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Supporting Information for

A novel K-ion battery; hexacyanoferrate(II)/graphite cell

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Experimental Section

Materials: K-MnHCFe and K-FeHCFe powder were synthesized by precipitation method. Firstly, 2 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 80 and 40 ml saturated KCl solution at 25 ^oC. Then, these two solutions were slowly dropped together with magnetic stirring under N_2 atmosphere at 60 ^oC. 4 hours later, the precipitate formed was centrifuged and washed thoroughly with 1 L deionized water. At last, the final product was obtained after drying in air under 80 ^oC for 12 h.

Electrochemical Characterization: The positive electrodes consisted of 70 wt% active materials, 20 wt% Ketjen black carbon, and 10 wt% polytetrafluoroethylene (PTFE). The negative electrodes for the full cell consisted 90 wt% nature graphite (average particle size ≈ 3 μm) and 10 wt% carboxymethyl cellulose (CMC) binder [1]. The positive and negative electrodes formed on Al mesh and foil, respectively, were dried at 150 ^oC under vacuum. For K half-cell, metallic potassium (Aldrich) was used as a negative electrode. The electrolyte solution was 0.7 mol dm^{-3} KPF_6 dissolved in EC:DEC (1:1) solvent (Kishida Chemical). A glass fiber filter (GB-100R, ADVANTEC) was used as a separator. R2032-type coin cells were assembled in Ar-filled glove box (dew point: < -70 ^oC).

Material Characterization: X-ray diffraction (XRD) data were collected using Multiflex (Rigaku Co., Ltd., Japan) with Cu Kα radiation at 40 kV and 20 mA. For operando XRD, in-situ battery cell equipped with Be window (Rigaku) was assembled and galvanostatically cycled at a current rate of 5 mA g^{-1}. The recording

time for one diffraction pattern is around 7 min. Morphology of as-prepared samples was observed by scanning electron microscope (SEM, S-5000, Hitachi). Thermal behavior of the synthesized powders (sample amount, 8 mg) was tested by TGA (Shimadzu DTG-60, Japan). Elemental ratio of K, Mn, and Fe was determined by ICP-AES analysis after dissolving the samples in HCl solutions.

Table S1 Structural parameters of K-MnHCFe and K-FeHCFe obtained from Rietveld analysis.

Sample K-MnHCFe

S.G. $P2_1/n$ a=10.1126(7) Å, b=7.3285(9) Å, c=6.9711(5) Å, β=90.06(9)°						
Atom	**Wyckoff.**	***x***	***y***	***z***	**B_{iso} / Å^2**	**Occ**
Mn	*2a*	0	0.5	0.5	0.5(7)	1
Fe	*2a*	0	0	0	0.5(7)	0.94(2)
N1	*4e*	0.4608(7)	0.2587(8)	0.8347(2)	1.2(1)	0.94(2)
N2	*4e*	0.0507(1)	0.3303(3)	0.7674(4)	1.2(1)	0.94(2)
N3	*4e*	0.1993(2)	0.4822(4)	0.3925(6)	1.2(1)	0.94(2)
C1	*4e*	0.5308(2)	0.6329(1)	0.2686(5)	1.2(1)	0.94(2)
C2	*4e*	0.9497(6)	0.7767(5)	0.1433(8)	1.2(1)	0.94(2)
C3	*4e*	0.6925(1)	0.5146(7)	0.5684(5)	1.2(1)	0.94(2)
K	*4e*	0.7549(4)	0.9368(7)	0.4817(4)	2.9(5)	0.89(5)
O1	*4e*	=*x*(N1)	=*y*(N1)	=*z*(N1)	1.2(1)	0.06(2)
O2	*4e*	=*x*(N2)	=*y*(N2)	=*z*(N2)	1.2(1)	0.06(2)
O3	*4e*	=*x*(N2)	=*y*(N2)	=*z*(N2)	1.2(1)	0.06(2)
O4	*4e*	0.2718(8)	0.0767(4)	0.5548(1)	1.2(1)	0.11(2)
R_p=9.79 %, R_{wp}=9.17 %, R_e=4.71 %, Chi2=3.785						

