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ARTICLE

Supplementary information for

Oxygen Defect Chemistry for the Reversible Transformation of Titanates for

Sizeable Potassium Storage

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Fig. S1 Structural representation and crystallographic information of LL-KTO. Schematic illustrations of plane (001), (100) and (010) and parameters of the unit cell.



Fig. S2 XPS spectra of Ti 2p in Anatase_{2-δ}. This shows Ti is composed of 12.9% Ti^{III} and 87.1% Ti^{IV} and suggests Anatase_{2-δ} has a chemical formula of Ti^{III}_{0.13}Ti^{IV}_{0.87}O_{1.935}. However, since the samples were exposed to air before XPS analysis, Ti^{III} may easily be oxidized during the process with somewhat misleading results. A general formula for Anatase_{2-δ}, TiO_{2-δ}, is used in this manuscript to present the nominal formula.



Fig. S3 Morphology and chemical distributions before and after the KOH_{aq} reaction. (A and C) SEM and STEM images and EDX elemental mapping before KOH_{aq} treatment. Anatase_{2-δ} with size smaller than 5 nm are embedded in carbon nanofibres as indicated by yellow arrows in (A) SEM image. (C) STEM images and elemental maps indicate Anatase_{2-δ} are uniformly distributed throughout the carbon nanofibres. (B and D) SEM and STEM images with elemental mapping after KOH_{aq} treatment. (B) SEM image shows that the highly cross-linked nanofibres around carbon nanofibres have an average diameter of 6 nm. (D) STEM images with elemental mapping confirm the thin nanofibres are LL-KTO while the thicker backbones are carbon nanofibres. (E) EDX results of LL-KTO show the stoichiometric ratio of between K and Ti on the LL-KTO nanofibres is 1: 4.08. Red: Carbon; Yellow: Potassium; Cyan: Titanium; Green: Oxygen. Scale bars: (C and D) 100 nm.



Fig. S4 Process of determine the chemical composition and structure for LL-KTO and KTO. (A) Schematic illustrations of simulated structures of lepidocrocite-type layered $K_4(TiO_2)_4(OH)_2$, $K_4(TiO_{1.75})_4(OH)_2$, $K_3(TiO_{1.75})_4(OH)_2$, $K_3(TiO_{1.75}$



Fig. S5 XPS survey of Anatase_{2- δ} and LL-KTO. XPS results of LL-KTO show the emergence of both a peak in the K 2s and 2p spectra at 387 and 293 eV, respectively, as compared to Anatase_{2- δ}.



Fig. S6 Evidence for OH group's presence. (A) FTIR results of LL-KTO showing the O-H stretching between $3550 - 2900 \text{ cm}^{-1.1}$ (B) TGA shows 4 regions of weight drop for LL-KTO. Region I represented the immediate weight loss of water molecules adsorbed on the sample surface. For Anatase_{2-ô}, region II was an extension of the region I where adsorbed water was continual being released from the pores. For LL-KTO, apart from the continue release of adsorbed water up until ~130 °C, this region also corresponded to the release of OH surface groups as well (indicated by the green box).² The huge weight loss below 100 °C is due to the sample being very hydrophilic. This phenomenon was found in other nano sized layered titanates as well.² Between ~280 and 480 °C, a rapid drop in weight indicated carbon combustion for all three samples. However, the blue box indicated a separate reaction happened for LL-KTO, the oxidation of potassium titanates. The content of LL-KTO is estimated to be 75.1 wt%.



Fig. S7 Nitrogen adsorption-desorption analysis before and after the KOH_{aq} reaction. Isotherm and pore size distribution of (A and B) Anatase_{2-δ} and (C and D) LL-KTO. The effect of KOH_{aq} can also be reflected by the significant increase in specific surface area (SSA) and pore volume. Based on the BET theory, the calculated SSA increase from 18.6 to 280.4 m² g⁻¹. Furthermore, the BJH shows an increase in average pore volume from 0.028 to 0.443 cm³ g⁻¹. The isotherm profile of LL-KTO lie between Type II and Type IV of BET model.³ Type II indicates no pores in the composites, however the hysteresis in Type IV indicates the presence of mesopore. Therefore, we concluded that LL-KTO has minimal mesopores. We will include this discussion in the supporting information.



Fig. S8 XRD spectra of other forms of anatase before and after the KOH_{aq} reaction. (A) Anatase nanoparticles less than 10 nm. (B) Pyrolysed TiO₂ – PVP sol-gel at 600 °C. (C) Pyrolysed electrospun PVP – TiO₂ nanofibre at 900 °C. Star indicates the LL-KTO phase.



