Electronic Supplementary Information (ESI)

Electrochemical Properties of a Titanium-Substituted KVPO$_4$F Cathode for K-Ion Batteries

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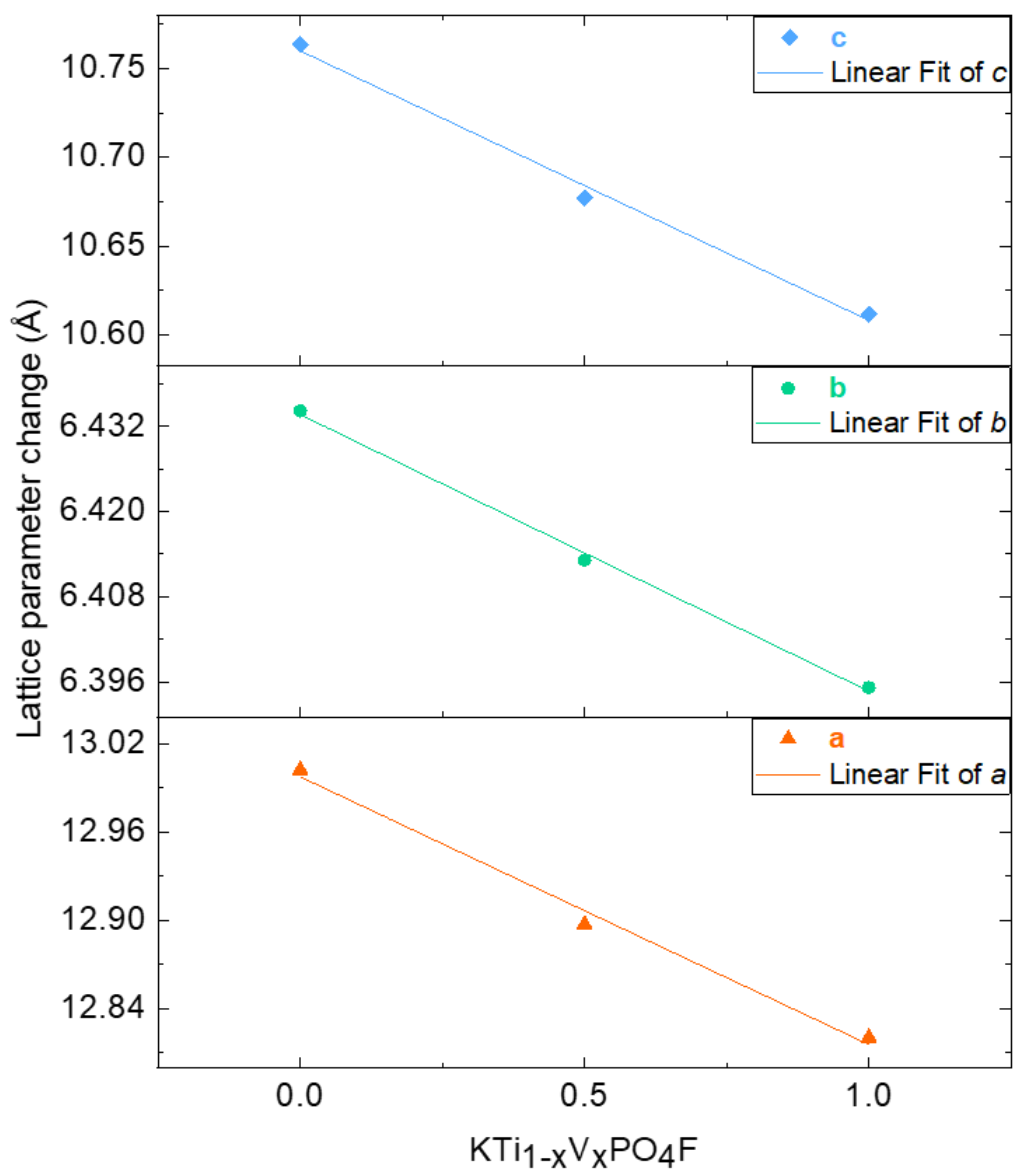[a]Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, NJ, 07030, USA

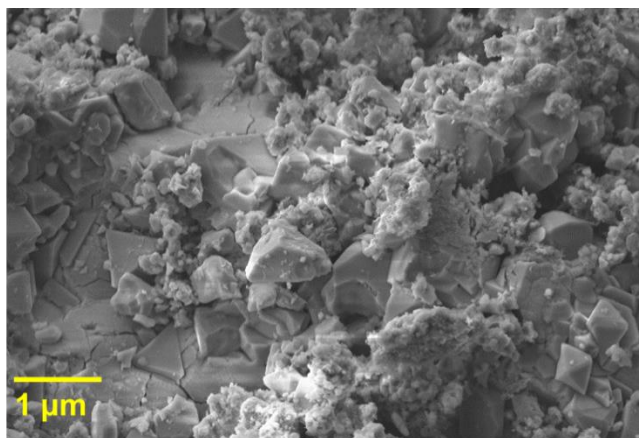**Figure S1.** Lattice parameters of $KTi_{1-x}V_xPO_4F$ obtained by Rietveld refinement.

