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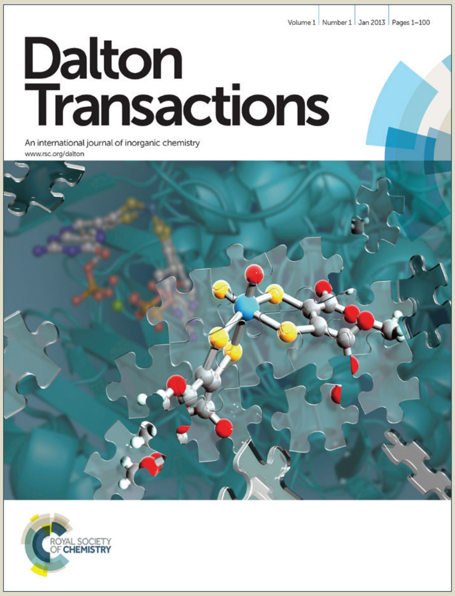

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Partial alkali-metal ion extraction from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ using PTFE as an extraction reagent[†]

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[†] Electronic supplementary information (ESI) available: Crystal structure drawing of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, the details of the PTFE derivative decomposition from PTFE_0.6_Ar, and the details of the dehydration and phase transformations of K^+- and/or Li^+-extracted $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by heating based on TG analysis, powder XRD and chemical analysis.

Abstract: Alkali-metal ion extraction ability of the inert material, polytetrafluoroethylene (PTFE; empirical formula CF_2), was clarified by characterizing a partially alkali-metal ion-extracted layered compound $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$. Washing $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ in water extracts only 44% of the interlayer K^+ and no intralayer Li^+; on the other hand, 53% of the interlayer K^+ and approximately 10% of the intralayer Li^+ ions were extracted from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by the reaction with PTFE at 350 °C under flowing Ar. A systematic decrease in the lattice parameters *a* and *c* along the intralayer directions and an increase in *b* along the interlayer direction were observed, consistent with the alkali-metal ion deintercalation amount as a function of the reaction temperatures and the reacted PTFE amounts. After the reaction with $K_{0.8}(Li_{0.27}Ti_{1.73-})O_4:CF_2$ = 1:0.6 in mol, the lattice parameter *b* increased to 1.5607(3) nm from 1.5522(2) of the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, and this change in the lattice parameter was approximately one order of magnitude larger than those in *a* and *c*.

Introduction

Deintercalation is one of the important processes to induce or enhance useful properties in various materials. For example, morphology transformation,[1] crystal structure transformation[2] and superconductivity[3-5] can be induced by deintercalation of various compounds.

Conventionally, deintercalation is performed by methods such as soft-chemical[6-10] and electro-chemical[11] reactions. Those conventional deintercalation reactions can be used to synthesize or modify chemical compositions of a variety of compounds. However, new approaches to deintercalation provide new directions for synthesis and a route to new properties that are not conventionally accessible.

Recently, we have discovered that alkali-metal ion-containing layered compounds can be transformed into binary metal oxide compounds, such as TiO_2 and SnO_2, by their reactions with polytetrafluoroethylene (PTFE; empirical formula CF_2) powder at relatively low temperatures around 400 °C in an inert atmosphere.[12, 13] The formation of binary metal oxide products and alkali-metal derivatives as secondary phases in those reactions suggests that complete extraction of alkali-metal ions from the layered compound precursors took place during the reactions. In those reactions, the completely alkali-metal ion-extracted intermediate framework transformed into structurally similar binary metal oxide products, such as brookite-type TiO_2, a metastable phase.[12]

These reactions are interesting in two aspects. First, PTFE, which is usually considered an inert material, is likely acting as an active reagent to extract alkali-metal ions. Second, completely alkali-metal ion-extracted intermediate states, which are often difficult to be induced by a conventional reaction approach, are produced during the reaction. These unique features of the reaction utilizing PTFE powder are likely driven by the high reactivity of alkali metals in the layered compounds and the fluorine in PTFE, leading to the formation of highly stable alkali-metal fluorides.

In addition, the relatively low temperature of those reactions prevents the recombination of alkali-metal containing byproducts and alkali-metal ion-extracted intermediates, providing products, including metastable ones, which cannot be accessed by high-temperature routes. However, deintercalation characteristics of such reactions using PTFE are not well understood yet, because complete alkali-metal ion-extracted intermediates cannot be isolated for characterization, as they transform into structurally different final products immediately.[12, 13] In order to understand and clarify the ability of PTFE to deintercalate alkali-metal ions from various compounds in these unique reactions, "partial" extraction of alkali-metal ions from layered compound reactants needs to be investigated by isolating or phase-purifying partially deintercalated products and characterizing them, without allowing their crystal structure transformation.