Fig. S9 Schematic illustrations of activation of LL-KTO.



Fig. S10 Ex situ TEM analysis of the potassium-storing mechanism at 200th cycle. (A) Discharged state. (B) Charged state.



Fig. S11 Ex situ XRD spectra of LL-KTO at charged and discharged state.



Fig. S12 Discharge-charge curve of LL-KTO at 100 mA g^{-1} . This shows the activation discharge and its capacity at 1180 mAh g^{-1} as illustrated in Fig. S9. From 1st discharge cycle to the 10th and 1,800th, the capacity gradually decayed from 392 to 287 and 201 mAh g^{-1} , corresponding to capacity decays of 0.027% and 0.017% per cycle from the 1st and 10th cycle.



Fig. S13 *Ex situ* XPS spectra of LL-KTO for Ti 2p at charged and discharged state. (A) Charged state. (B) Discharged state. The peaks at the binding energy of 458.8 and 464.4 eV at charge state are attributed to the Ti^{IV} 2p 3/2 and Ti^{IV} 2p 1/2, respectively. At discharged stage, chemical shifts of the binding energy for Ti^{IV} 2p 3/2 and Ti^{IV} 2p 1/2 are observed and moved to 458.6 and 464.2 eV. Two new peaks were observed at the binding energy of 457.8 and 462.8 eV for Ti^{III} 2p 3/2 and Ti^{III} 2p 1/2, respectively. These suggest some Ti^{IV} are reduced to Ti^{III}.



Fig. S14 Capacity contribution analysis towards K⁺ for LL-KTO. (A) CV curves at various scan rates from 0.1 to 1.0 mV s⁻¹. (B) Contribution ratio of pseudocapacitive and diffusive charge versus various scan rates.



Fig. S15 Rate performance of LL-KTO. It has reversible capacities of 209, 181, 164 and 134 mAh g^{-1} at current density of 100, 200, 500, 1,000 mA g^{-1} , respectively. A recovery rate of 94.7% (198 mAh g^{-1}) when the current density was decreased back to 100 mA g^{-1} .



Fig. S16 Performance comparison of LL-KTO. Compared with other titanium-based materials KIBs,³⁻⁷ NIBs ^{5-7,12-15} and LIBs ^{7,8-11} in terms of number of cations stored per transition metal. Grey: LIBs; Blue: NIBs; Pink: KIBs; Orange: KIBs with LL-KTO. See expanded dataset including reported electrode materials and references in Table S2-S4.



Fig. S17 Electrochemical performances of CNF. (A and B) Cycling performances with reversible capacities of 11 and 4 mAh g^{-1} at current density 100 and 500 mA g^{-1} after 20 cycles, respectively.



Fig. S18 Morphological analysis of KTO. (A and B) SEM images of different magnifications. Both showing highly crosslinked potassium titanate nanofibres around carbon nanofibres, a morphology similar to that of LL-KTO. (C) TEM images showing that KTO are nanofibres with laminar structure that has a d-spacing of 7.9 Å (Inset). (D and E) STEM images with elemental mapping confirm the thin nanofibres are KTO while the thicker backbones are carbon nanofibres. Red: Carbon; Yellow: Potassium; Cyan: Titanium; Green: Oxygen. Scale bars: (D and E) 100 nm.



Fig. S19 Structural representation and crystallographic information of KTO. (A) Schematic illustrations of plane (001), (100) and (010) and parameters of the unit cell. (B) XRD patterns. (020) peak position is at 10.9° and corresponds to an interlayer spacing of 8.01 Å, which is similar to what was observed from TEM. The diffraction peaks at 24.1° and 28.3° represent the in-plane structure of the titanates ((210) and (230), respectively).



Fig. S20 *Ex situ* TEM analysis of KTO at discharged and charged state. (A) Discharged sate showing laminar structure with d-spacing of 9.3 Å. (B) Charged sate showing laminar structure with d-spacing of 8.4 Å. The laminar structure was observed in both charge and discharge state without any nanodots that represent titania nuclei. Furthermore, the increase in d-spacing after discharging indicates intercalation of K⁺ ions into the laminar structure.



Fig. S21 Electrochemical performances of KTO. (A and B) Cycling performances with reversible capacities of 104 and 34 mAh g⁻¹ at current density 100 and 500 mA g⁻¹ after 1,800 cycles, respectively. (C and D) Performance comparison of LL-KTO with other titanium oxide-based materials for KIBs,³⁻⁷ NIBs ^{5-7,12-15} and LIBs.^{7,8-11} In terms of (C) specific capacities and (D) number of cations stored per transition metal. Grey: LIBs; Blue: NIBs; Pink: KIBs; Brown: KIBs with KTO. See expanded dataset including reported electrode materials and references in Table S2-S4.