Sample K-FeHCFe

S.G. $P2_1/n$ a=10.1250(9) Å, b=7.2562(9) Å, c=7.0238(1) Å, β=89.68(3)°						
Atom	**Wyckoff.**	***x***	***y***	***z***	**B_{iso}/ Å^2**	**Occ**
Fe1	*2a*	0	0.5	0.5	1.0(9)	1
Fe2	*2a*	0	0	0	1.0(9)	0.89(7)
N1	*4e*	0. 4905(3)	0. 2376(3)	0. 7926(7)	0.2(2)	0.89(7)
N2	*4e*	0. 0168(3)	0.2737(2)	0.7880(3)	0.2(2)	0.89(7)
N3	*4e*	0.2202(2)	0.5209(1)	0.4459(2)	0.2(2)	0.89(7)
C1	*4e*	0.5130(7)	0.6040(6)	0.2891(5)	0.2(2)	0.89(7)
C2	*4e*	0.9159(1)	0.7654(4)	0.1342(1)	0.2(2)	0.89(7)
C3	*4e*	0.6919(7)	0.5343(3)	0.5564(3)	0.2(2)	0.89(7)
K	*4e*	0.7536(4)	0.9444(7)	0.4832(2)	4.3(1)	0.82(4)
O1	*4e*	=*x*(N1)	=*y*(N1)	=*z*(N1)	0.2(2)	0.11(2)
O2	*4e*	=*x*(N2)	=*y*(N2)	=*z*(N2)	0.2(2)	0.11(2)
O3	*4e*	=*x*(N2)	=*y*(N2)	=*z*(N2)	0.2(2)	0.11(2)
O4	*4e*	0.3478(7)	-0.0665(1)	0.7978(5)	0.2(2)	0.16(1)
R_p=11.7 %, R_{wp}=9.87 %, R_e=7.7 %, Chi2=1.644						

Table S2 ICP results.

K-MnHCFe			
element	**K**	**Mn**	**Fe**
Mole ratio	**1.75**	**1**	**0.93**
K-FeHCFe			
element	**K**		**Fe**
Mole ratio	**0.88**		**1**