In this study, we attempted such partial alkali-metal ion extraction from a layered compound $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, whose crystal structure is described in ESI S1†, by mid-temperature reactions with PTFE under carefully chosen conditions, and characterized the products in order to understand and clarify the ability of PTFE to extract alkali-metal ions.

Experimental

Material synthesis

$K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was synthesized by solid-state reaction of K_2CO_3, Li_2CO_3 and TiO_2 as described elsewhere.[6] K_2CO_3 and Li_2CO_3 were heated at 200 °C overnight before use in order to dehydrate them. Alkali-metal ion deintercalation reactions of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ were attempted at various temperatures between 100 and 400 °C at various ratios of F in PTFE to alkali metals in $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ under 100 mL min^{-1} flow of Ar for 12 h.

Measurements and analysis

Powder X-ray diffraction (XRD) profiles of the reactants, intermediates and products were obtained using Cu K_α radiation on a Rigaku RINT2200V/PC diffractometer. The diffraction peaks were indexed, and the lattice parameters were refined using APPLEMAN software.[14]

K, Li and Ti compositions in $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and its reaction products were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Hitachi High-Tech SPS3520UV-DD. Samples were dissolved in sulfuric acid under heating and diluted with water before characterizations. The F content was analyzed by the lanthanum-alizarin complexone method using a JASCO Ubest-35. For this analysis, sulfuric acid was added to the samples, and the F component was separated as hexafluorosilicic acid by steam distillation, and quantified.

Results and discussion

We first studied the effect of the different temperatures in the reactions between PTFE and $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ on the K^+ and Li^+ deintercalation amounts in terms of the lattice parameter changes in the products. For this study, the molar ratio of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4:CF_2 = 1:1.8$, which is the same as that was used in the previously reported complete transformation of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ into brookite-type TiO_2,[12] was used. This molar ratio was equivalent to F / (K + Li) = 3.4 in mol, so F in PTFE was far in excess of the alkali-metal ions in $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$.

Fig. 1 shows the powder XRD patterns of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and that reacted with PTFE at various temperatures under flow of Ar. For all the products, a peak originating from the remaining PTFE was observed around 18°. Up to 350 °C, no trace of brookite-type TiO_2 was observed in the products, and the complete transformation from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ to brookite-type TiO_2 was observed at 400 °C, consistent with the previous report.[12] Most of the diffraction peaks of the products from the reactions at 350 °C and below can be indexed based on the crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$.[6, 15] This indicates that the fundamental crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was retained in the primary products after the reactions at 350 °C and below. However, the product obtained by the reactions with PTFE at 350 °C showed the diffraction peaks that cannot be indexed based on the crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$.[6] The peak around 41° is attributed to a PTFE derivative, which can be removed by re-heating in air. The peak around 31° corresponds to K_2CO_3,[16, 17] and the peaks around 39 and 45° correspond to LiF.[18] We have attempted to quantitatively analyze the produced K_2CO_3 and LiF amounts from their relative diffraction intensities. However, it was not successful due to the preferred orientation effect on the diffraction pattern of the $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ reacted with PTFE, the low intensity and broadness of the diffraction peaks from K_2CO_3 and LiF, and the uncertain quantities such as c, d, x, y and z in the following expected reaction:

$$
\begin{aligned}
K_{0.8}(Li_{0.27}Ti_{1.73})O_4 + xCF_2 \rightarrow\ & K_{0.8-c}(Li_{0.27-d}Ti_{1.73})O_{4-y-z}F_z \\
& + cK^+ \text{ derivative (including } K_2CO_3) \\
& + dLi^+ \text{ derivative (including LiF)} \\
& + \text{PTFE derivative} \qquad (1)
\end{aligned}
$$

We were not able to identify the compound contributing to the peak around 19°. However, we found that this peak and those from K_2CO_3 and LiF diminish when the sample is washed in water.[12, 13] Therefore, we expect that it is also from K^+- or Li^+-containing compound that was produced as a result of the K^+ and/or Li^+ deintercalation as in the chemical equation (1). In addition, some other K^+- and/or Li^+-containing byproducts might also exist as amorphous phases, not appearing in the XRD pattern. We expect that charge balancing for the extracted K^+ and Li^+ is achieved by the partial replacement of zO^{2-} with zF^-. Furthermore, small but finite amount y of O^{2-} deficiency might have been induced in the $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ reacted with PTFE under flowing Ar. Those O^{2-} from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ must be the source of O^{2-} in the K_2CO_3 byproduct. Further discussion on the reaction stoichiometry is provided in the later section along with the chemical analysis results.