Fig. S22 Diffusion kinetic analysis of LL-KTO and KTO. (A and B) EIS curves and the linear fits of Z' v.s. $\omega^{-0.5}$ for LL-KTO). (C and D) EIS curves and the linear fits of Z' v.s. $\omega^{-0.5}$ for KTO).



Fig. S23 Electrochemical performances of Anatase_{2- δ}. (A and B) Cycling performances with reversible capacities of 117 and 102 mAh g⁻¹ at current density 200 and 500 mA g⁻¹ after 600 cycles, respectively.



Fig. S24 Peukert's constant. (A) LL-KTO. (B) KTO. Peukert's constant is calculated by taking log on the formula CI^{k} =constant.¹⁷ Where C is the capacity, I is the current density and k is the Peukert's constant. We then plot log(C) against log (I) base on the formula – log (C) = -klog (I) + constant.

Structures	La	Lattice Constant (Å)			Angles (°)	
	а	b	С	α	β	χ
K ₄ (TiO ₂) ₄ (OH) ₂	3.92	21.48	3.02	87.00	90.00	90.00
K ₄ (TiO _{1.75}) ₄ (OH) ₂	3.83	21.95	3.00	87.00	90.00	90.00
K ₃ (TiO _{1.75}) ₄ (OH) ₂	3.73	21.79	3.02	86.05	90.00	90.00
K ₃ (TiO _{1.75}) ₄ OH	3.84	18.56	3.00	83.43	90.00	90.00
K ₂ (TiO _{1.75}) ₄ OH	3.73	18.35	3.02	82.66	90.00	90.00
K(TiO _{1.875}) ₄ OH – LL-KTO	7.40	17.91	3.01	82.88	89.94	91.07
K(TiO₂)₄·0.5H₂O − KTO	7.58	16.19	3.01	81.29	89.88	91.60

 Table S1 Details of the obtained structures during the process of determine the chemical composition.

Systems	Materials	Cycling capacity (mAh g ⁻¹) / Current	Cations	Ref.
		density (mA g ⁻¹) / Cycle number	per TM	
	LL-KTO	201 / 100 / 1800	0.62	
Ours		183 / 500 / 1800	0.56	This
	кто	104 / 100 / 1800	0.36	work
		34 / 500 / 1800	0.12	
	K ₂ Ti ₄ O ₉	80 / 30 / 30	0.31	4
		45 / 100 / 10	0.17	
	K ₂ Ti ₈ O ₁₇	110.7 / 20 / 50	0.38	5
KIBs	MXene-derived K ₂ Ti ₄ O ₉	50 / 200 / 900	0.19	6
	KTO/rGO	75 / 2000 / 2000	0.29	7
	Lepidocrocite-Type Layered TiO ₂	37 / 25 / 45	0.14	8
	MXene-derived NaTi _{1.5} O _{8.3}	130 / 200 / 150	0.74	6
	NTO/rGO	72 / 5000 / 10000	0.28	7
	Lepidocrocite-Type Layered TiO ₂	90 / 25 / 45	0.33	8
	Na ₂ Ti ₆ O ₁₃	145 / 100 / 200	0.49	13
NIBs	Anatase	153 / 335 / 1000	0.46	14
		108 / 1675 / 1000	0.32	
	Na ₂ Ti ₃ O ₇	108 / 354 / 1200	0.41	15
		85 / 3540 / 10000	0.32	
	TiO ₂ (B)	77 / 50 /100	0.23	16
	Lepidocrocite-Type Layered TiO ₂	165 / 25 / 45	0.61	8
		150 / 150 / 50	0.55	12
		110 / 600 / 50	0.40	
LIBs	TiO ₂ (B)	200 / 50 / 100	0.60	9
	LTO	191 / 340/ 15	0.65	10
		155 / 1700 / 150	0.53	
	Anatase	169 / 170 / 100	0.50	11
		155 / 340 / 100	0.46	
		120 / 1700 / 100	0.36	

 Table S2 Long cycle performance and number of cations stored per transition metal.

Table S3 Rate performance.