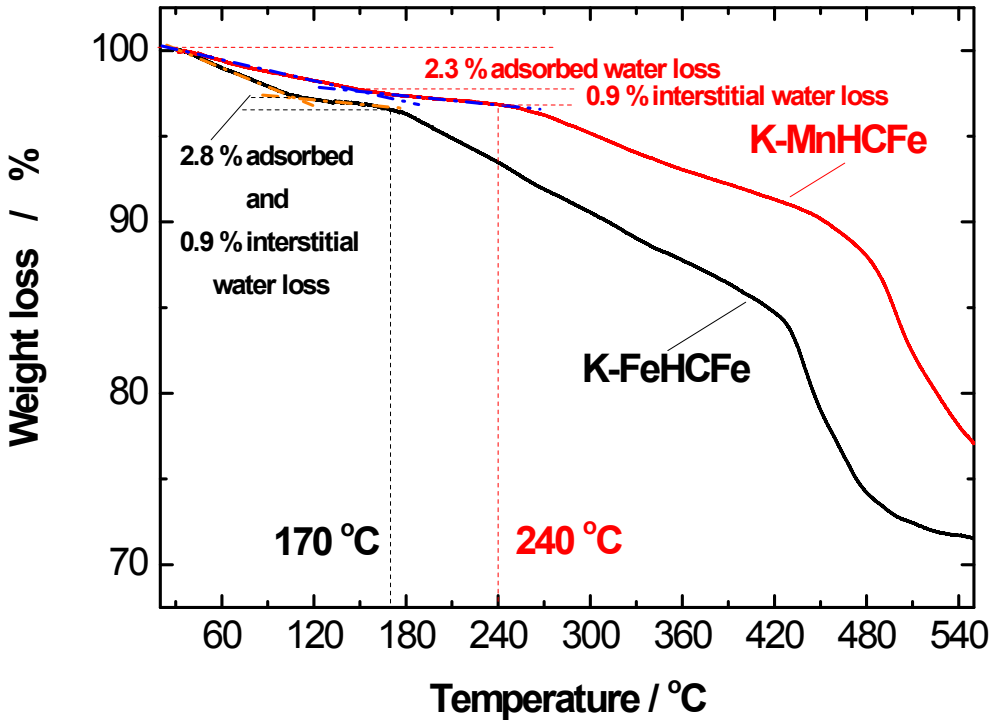

Figure S1 TG curves of K-MnHCFe and K-FeHCFe. The TGA test was conducted at a heating rate of 1 °C min^{-1} under Ar gas flow. K-MnHCFe shows two slopes from room temperature to 240 °C, which are corresponding to 2.3% adsorbed and 0.9% interstitial water loss. And a rapid weight loss was observed above 240 °C, which indicates the compound decomposition. Similar behavior is found in the TGA curve of K-FeHCFe.

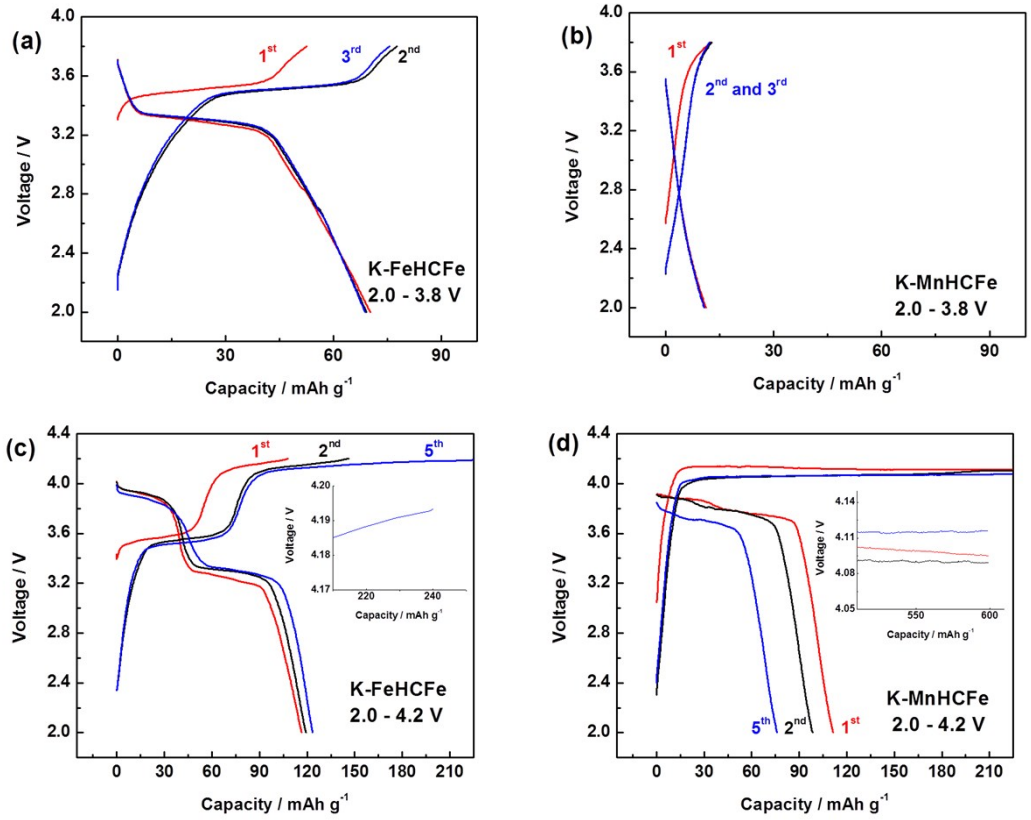

Figure S2 Charge-discharge profiles of (a,c) K-FeHCFe and (b,d) K-MnHCFe electrode in K half-cell with 1 M KFSI in EC: DEC (1:1) electrolyte under voltage range of (a,b) 2.0-3.8 and (c,d) 2.0-4.2 V.

