

Electronic Supplementary Information (ESI)

Partial alkali-metal ion extraction from $\text{K}_{0.8}(\text{Li}_{0.27}\text{Ti}_{1.73})\text{O}_4$ using PTFE as an extraction reagent

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S1. Crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$

The crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ consists of edge-shared Li^+ -substituted TiO_6 octahedral layers interspersed with K^+ .

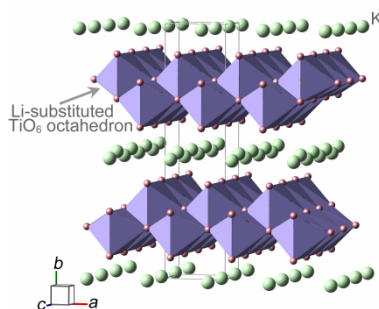


Fig. S1. Schematic drawing of the crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ based on the previously published data.^{1,2}

S2. Optimization of the reaction duration to decompose PTFE derivatives from PTFE_0.6_Ar

PTFE_0.6_Ar was re-heated at 350 °C under flowing air in order to oxidatively decompose PTFE derivatives in PTFE_0.6_Ar. After 24 h of re-heating, the color of the product turned white (Fig. S2a inset) indicating the successful decomposition of the PTFE derivatives. When the reaction duration was extended over 24 h, the intensities of the powder X-ray diffraction (XRD) peaks attributed to the alkali-metal derivatives (K_2CO_3 and LiF) decreased significantly as shown in Fig. S2a. Furthermore, the lattice parameters of the re-heated products got closer to those of the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ as the reaction duration was increased as shown in Fig. S2b. These results indicate that the extracted alkali-metal ions intercalated back into the phase when the re-heating duration in air was too long. Therefore,

24 h was considered as the optimum duration to decompose the PTFE derivatives in PTFE_0.6_Ar.

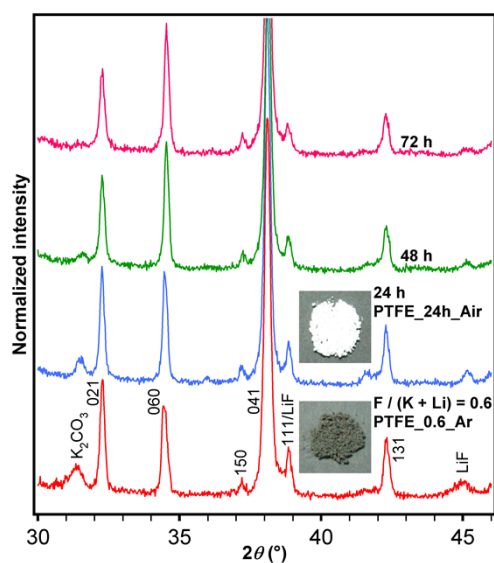


Fig. S2a. Powder XRD profiles of PTFE_0.6_Ar and that re-heated at 350 °C under flowing air for 24 (PTFE_24h_Air), 48 and 72 h. (Inset) Photographs of PTFE_0.6_Ar and that re-heated at 350 °C in air for 24 h.

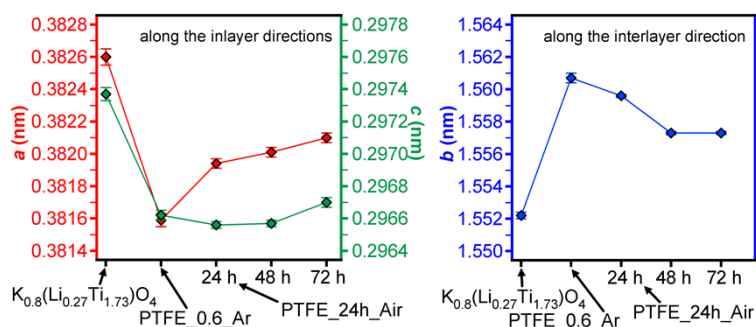


Fig. S2b. Refined lattice parameters of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, PTFE_0.6_Ar and that re-heated at 350 °C under flowing air for 24 (PTFE_24h_Air), 48 and 72 h.