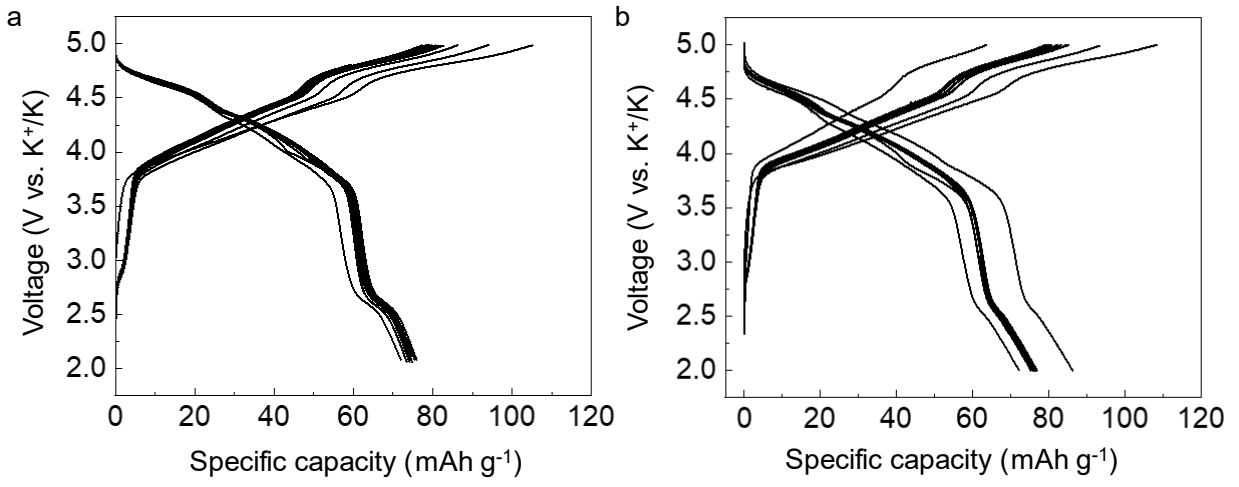**Figure S2.** SEM image of as-synthesized $KV_{0.5}Ti_{0.5}PO_4F$

Figure S3. Voltage vs. capacity curves for (a) micron-sized (pristine) and (b) nano-sized (ball-milled) $KV_{0.5}Ti_{0.5}PO_4F$ at C/10 for 10 cycles