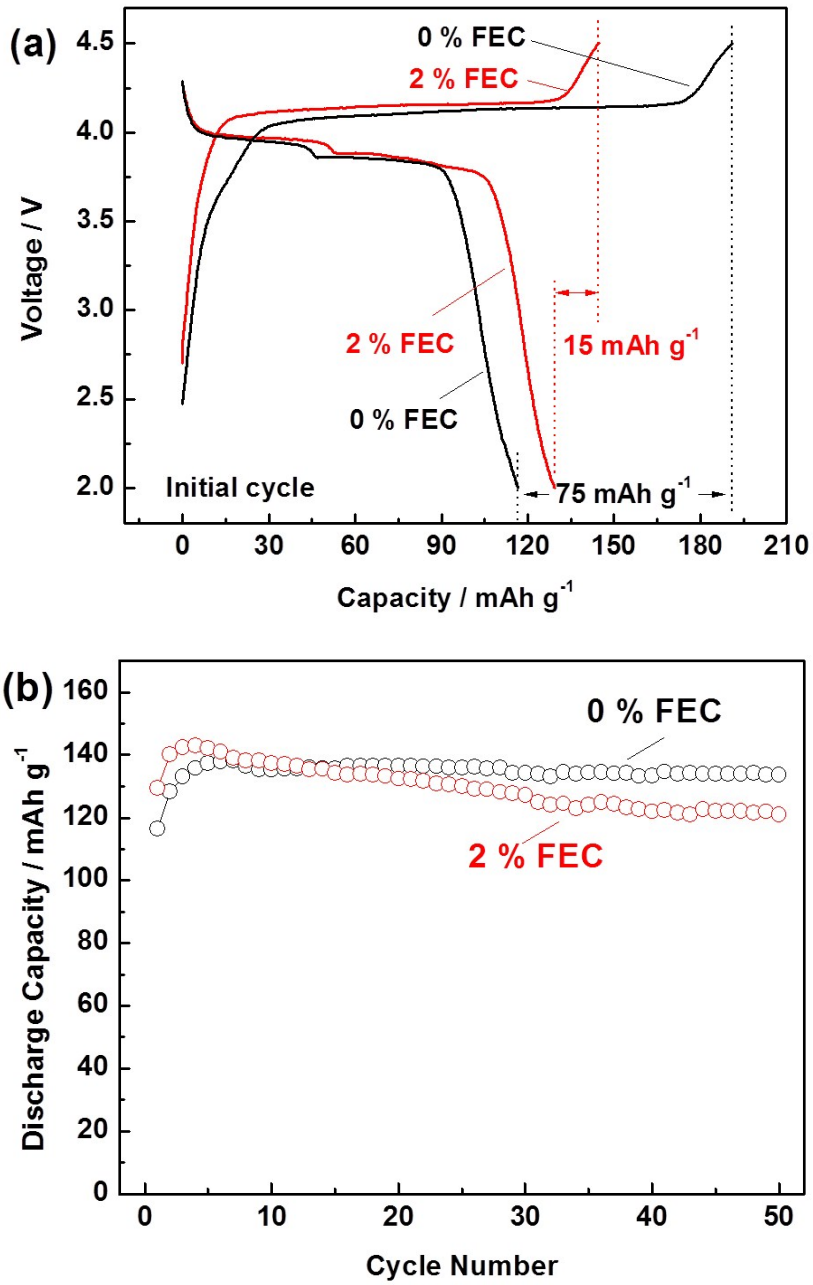

Figure S3 (a) Initial charge-discharge profiles and **(b)** cycle performance of K-MnHCFe electrode in K half-cell with 0.7 M KPF_6 in EC:DEC (1:1) electrolyte with 0 % and 2 % FEC additive.