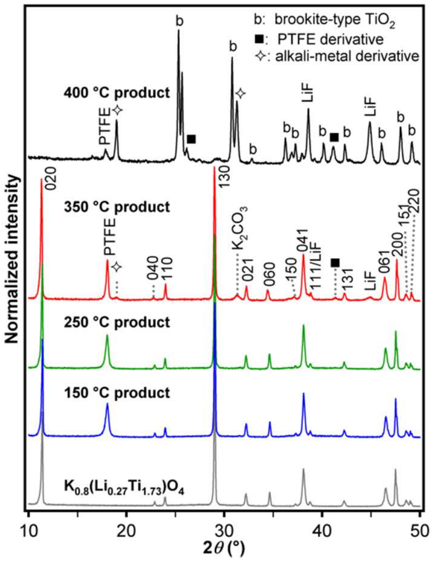


Fig. 1. Powder XRD profiles of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and that reacted with PTFE (F / (K + Li) = 3.4) at selected temperatures.

The refined lattice parameters of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and those reacted with PTFE (F / (K + Li) = 3.4) at various temperatures are shown in Fig. 2. The lattice parameter *b* along the interlayer direction increased systematically for the reactions above 200 °C. On the other hand, the lattice parameters *a* and *c* along the intralayer directions decreased systematically above 250 °C. Considering the crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, it is reasonable to expect that the change in the interlayer K^+ content mainly influences the lattice parameter *b* along the interlayer direction, and the change in the intralayer Li^+ content mainly influences the lattice parameters *a* and *c* along the intralayer directions.

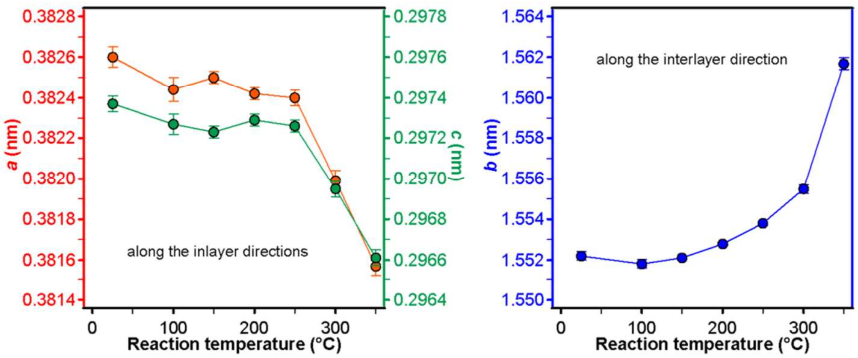


Fig. 2. Refined lattice parameters of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and its reaction products as functions of reaction temperatures from the reactions with F / (K + Li) = 3.4.

Similar lattice parameter trends were observed in another layered compound, α-$NaFeO_2$-type Li_xCoO_2, where *x* is the electro-chemically deintercalated Li^+ amount.[19, 20] In the case of Li_xCoO_2, the changes in the lattice parameters with respect to *x* are attributed to the following mechanisms. When interlayer Li^+ is deintercalated, the Coulomb repulsion between O^{2-} of the adjacent layers increases. That is why the lattice parameter along the interlayer direction increases with respect to *x*. On the other hand, the decrease in the lattice parameters along the intralayer directions with respect to *x* is attributed to the partial oxidation of relatively larger Co^{3+} (radius = 0.0670 nm) to smaller Co^{4+} (radius = 0.0605 nm),[21] charge compensating for the deintercalated Li^+.