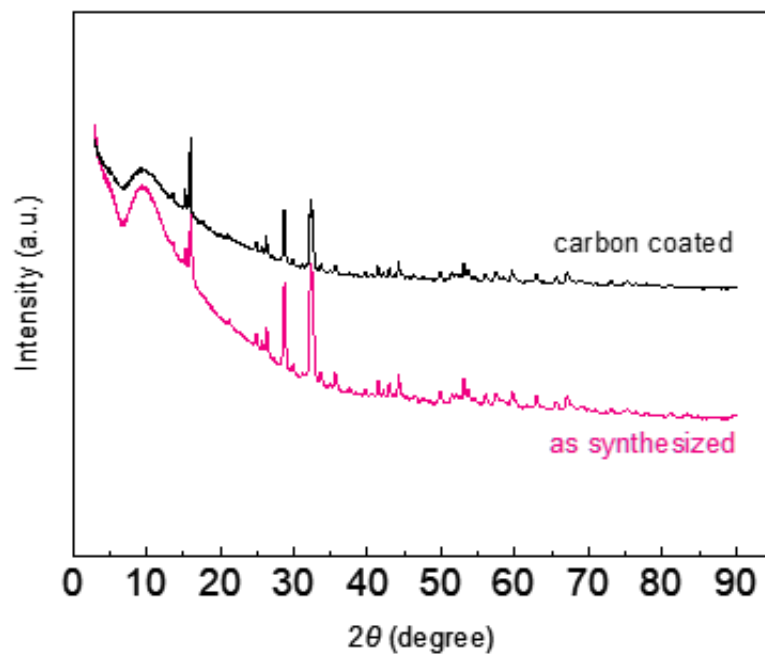
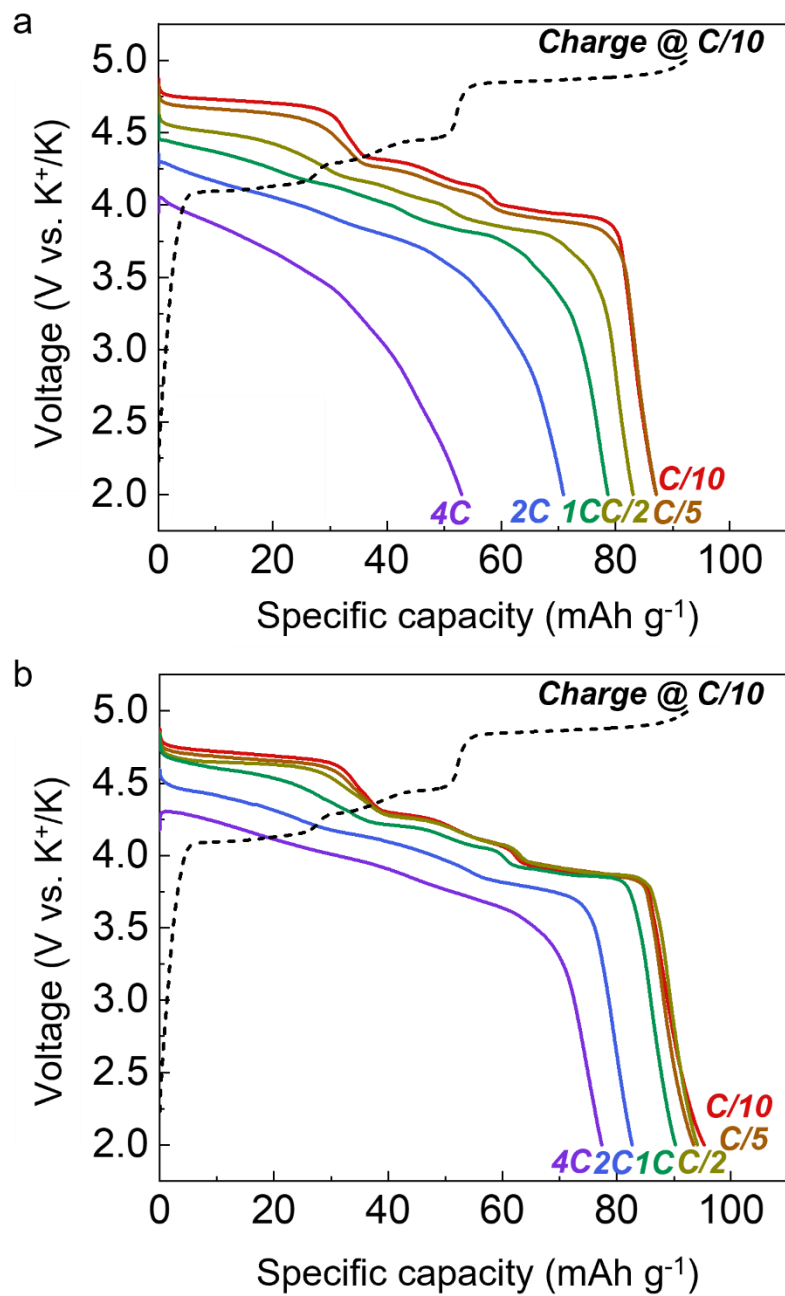**Figure S4.** XRD patterns of $KV_{0.5}Ti_{0.5}PO_4F$ before and after carbon coating

Figure S5. Discharge rate capability of KVPO$_4$F/C at (a) 25°C and (b) 35°C. The cells were charged at C/10 after each discharge.