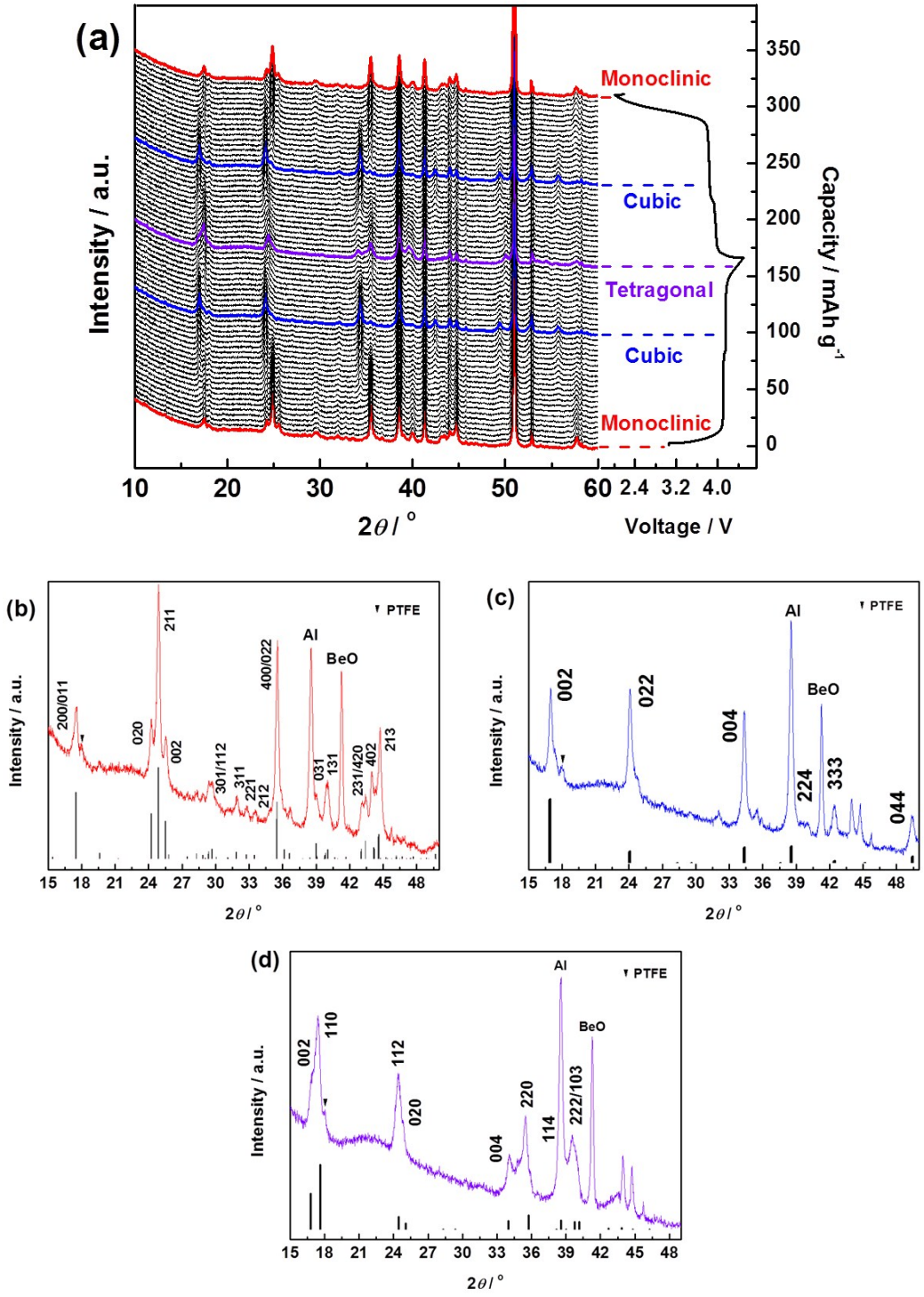

Figure S4 (a) In-situ XRD patterns of K-MnHCFe during initial cycle and indexed XRD patterns of K-MnHCFe electrodes under different charge state: **(b)** pristine electrode (monoclinic), **(c)** half charged electrode (cubic) and **(d)** fully charged (tetragonal).