The increase in the lattice parameter along the interlayer direction in our products might follow the same mechanism as that for Li_xCoO_2. Such speculation is based on an assumption that the deintercalated amount of the interlayer K^+ increased as the reaction temperatures increased; thus, the repulsion between O^{2-} of the adjacent layers increased. However, the mechanism of the changes in the lattice parameters along the intralayer directions cannot be analogous between Li^+-deintercalated Li_xCoO_2 and our reaction products from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ because Ti^{4+} in $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ cannot be further oxidized. In addition, the changes in the lattice parameters along the intralayer directions of our reaction products with respect to the increase in the reaction temperatures are approximately one order of magnitude smaller than those in the lattice parameters along the interlayer direction. Such small changes in the lattice parameters along the intralayer direction might be caused by slight and systematic distortion of the Li^+-substituted TiO_6 octahedra, assuming that the Li^+ deintercalation amount increased systematically as the reaction temperatures increased.

If these assumptions are correct, these lattice parameter trends indicate that partial K^+ and Li^+ deintercalation from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ using PTFE as the extraction reagent was successful, and the deintercalation amounts are proportional to the reaction temperatures. In order to further confirm such deintercalation from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, chemical compositions of the reaction products must be analyzed. However, these reaction products contain significant amounts of secondary phases, particularly PTFE derivatives, and they prevent meaningful and quantitative chemical composition analysis. Therefore, we then systematically optimized the amount of PTFE to deintercalate as much K^+ and Li^+ as possible from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ while minimizing the co-production of the secondary phases in the reactions at 350 °C.

Fig. 3 shows the powder XRD patterns of the products from the reactions between $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and various amounts of PTFE at 350 °C for 12 h under flowing Ar. Most of the reflections can be indexed based on the crystal structure of the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, indicating that the fundamental crystal structure of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was retained in all these products. However, other reflections attributed to trace amounts of PTFE and alkali-metal derivatives were also observed in the reaction products, and their diffraction intensities increased as the amount of the reacted PTFE increased.

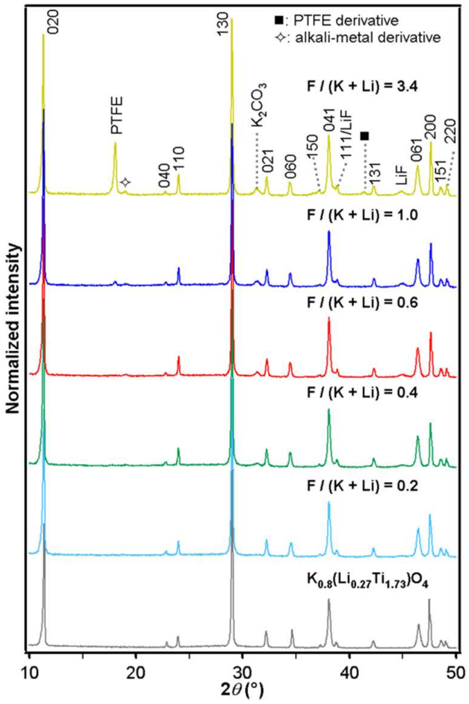


Fig. 3. Powder XRD profiles of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and that reacted with various amounts of PTFE at 350 °C for 12 h under flowing Ar.

Lattice parameter trends of these products are shown in Fig. 4. The lattice parameters *a* and *c* along the intralayer directions decreased and *b* along the interlayer direction increased as F / (K + Li) in the reactions increased up to 0.6, and the changes became quite small for F / (K + Li) > 0.6. These changes in the lattice parameters suggest that partial deintercalation proceeded proportional to the amount of reacted PTFE, particularly up to F / (K + Li) = 0.6. The mechanism of these lattice parameter trends is likely analogous to that for the previously discussed temperature dependence of the reactions between $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and PTFE. Therefore, this result, along with the formation of alkali-metal derivatives, such as K_2CO_3 and LiF, again suggests that alkali-metal ions are in fact partially deintercalated from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ using PTFE as the alkali-metal ion extraction reagent.