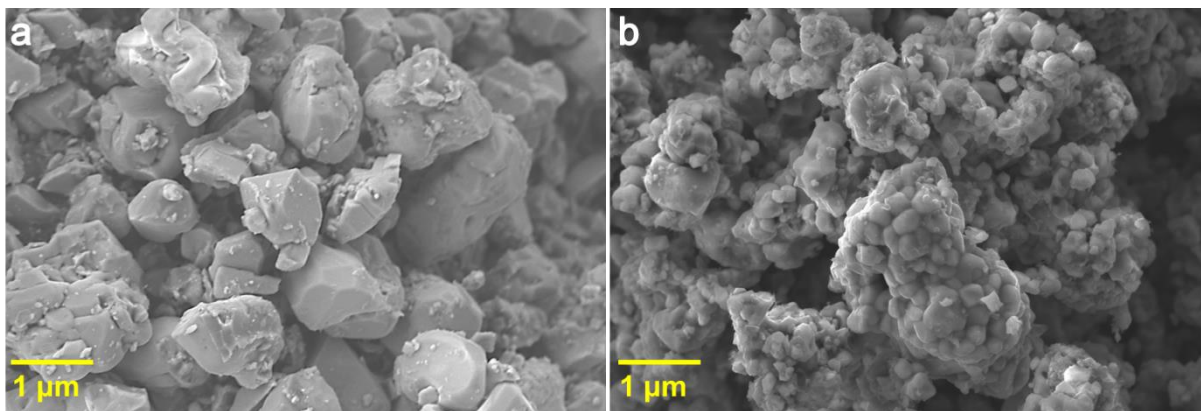
Figure S6. SEM images of (a) as-synthesized and (b) carbon-coated $KVPO_4F$

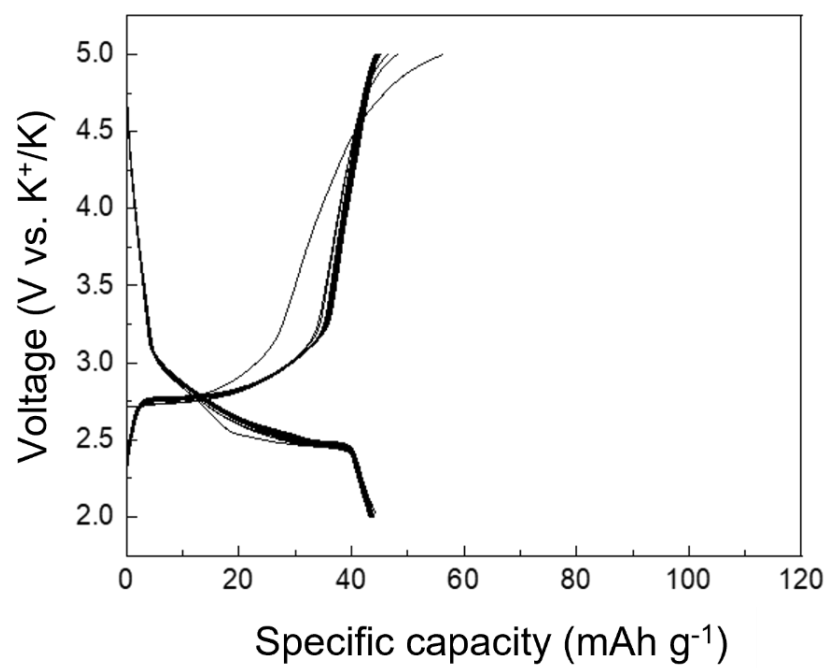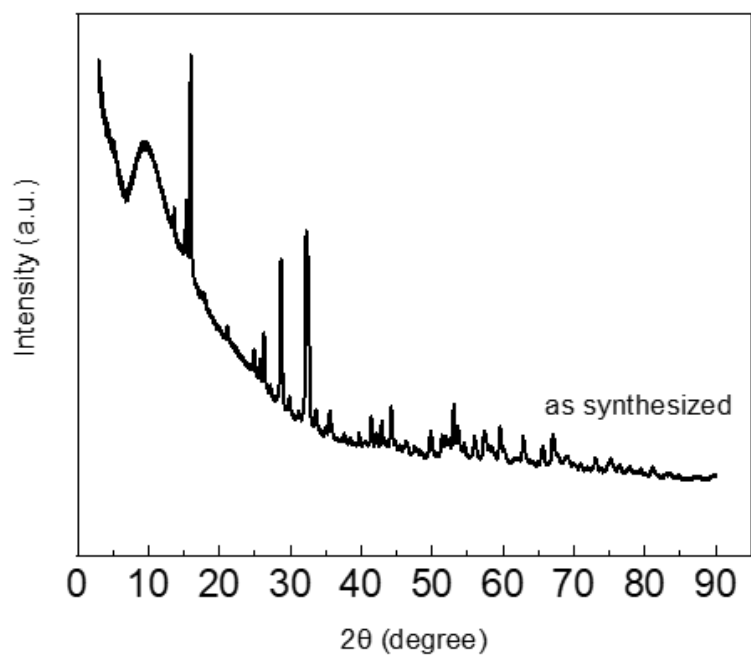**Figure S7.