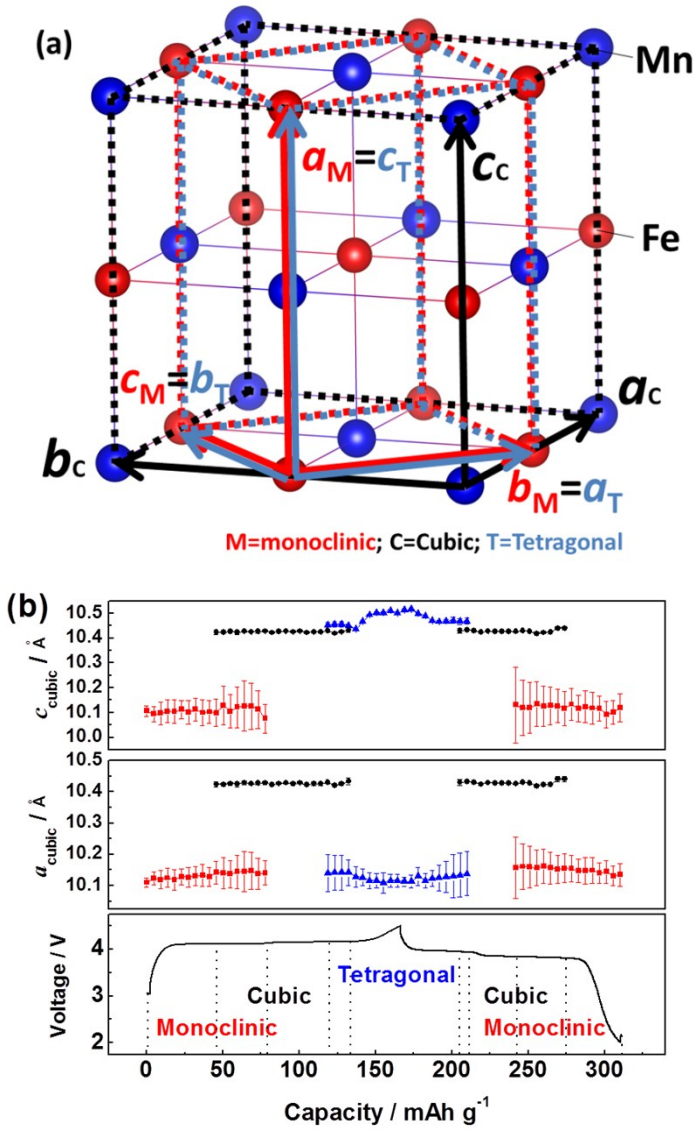

Figure S5 (a) Scheme of K-MnHCFe framework with monoclinic (M), cubic (C) and tetragonal (T) lattices. **(b)** The evolution of lattice parameters along cubic axis *a* and *c* directions during initial charge-discharge. According to the scheme, lattice parameters of monoclinic and tetragonal could be normalized to those in a cubic lattice as:

$$a_C = \sqrt{{b_M}^2 + {c_M}^2} = \sqrt{{a_T}^2 + {b_T}^2}$$

$$c_C = a_M \times sin\beta_M = c_T$$

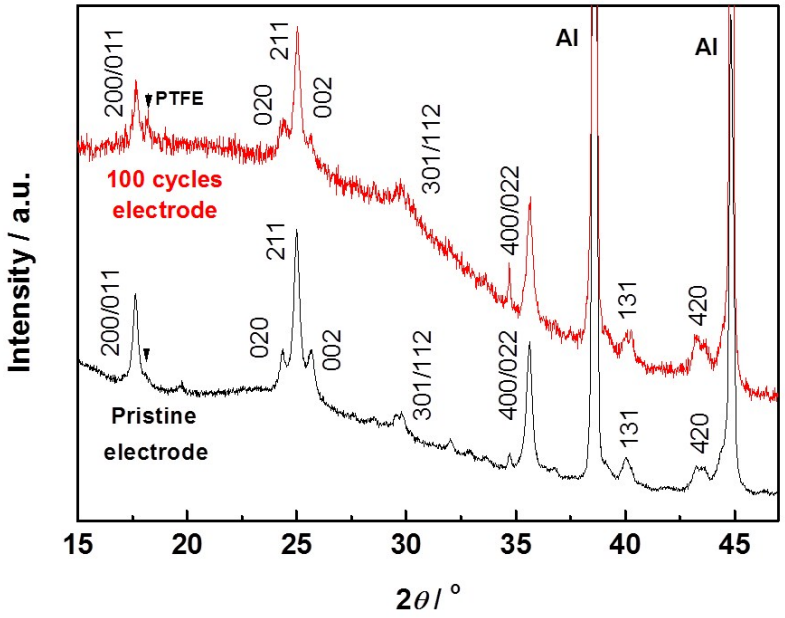

Figure S6 XRD patterns of K-MnHCFe pristine electrode and the electrode after 100 cycles in the voltage range of 2.0-4.5 V at a current density of 30 mA g^{-1}.

