Electronic supplementary information (ESI)

Beyond soft chemistry - bulk and surface modifications of polycrystalline lepidocrocite titanate induced by post-synthesis thermal treatment

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Table S1. Unit cell parameters a, b, and c of the orthorhombic symmetry for several samples of lepidocrocite titanate, including the nominal layer charge density CD and the chemical composition.

Sample	a/ nm	<i>b/</i> nm	<i>c</i> / nm	CD ^a /	Composition ^b
				<i>e</i> nm ⁻²	
K _{0.8} Zn _{0.4} Ti _{1.6} O ₄					
Groult et al ¹	0.38064(5)	1.5692(5)	0.29850(5)	3.520	"K _{0.8} Zn _{0.4} Ti _{1.6} O ₄ "
As-made powder	0.3798(1)	1.5681(5)	0.29854(9)	3.559	$K_{0.81}Zn_{0.40}Ti_{1.58}O_4$
Pellet, 950 °C	0.3801(2)	1.5700(8)	0.2971(1)	2.856	$K_{0.65}Zn_{0.32}Ti_{1.30}O_4$
Powder, ^c 950 °C	0.3816(3)	1.5707(9)	0.2976(2)	2.840	$K_{0.65}Zn_{0.32}Ti_{1.30}O_4$
Pellet, 990 °C	0.3806(2)	1.5724(10)	0.2973(2)	2.678	$K_{0.61}Zn_{0.29}Ti_{1.21}O_4$
Powder, ^c 990 °C	0.3810(4)	1.5728(8)	0.2976(2)	2.672	$K_{0.61}Zn_{0.29}Ti_{1.21}O_4$
K _{0.8} Cu _{0.4} Ti _{1.6} O ₄					
Groult et al ¹	0.38054(5)	1.5630(5)	0.29857(5)	3.521	"K _{0.8} Cu _{0.4} Ti _{1.6} O ₄ "
As-made powder	0.3805(5)	1.561(2)	0.2981(3)	3.466	$K_{0.79}Cu_{0.47}Ti_{1.55}O_4$
Pellet, 940 °C	0.3813(7)	1.561(2)	0.2966(5)	3.130	$K_{0.71}Cu_{0.37}Ti_{1.43}O_4$
Pellet, 950 °C	0.3815(8)	1.564(2)	0.2970(5)	2.992	$K_{0.68}Cu_{0.37}Ti_{1.44}O_4$
Pellet, 1,000 °C	0.3828(10)	1.571(3)	0.2979(5)	2.960	$K_{0.68}Cu_{0.38}Ti_{1.46}O_4$
K _{0.8} Ni _{0.4} Ti _{1.6} O ₄					
Groult et al ¹	0.38361(5)	1.5559(5)	0.29648(5)	3.517	"K _{0.8} Ni _{0.4} Ti _{1.6} O ₄ "
As-made powder	0.3840(2)	1.5517(5)	0.29676(8)	3.484	$K_{0.79}Ni_{0.41}Ti_{1.64}O_4$
Pellet, 960 °C	0.3829(5)	1.552(2)	0.2969(4)	N/A	N/A
Pellet, 980 °C	0.3833(5)	1.554(1)	0.2974(4)	3.294	$K_{0.75}Ni_{0.37}Ti_{1.51}O_4$
Pellet, 1,000 °C	0.3843(5)	1.5580(9)	0.2975(2)	3.023	$K_{0.69}Ni_{0.33}Ti_{1.31}O_4$

^{*a*} Nominal layer charge density CD = x/(2ac) where *x* is the number of potassium ions per formula unit obtained from XRF measurement, *a* and *c* is the respective cell edge determined from PXRD.

^b Assuming 4 oxygen atoms per formula unit as in the "starting composition". The calculated compositions are *not* charge-balanced and require the presence of oxygen vacancy defects. (See text for discussion.)

^{*c*} The measurement was performed on the powder, crushed from the respective thermallytreated pellet, with the addition of the LaB₆ internal standard.



Fig. S1 Representative SEM images of (a) $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ powder, and the pellet thermally treated at (b-d) 990 °C. Images (b,c) are from the top surfaces while image (d) is the cross-section, all from the unpolished pellet.



Fig. S2 Wide-scan XPS spectra of: (a) $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ powder, and the pellets thermally treated at (b) 950 °C, and (c) 990 °C.



Fig. S3 The mass loss curves of (a) $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ powder, and the pellets thermally treated at (b) 950 °C, and (c) 990 °C. The inset is a zoom-in to curve (b) and (c). Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 1 instrument. The samples were heated from RT to 900 °C (10 °C min⁻¹) under nitrogen gas flowing at 20 mL min⁻¹.



Fig. S4 (a) Volumetric change $\Delta V/V$, and (b) apparent density relative to the theoretical value for the K_{0.8}M_{0.4}Ti_{1.6}O₄ (M = Zn, Cu, Ni) pellets thermally treated at 940-1000 °C.

The apparent density D_{app} was calculated as the ratio of mass (*m*) to volume (*V*) of the pellet, i.e., $D_{app} = m/V$. *V* was calculated from the radius (*r*) and the thickness (*d*) of the pellet following the equation $V = \pi r^2 d$. Then, the obtained D_{app} can be compared to the theoretical density (3.6898 g/cm³ for K_{0.8}Zn_{0.4}Ti_{1.6}O₄, 3.6687 g/cm³ for K_{0.8}Ni_{0.4}Ti_{1.6}O₄, and 3.6906 g/cm³ for K_{0.8}Cu_{0.4}Ti_{1.6}O₄) calculated from the reported¹ unit cell parameters. The change in volume ($\Delta V/V$) was then determined from the difference in volume before (V_i) and after (V_f) the thermal treatment, which is $\Delta V/V = [(V_f - V_i)/V_i] \times 100\%$.



Fig. S5 PXRD patterns of (a) as made powder $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$, and the proton exchange product prepared from (b) potassium precursor without the post-synthesis thermal treatment, and (c) from potassium precursor thermally-treated at 990 °C 4 h.

The exchange of interlayer K⁺ cations for (solvated) protons was done following the reported² procedure. The powder was repeatedly (3 times) equilibrated with 1 M HCl overnight at the solid-to-solution ratio of 1 g 100 mL⁻¹, with the acid renewed every day. The product was washed with deionized water until it is free from excess acid, and was dried at room temperature. The starting material was either (i) as made $K_{0.8}Zn_{0.4}Ti_{1.6}O_4$ powder, and (ii) the powder crushed from the pellet thermally treated at 990 °C. In both cases, the PXRD patterns characteristic of the protonated form are obtained as shown in Fig. S5, similar to the previous work² by Sasaki et al. The product has d_{020} of ~0.90 nm (vs ~0.78 nm prior to the exchange), suggesting the successful exchange of K⁺ with solvated protons.

References

¹ Groult, D.; Mercey, C.; Raveau, B. Nouveaux oxydes à structure en feuillets: Les titanates de potassium non-stoechiométriques $K_x(M_yTi_{2-y})O_4$. *J. Solid State Chem.* **1980**, *32*, 289-296. ² Sasaki, T.; Watanabe, M.; Michiue, Y.; Komatsu, Y.; Izumi, F.; Takenouchi, S. Preparation and acid-base properties of a protonated titanate with the lepidocrocite-like layer structure. *Chem. Mater.* **1995**, *7*, 1001-1007.