** Voltage profile (10 cycles) of $KTiPO_4F/C$ at C/10

Figure S8. XRD pattern of as-synthesized $KTiPO_4F$
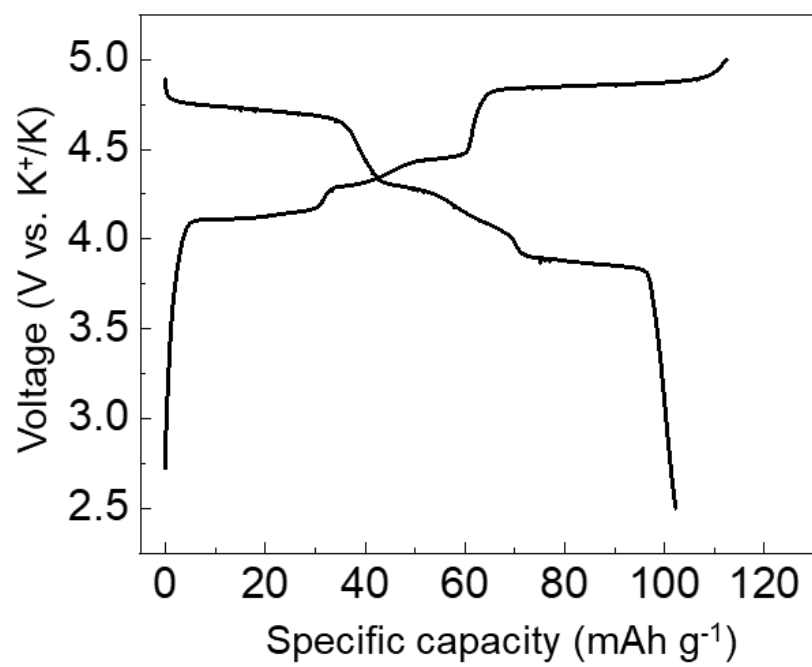
Figure S9. Voltage vs. capacity of $KVPO_4F/C$ at C/10 (the second cycle)