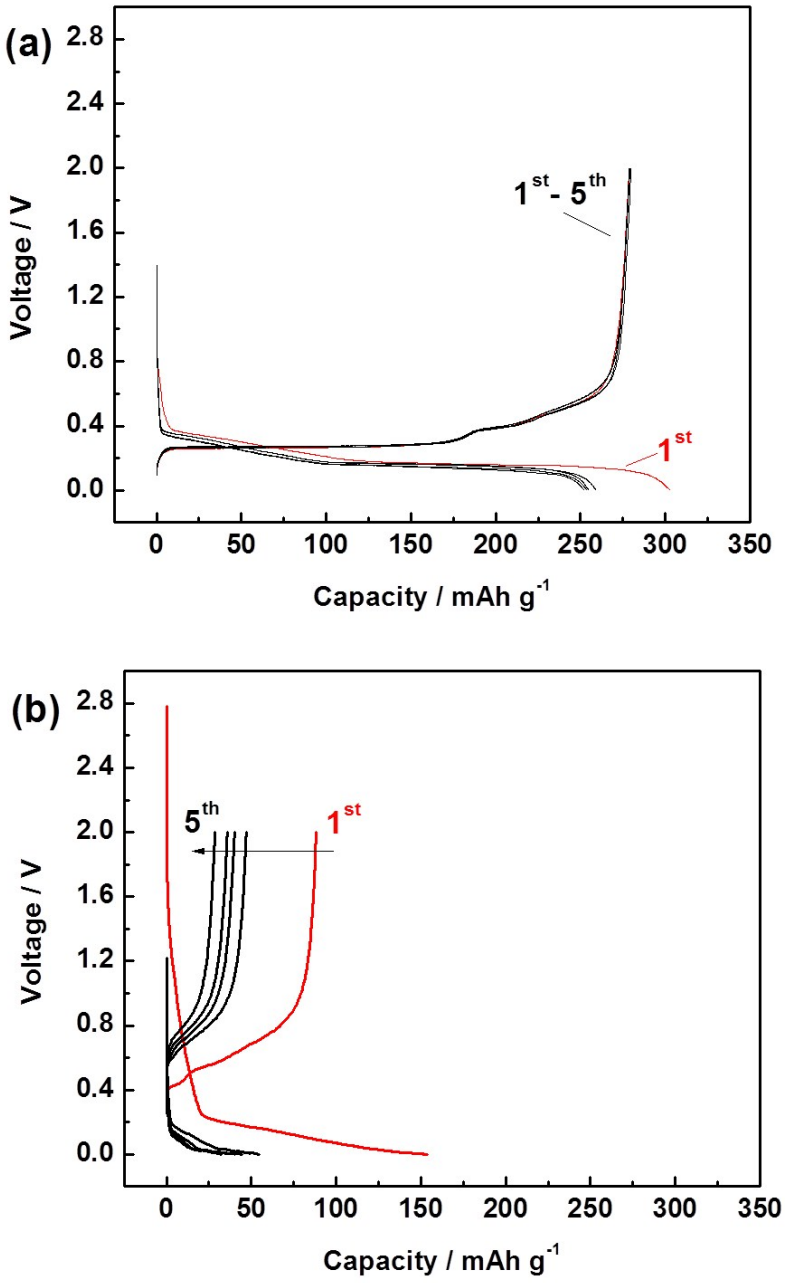

Figure S7 Charge-discharge profiles of graphite negative electrode in K half-cell with 0.7 M KPF_6 in EC:DEC (1:1) electrolyte with **(a)** 0 % FEC and **(b)** 2 % FEC additive.

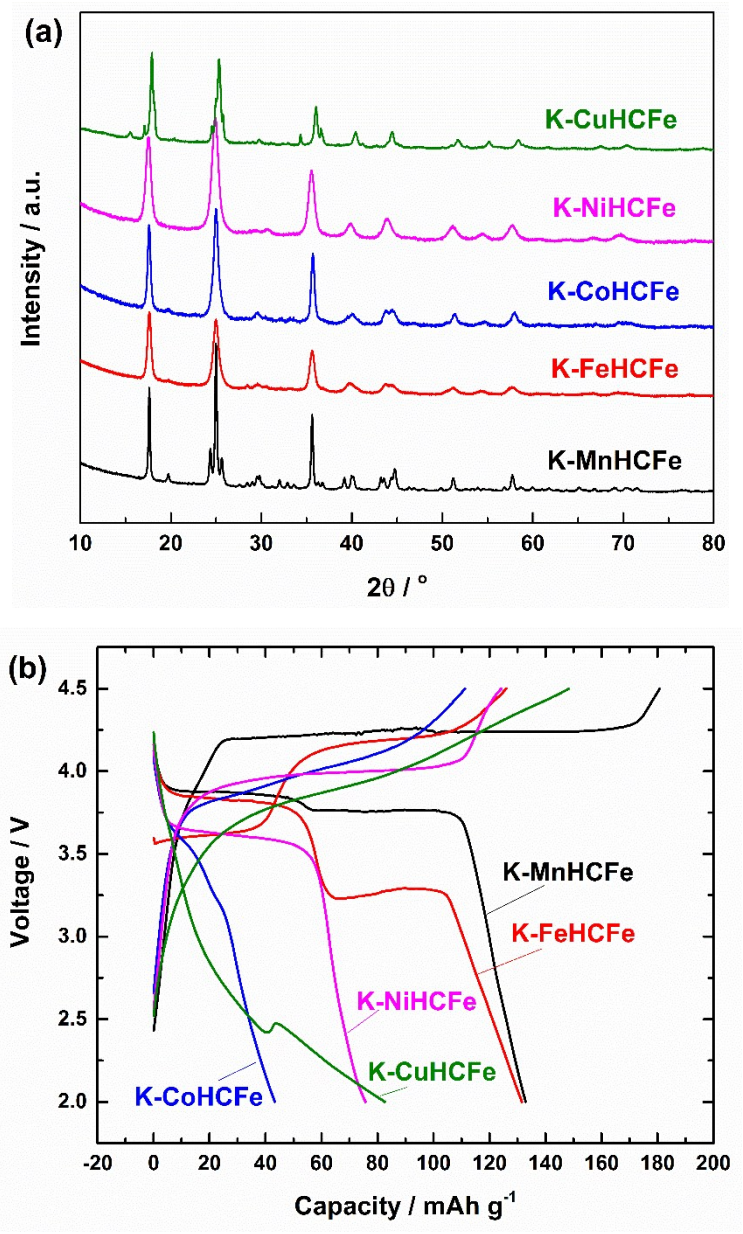

Figure S8 (a) XRD patterns of K-MHCFe (M=Mn, Fe, Co, Ni, Cu), (b) initial charge-discharge curves of K-MHCFe.

Reference:

1. S. Komaba, T. Hasegawa, M. Dahbi and K. Kubota, *Electrochem. Commun.* 2015, **60,** 172-175.