S3. Dehydration and phase transformations of K^+ - and/or Li^+ -extracted $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ characterized by powder XRD

We have studied the dehydration and phase transformation behaviors of KTLO_Washed_RT and PTFE_Washed_RT by heating them and characterizing their powder XRD patterns.

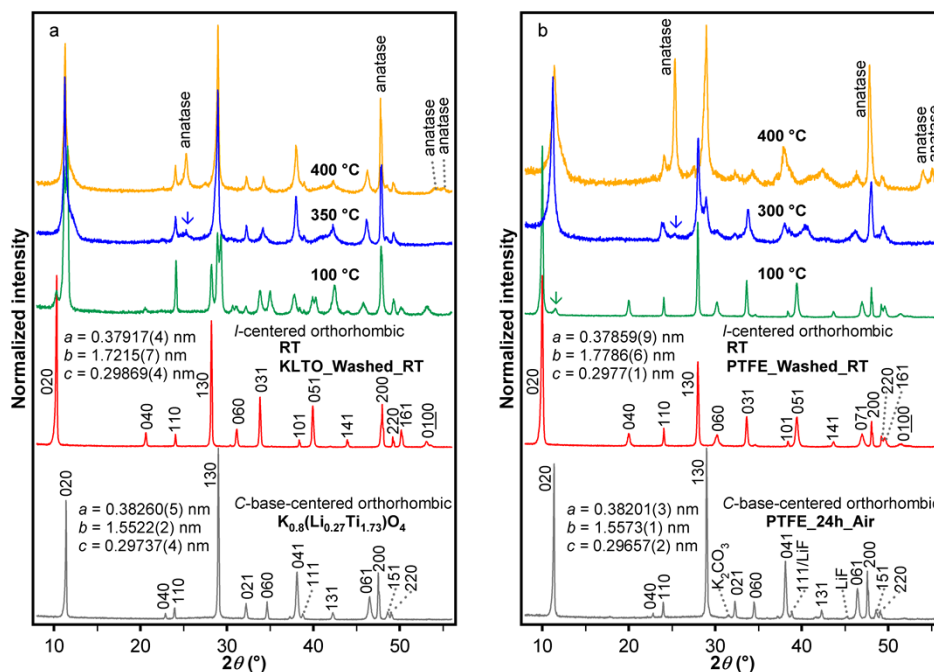


Fig. S3. Powder XRD profiles of (a) $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and that washed in water and dried or heated in air at selected temperatures and (b) PTFE_24h_Air and that washed in water and dried or heated in air at selected temperatures.

S4. Further characterizations of the dehydration and phase transformation behaviors of PTFE_Washed_RT by thermogravimetric analysis, powder XRD and chemical analysis of PTFE_Washed_RT heated at 1000 °C

We have also studied the sample weight and crystal structure changes with respect to heating temperatures in order to further understand the dehydration behavior of PTFE_Washed_RT. The thermogravimetric (TG) profile of PTFE_Washed_RT is shown in Fig. S4a. The TG analysis was performed using a Rigaku Thermo plus TG8120 at a heating rate of 10 °C min⁻¹ under 20 mL min⁻¹ flow of air. Approximately 8% weight loss up to around 200 °C and a further 2% loss up to around 370 °C are attributed to overlapped two-step dehydration. The first step (I) of the weight loss is attributed to the evaporation of interlayer H₂O, represented by w in the chemical equation (3). The second step (II) is attributed to the loss of H⁺, which partially replaced K⁺ and Li⁺ during washing in water, represented by $\nu+t$ in the chemical equation (3); such loss of H⁺ is expected to take place in the form of H₂O like the cases of the H⁺-exchanged layered metal oxide compounds.^{2, 3} Between 370 and 700 °C (region III in Fig. S4a), the weight change is very small. The results of the XRD (Figs. S3b and S4b) indicate that the sample in this temperature range consists of the partially K⁺- and Li⁺-extracted and H⁺-exchanged K_{0.8}(Li_{0.27}Ti_{1.73})O₄, anatase-type TiO₂, spinel-type Li_{1.33}Ti_{1.67}O₂⁴ and a trace amount of hollandite-type K_{3x}(Li_xTi_{8-x})O₁₆¹. Above 700 °C, the sample weight again decreased approximately 0.5% up to 1000 °C.

