thompson, and J. Trotter, The structure of potassium difluorophosphate. *J. Chem. Soc. A* **1966**, 1775-1780.