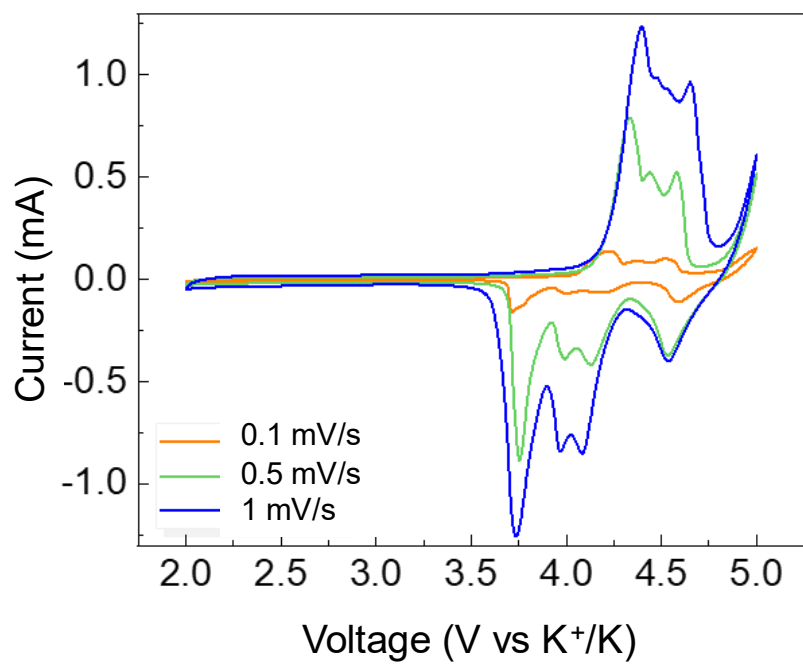
Figure S10. CV of KVPO$_4$F/C at different scan rates
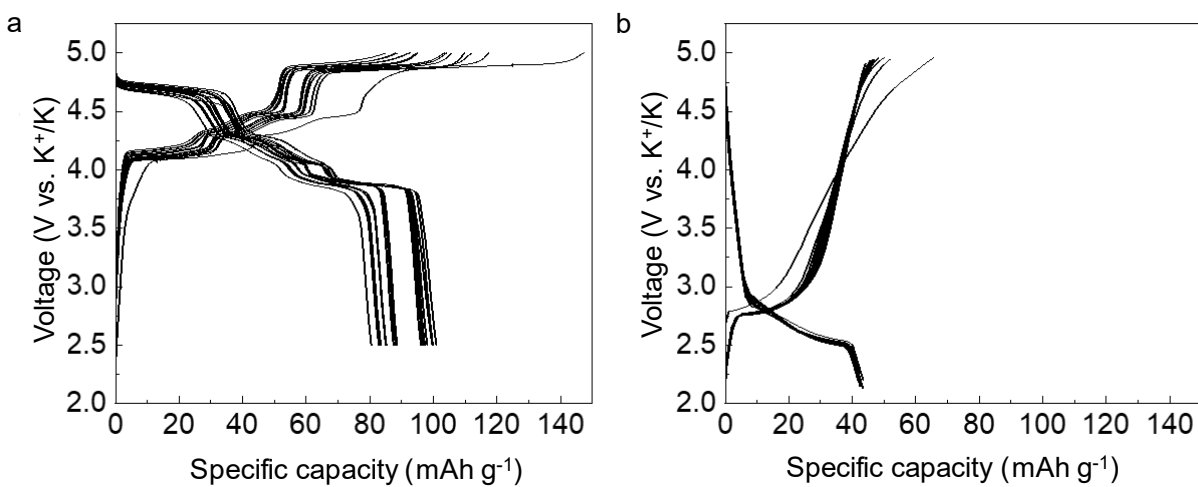
Figure S11. The voltage vs. capacity curves of (a) KVPO$_4$F and (b) KTiPO$_4$F at C/10 for 30 cycles.