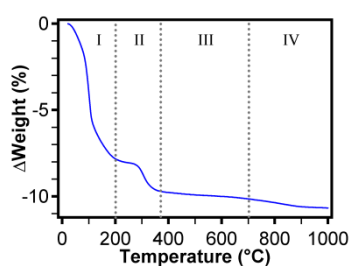


Fig. S4a. TG curve of PTFE_Washed_RT.

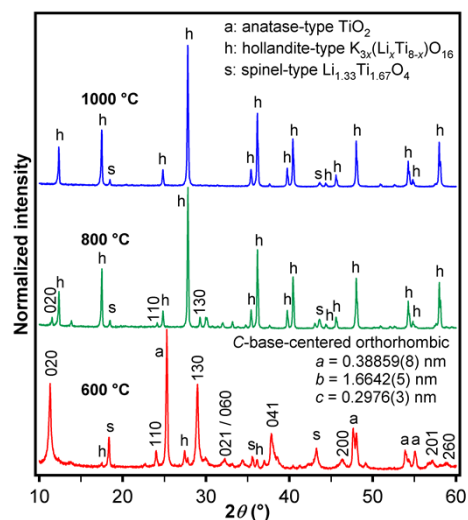


Fig. S4b. Powder XRD profiles of PTFE_Washed_RT heated at 600, 800 and 1000 °C. The indices are for the partially K^+ - and Li^+ -extracted and H^+ -exchanged $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$.

The elemental composition of PTFE_Washed_RT heated at 1000 °C is shown in Table S1. The contents of K, Li and F in the sample heated at 1000 °C decreased with respect to those in PTFE_Washed_RT (Table 1), consistent with the weight loss above 700 °C in the TG analysis (Fig. S4a). PTFE_Washed_RT heated at 800 °C consists of hollandite-type $K_{3x}(Li_xTi_{8-x})O_{16}$, spinel-type $Li_{1.33}Ti_{1.67}O_2$ and a trace amount of the partially K^+ - and Li^+ -extracted and H^+ -exchanged $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$; no trace of anatase-type TiO_2 was observed (Fig. S4b). Furthermore, PTFE_Washed_RT heated at 1000 °C consists of hollandite-type $K_{3x}(Li_xTi_{8-x})O_{16}$ and spinel-type $Li_{1.33}Ti_{1.67}O_2$; and no trace of the partially K^+ - and Li^+ -extracted and H^+ -exchanged $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was observed. This result is in clear contrast to the case of the complete alkali-metal ion-extracted $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$. When all the alkali-metal ions were completely extracted from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by reaction with PTFE at the ratio of $F / (K + Li) = 3.4$ in mol at 400 °C, it was transformed into brookite-type TiO_2 .⁵ A sign of partial rutile-type TiO_2 formation was observed when it was further heated at 750 °C

in air. At 800 °C, XRD peaks of a trace amount of hollandite-type titania^{6, 7} were observed, but this was completely transformed into single phase rutile-type TiO₂ above 800 °C.⁵

Table S1. Analytically Determined Molar Elemental Composition^{*1} of PTFE Washed RT heated at 1000 °C

	K	Li	Ti	F
PTFE Washed RT heated at 1000 °C	0.37	0.24	1.73	0 ^{*2}

*¹ All the compositions are normalized to 1.73 mol of Ti.

*² Within the limits of the analysis.

References

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