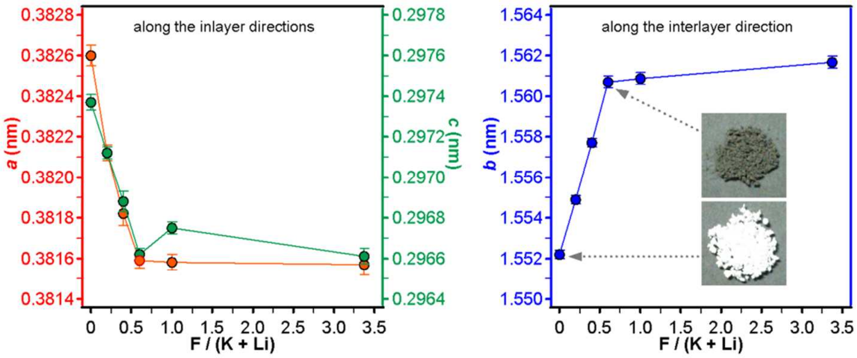
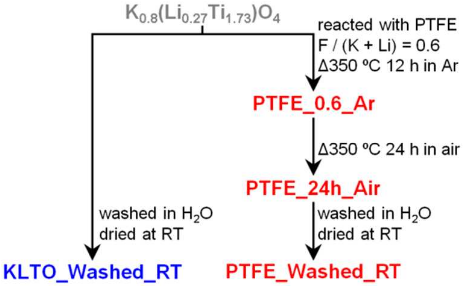


Fig. 4. Refined lattice parameters of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and its reaction products as functions of F / (K + Li) in the reactants at 350 °C. (Inset) Photographs of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and that reacted with PTFE (F / (K + Li) = 0.6) at 350 °C under flowing Ar for 12 h.

The color of the $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ reacted with PTFE is gray while that of the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ is white (Fig. 4 inset). The origin of this gray color is attributed to the PTFE derivatives, which are some organics, as in the previous studies in the reactions using PTFE.[12, 13] Therefore, we then attempted to remove the PTFE derivatives in the product by oxidative thermal decomposition in air. For this study, F / (K + Li) = 0.6 reaction product was chosen because it has almost maximum lattice parameter differences from those of the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, whereas the amounts of remaining PTFE and undesired derivatives are minimal. This reaction product from the F / (K + Li) = 0.6 reactant ratio is denoted as PTFE_0.6_Ar, and the processes to remove the secondary phases from it are shown in Scheme 1.

Scheme 1. Alkali-Metal Ion Extraction and Phase Purification Processes for $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$



After re-heating PTFE_0.6_Ar for 24 h under flowing air at 350°C, no trace of the diffraction peak attributed to the PTFE derivatives were observed, and the color of the product (PTFE_24h_Air) turned white. The photographs showing the change in the colors in these samples and the detail of the reaction duration optimization to decompose PTFE derivatives from PTFE_06_Ar are provided in ESI S2†. These results indicate the successful decomposition of the PTFE derivatives from PTFE_0.6_Ar, and we proceeded to remove the alkali-metal derivatives from PTFE_24h_Air.

The alkali-metal derivatives from the reaction using PTFE are usually water-soluble salts.[12, 13] Therefore, we attempted to wash away the alkali-metal derivatives from PTFE_24h_Air. PTFE_24h_Air was mixed with water, agitated, allowed to settle for more than 8 h, centrifuged and supernatant fluid was decanted. These processes were repeated to the centrifuged sediment until the conductivity of the supernatant fluid became less than 5 mS m^{-1}. In addition, our preliminary study of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ indicated that its alkali-metal ions tended to ion-exchange with H^+ to some extent when it was soaked in water. Thus, the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was also washed in the same way as that for PTFE_24h_Air for comparison (Scheme 1). The powder XRD profiles of PTFE_24h_Air and that washed in water and dried at room temperature (RT), denoted as PTFE_Washed_RT, are shown in Fig. 5. The diffraction peaks from the alkali-metal derivatives (K_2CO_3 and LiF) in PTFE_24h_Air disappeared after washing. This indicates the successful removal of the alkali-metal derivatives from PTFE_24h_Air. However, diffraction patterns of the washed products of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, denoted as KLTO_Washed_RT, and PTFE_Washed_RT were quite different from those before washing due to the interlayer hydration (Figs. 5 and S3 in ESI[†]).

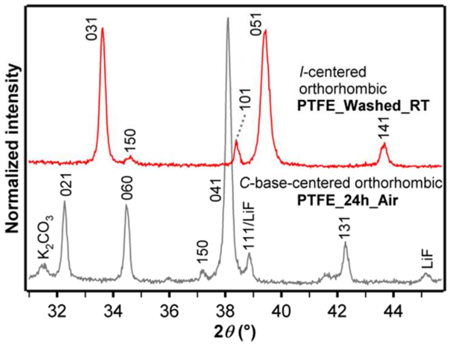


Fig. 5. Magnified powder XRD profiles of PTFE_24h_Air and PTFE_Washed _RT.