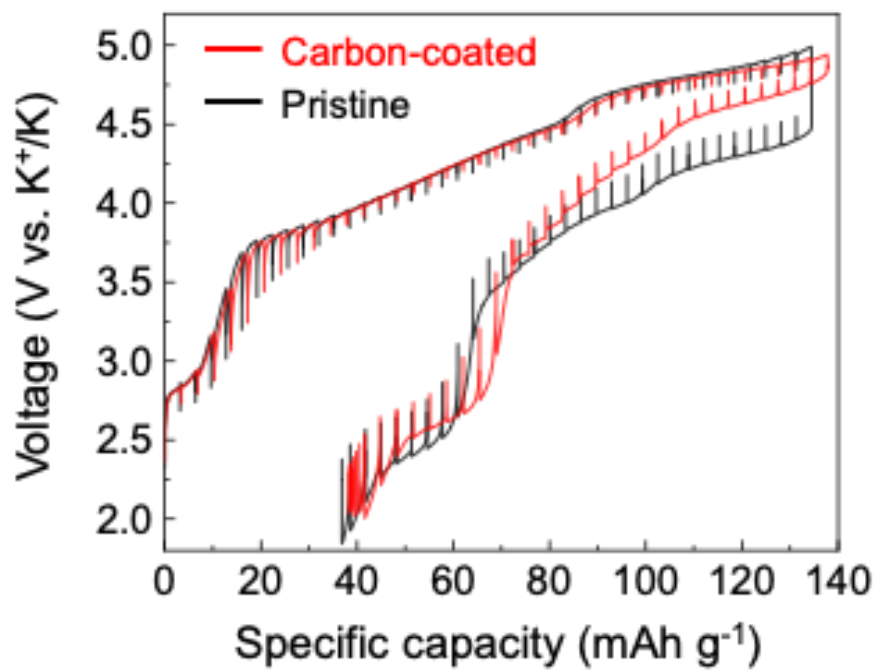
Figure S12. Calculated chemical diffusion coefficients of $KTi_{0.5}V_{0.5}PO_4F/C$ and $KTi_{0.5}V_{0.5}PO_4F$ upon (a) charge and (d) discharge.
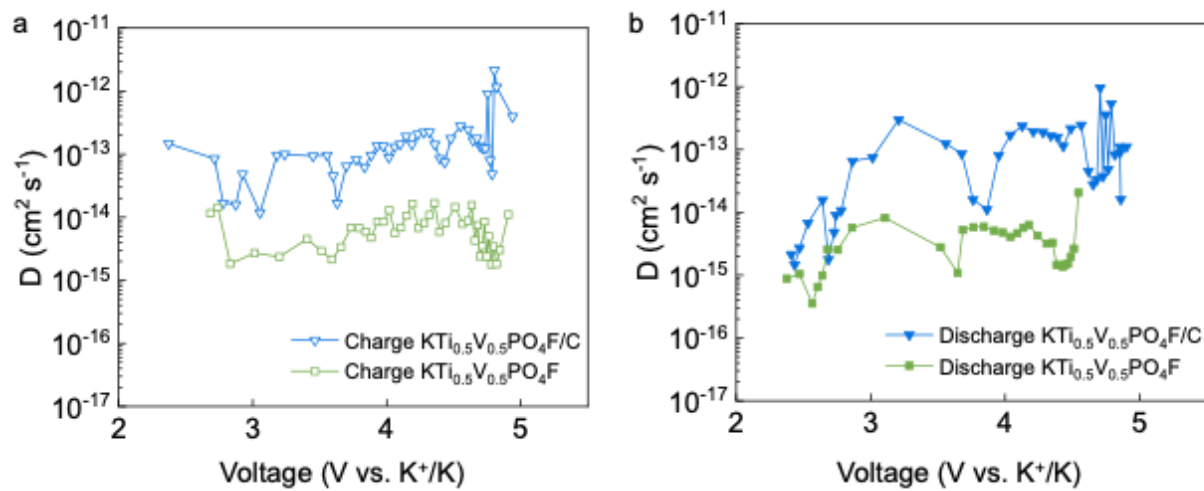
Figure S13. Calculated chemical diffusion coefficients of $KTi_{0.5}V_{0.5}PO_4F/C$ and $KTi_{0.5}V_{0.5}PO_4F$ upon (a) charge and (d) discharge.

Figure S14. Nyquist plots for two K metal half cells with the carbon-coated and pristine KTi$_{0.5}$V$_{0.5}$PO$_4$F cathodes (after one C/5 cycle).

Table S1. Crystallographic data obtained from Rietveld refinement for $KTi_{0.5}V_{0.5}PO_4F$.