These differences in the diffraction patterns are attributed to the gliding of the adjacent host layers along the *c*-axis by *c* / 2 due to the interlayer hydration by washing in water. Such gliding of the host layers transforms *C*-base-centered orthorhombic unit cells ($h + k = 2n$ reflections only) of the pre-washed phases into *I*-centered orthorhombic unit cells ($h + k + l = 2n$ reflections only) of the washed phases, and the analogous gliding of the host layers was also reported for the completely H^+-exchanged $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ produced by acid leaching.[6, 22] The lattice parameter *b* along the interlayer direction elongated more than 10% after washing $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and PTFE_24h_Air in water due to the interlayer hydration, while the changes in the lattice parameters *a* and *c* along the intralayer directions were less than 1% (see Fig. S3 in ESI†). After heating PTFE_Washed_RT at 100 °C, the diffraction peak of the dehydrated phase appeared as indicated by the green arrow in Fig. S3b in ESI†. However, a single-phase of the completely dehydrated phase was not obtained because the phase transformation to anatase-type TiO_2 (indicated by the blue arrow in Fig. S3b in ESI†) took place at 300 °C and above where dehydration was still incomplete.[22] Similarly, phase transformation to anatase-type TiO_2 was observed for KLTO_Washed_RT when it was heated at 350 °C and above, indicated by the blue arrow in Fig. S3a in ESI†. The relative amount of anatase-type TiO_2 is more significant in the sample transformed from PTFE_Washed_RT than that from KLTO_Washed_RT. These behaviors might reflect the fact that PTFE_Washed_RT and KLTO_Washed_RT are chemically different, where we expect that more alkali-metal ions were extracted from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ reacted with PTFE than that simply washed in water. The further details of the dehydration and phase transformation behaviors of PTFE_Washed_RT characterized by thermogravimetric (TG) analysis and powder XRD are provided in the section S4 in ESI† along with the result of the chemical analysis of PTFE_Washed_RT heated at 1000 °C.

In order to understand and confirm the ability of PTFE as an alkali-metal ion extraction reagent, we have performed chemical analysis of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, KLTO_Washed_RT and PTFE_Washed_RT; their estimated elemental compositions are summarized in Table 1. The estimated molar elemental contents in the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ are very close to nominal. While washing $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ to form

KLTO_Washed_RT reduced the K content, Li content remained unchanged within the experimental uncertainty. It is likely that the interlayer K^+ in $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was readily ion-exchanged with H^+ just by washing it in water due to its structural accessibility. On the other hand, the intralayer Li^+ was not extracted or not ion-exchanged with H^+ by water washing because Li^+ is more tightly bound to the layer unit of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ than the interlayer K^+. In order to extract or H^+-exchange such tightly bound Li^+ by soft-chemical approach, a reaction with an acidic solution rather than water is required.[6, 22] These results suggest that the following reaction took place by water washing of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$:

$$K_{0.8}(Li_{0.27}Ti_{1.73})O_4 + (v+w)H_2O \rightarrow K_{0.8-v}H_v(Li_{0.27}Ti_{1.73})O_4{\cdot}wH_2O + vK^+ + vOH^-$$

$$\text{where } v \approx 0.35 \qquad (2)$$

Table 1. Analytically Determined Molar Elemental Compositions[*1] of $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ and its Processed Samples

	K	Li	Ti	F
$K_{0.8}(Li_{0.27}Ti_{1.73})O_4$	0.80	0.29	1.73	–
KLTO_Washed_RT	0.45	0.28	1.73	–
PTFE_Washed_RT	0.38	0.26	1.73	0.04

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

In contrast, a decrease in both K and Li contents was observed in the PTFE treated sample (PTFE_Washed_RT). These chemical analysis results along with the XRD and TG analysis data of PTFE_Washed_RT (sections S3 and S4 in ESI†) suggest that the following H^+-exchange and hydration reaction took place during the water washing of PTFE_24h_Air to form PTFE_Washed_RT:

$$K_{0.8-c}(Li_{0.27-d}Ti_{1.73})O_{4-y-z}F_z + (v+t+w)H_2O$$

$$\rightarrow K_{0.8-c-v}H_v(Li_{0.27-d-t}H_tTi_{1.73})O_{4-y-z}F_z{\cdot}wH_2O + vK^+ + tLi^+ + (v+t)OH^-$$

$$\text{where } c+v \approx 0.42 \text{ and } d+t \approx 0.03 \qquad (3)$$

The difference in the elemental compositions between KLTO_Washed_RT and PTFE_Washed_RT indicates that at least 9% K^+ was extracted from the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by the reaction with PTFE and the total of 53% K^+ was extracted after the phase purification processes causing the ion-exchange with H^+. Similarly, approximately 10% of Li^+ was extracted from the pristine $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by the reaction with PTFE and no further Li^+ extraction through H^+-exchange was observed within the experimental uncertainty.