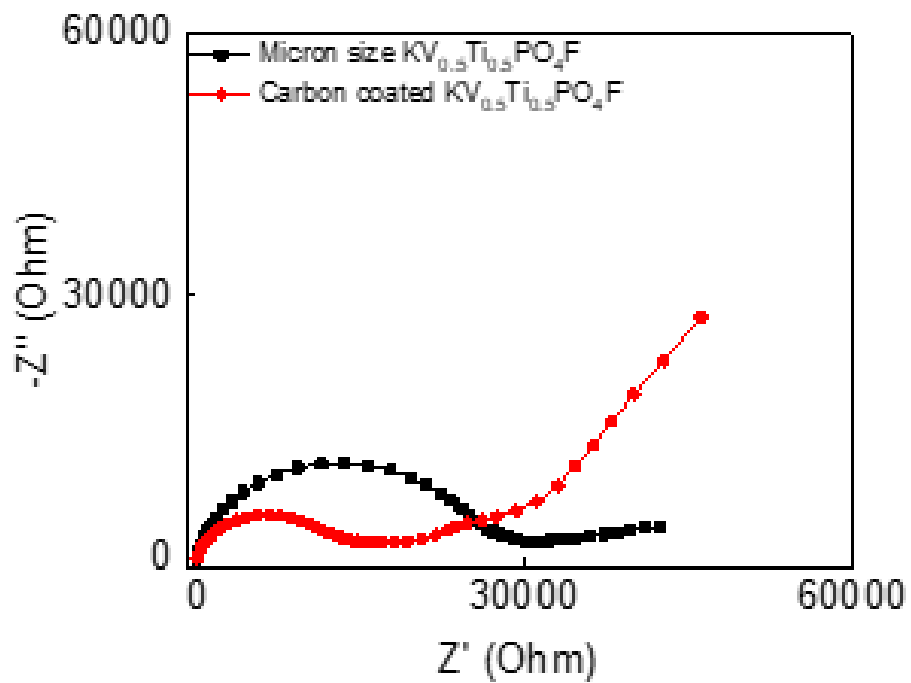
Formula	$KTi_{0.5}V_{0.5}PO_4F$
Space group	*Pna2₁*
***a*, Å**	12.8911
***b*, Å**	6.411
***c*, Å**	10.665
***V*, Å³**	881.4067
Radiation	X-rays, Cu-K$_\alpha$, λ_1 = 1.540598 Å, λ_2 = 1.54433 Å
Two theta range, step, deg.	10–75, 0.01
***R$_E$*, %**	0.71987
***R$_p$*, *R$_{wp}$*, %**	8.02992, 12.55658

Atom	Wycoff position	Atomic position			Occupancy
		x	y	z	
K0	4a	0.10325	0.70147	0.06001	1
K1	4a	0.12164	0.27556	0.80093	1
V2	4a	0.11553	0.99470	0.50315	0.5
V3	4a	0.24666	0.24953	0.25214	0.5
Ti2	4a	0.11553	0.99470	0.50315	0.5
Ti3	4a	0.24666	0.24953	0.25214	0.5
P4	4a	0.00124	0.83393	0.75416	1
P5	4a	0.18045	0.49762	0.50419	1
O6	4a	0.01019	0.02722	0.37057	1
O7	4a	0.01634	0.98539	0.64401	1
O8	4a	0.09415	0.30214	0.23167	1
O9	4a	0.09759	0.69671	0.77284	1
O10	4a	0.11115	0.30836	0.53029	1
O11	4a	0.11218	0.68635	0.47816	1
O12	4a	0.24673	0.95382	0.89279	1
O13	4a	0.24907	0.03340	0.11931	1
F14	4a	0.23030	0.98003	0.62994	1
F15	4a	0.23099	0.02362	0.38101	1

Note that the reference structure for Rietveld refinement was obtained from computation that assumes equal population of K over the two K sites and equal population of transition metals over the two transition metal sites per formula unit. The difference between observed and calculated peak intensities in Figure 1 in the manuscript implies that K, Ti, and V in synthesized $KTi_{0.5}V_{0.5}PO_4F$ may have different site occupancies from the reference structure.