When positively charged alkali-metal ions are deintercalated from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, some other change in the chemical composition must take place in order to maintain the charge neutrality. The TG analysis result (Fig. S4a in ESI†) indicates that some portions (v+t) of K^+ and Li^+ were H^+-exchanged during washing in water as in the chemical equation (3).

In addition, a small but finite amount of F content was detected in PTFE_Washed_RT (Table 1). It has been reported that some portion of O^{2-} in oxide compounds tends to be replaced with F^- when those compounds are reacted with PTFE.[23-27] Therefore, zO^{2-} of PTFE_Washed_RT is likely replaced with zF^- as in the chemical equations (1) and (3), contributing to the charge re-balancing in the K^+- and Li^+-deintercalated $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$. Furthermore, the additional deficiency y in the O^{2-}-site was likely induced when $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ was reacted with PTFE as explained for the chemical equation (1).

These results quantitatively proved that PTFE functioned as an effective alkali-metal ion extraction reagent, and that not only interlayer alkali-metal ions, but also intralayer alkali-metal ions can be extracted by this approach, utilizing PTFE powder as the active reagent. Furthermore, these results suggest that the previously discussed systematic changes in the lattice parameters with respect to the reaction temperatures and F / (K +

Li) ratios actually reflect a systematic increase in the alkali-metal ion deintercalation amounts.

Assuming that the K^+ and Li^+ extraction amounts in the chemical equation (1) can be estimated by taking the difference between the chemical compositions of PTFE_Washed_RT and KLTO_Washed_RT or $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, the chemical equation (1) can be simplified into the following for the F / (K + Li) = 0.6 reaction at 350 °C:

$$K_{0.8}(Li_{0.27}Ti_{1.73})O_4 + 0.32CF_2 \rightarrow K_{0.73}(Li_{0.24}Ti_{1.73})O_{3.93}F_{0.04}$$

$$+ 0.07\ K^+ \text{ derivatives (mainly } K_2CO_3\text{)}$$

$$+ 0.03\ Li^+ \text{ derivatives (mainly LiF)}$$

$$+ \text{PTFE derivative} \qquad (4)$$

Such a simplified model provides approximate estimation of the O^{2-} deficiency and F^- substitution amounts in the $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ reacted with PTFE. The highly O^{2-} deficient and F^- substituted non-stoichiometric product in the chemical equation (4) and the additionally alkali-metal ion extracted and H^+-exchanged product in the chemical equation (3) are uniquely accessible by the AEP (*Alkali-metal ion Extraction using PTFE*) reactions. It would be interesting to study properties of such deintercalated non-stoichiometric compounds produced by the AEP reactions of various other compounds.

In conclusion, the systematic changes in the lattice parameters with respect to the reaction temperatures and the reacted PTFE amounts, and the chemical analysis results of the reaction products from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$, unambiguously and quantitatively indicated that both intralayer and interlayer alkali-metal ions can be deintercalated using PTFE as the extraction reagent without allowing its crystal structure transformation. Unlike other conventional deintercalation methods, such as soft-chemical and electro-chemical reactions, AEP reactions can be performed in inert atmosphere without involving any liquid phase. Such a unique feature of the AEP reaction might enable deintercalation of alkali-metal ions from compounds that are highly air-sensitive and/or reactive toward liquid media, unlike the conventional deintercalation methods. In addition, alkali-metal ion extracted products from the AEP reaction tend to have unique non-stoichiometric chemical compositions. Furthermore, the results of this and previous[12, 13] studies indicated that transformation into various phases, including a metastable one, can be induced by the AEP reaction depending on the reaction parameters such as PTFE amounts and temperatures. These exceptional characteristics of the AEP reaction provide a new route for materials design through the modification of chemical composition, optionally followed by the crystal structure transformation.

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53% of interlayer K^+ and 10% of intralayer Li^+ were extracted from $K_{0.8}(Li_{0.27}Ti_{1.73})O_4$ by the reaction with PTFE.