Systems	Materials	Rate capacities (mAh g ⁻¹) /	Ref.
		Current density (mA g ⁻¹)	
	LL-KTO	207-180-163-142 /	
Ours		100-200-500-1000	This
	кто	86-66-51-41 /	work
		100-200-500-1000	
	K ₂ Ti ₄ O ₉	97-80-65-56-50-42-20 /	4
		30-100-250-500-1000-1500-2000	
	K ₂ Ti ₈ O ₁₇	175-105-90-80-75-60-50-40 /	5
		20-40-80-100-150-200-400-500	
KIBs	MXene-derived K ₂ Ti ₄ O ₉	150-119-105-97-89-81 /	6
		20-50-100-150-200-300	
	KTO/rGO	228-162-116-84 /	7
		100-200-500-1000	
	MXene-derived NaTi _{1.5} O _{8.3}	196-169-153-134-119-109-101 /	6
		50-100-200-500-1000-1500-2000	
	NTO/rGO	302-226-197-174-147-127-97 /	7
		100-200-500-1000-2000-3000-5000	
	$Na_2Ti_6O_{13}$	160-145-133-123-119 /	13
		100-200-400-800-1000	
NIBs	Anatase	180-177-174-158-132-108-84-68-52 /	14
		34-85-170-340-850-1700-3400-5100-8500	
	Na ₂ Ti ₃ O ₇	108-100-90-85 /	15
		354-885-1770-3540	
	TiO ₂ (B)	77-55-42-33 /	16
		50-100-200-400	
	Lepidocrocite-Type Layered TiO ₂	170-150-130-110 /	12
LIBs		20-150-300-600	
	TiO ₂ (B)	200-155-125-100-85 /	9
		200-500-1000-2000-3000	
	LTO	191-170-135-125 /	10
		340-850-3400-5100	
	Anatase	224-192-170-150 /	11

85-170-850-1700

Table S4 Peukert's constant (k), i	fractal dimension (d) and I	host-to-guest ion ratio (r)	at 100 and 1,000 mA g ⁻¹	based on
table S3 using Peukert's law. ¹⁷				

Systems	Materials	k	d	Cations per	r at 100	Cations per	r at 1000	Ref.
				TM at 100	mA g⁻¹	TM at 1000	mA g⁻¹	
				mA g ⁻¹		mA g⁻¹		
Ours	LL-KTO	0.16	2.16	0.62	1.61	0.43	2.30	This
	кто	0.32	2.32	0.29	3.45	0.14	7.14	work
	$K_2 Ti_4 O_9$	0.30	2.30	0.31	3.24	0.19	5.18	4
	K ₂ Ti ₈ O ₁₇	0.41	2.41	0.27	3.66	0.11	9.44	5
KIBs	MXene-derived	0.22	2.22	0.41	2.47	0.24	4.16	6
	K ₂ Ti ₄ O ₉							
	KTO/rGO	0.42	2.42	0.88	1.14	0.32	3.09	7
	Mxene-derived	0.17	2.17	0.96	1.05	0.67	1.48	6
	NaTi _{1.5} O _{8.3}							
NIBs	NTO/rGO	0.26	2.26	1.13	0.88	0.65	1.53	7
	$Na_2Ti_6O_{13}$	0.13	2.13	0.54	1.86	0.40	2.50	13
	Anatase	0.24	2.24	0.53	1.90	0.35	2.84	14
	Na ₂ Ti ₃ O ₇	0.11	2.11	0.47	2.15	0.36	2.75	15
	TiO ₂ (B)	0.41	2.41	0.16	6.10	0.07	14.78	16
LIBs	Lepidocrocite-Type Layered TiO ₂	0.12	2.12	0.53	1.88	0.40	2.47	12
	TiO ₂ (B)	0.31	2.31	0.75	1.33	0.37	2.68	9
	LTO	0.16	2.16	0.80	1.25	0.56	1.79	10
	Anatase	0.12	2.12	0.64	1.57	0.48	2.08	11

Note S1 Determination of crystal structure and chemical composition. PANalytical HighScorePlus was first employed to index the as-prepared LL-KTO sample, however, none of the available titanate structures ($K_2Ti_2O_5$ · H_2O , $K_2Ti_2O_5$, $K_2Ti_4O_9$, and $K_2Ti_8O_{17}$) in ICDD/JCPDF/PCPDF database were with good agreement with the diffractions of LL-KTO. The major differences were the relative intensities of (020) and (230), indicating orientation preference lied within LL-KTO.

To determine the crystal structure and chemical composition, we constructed structures base on our estimation from XRD, EDX and optimized them using DFT calculations to ultimately determine the most suitable chemical structure for LL-KTO using the following procedures:

In the first step, lepidocrocite laminar structure with inserted K⁺ and OH⁻ ions between the layers was constructed to form $K_4(TiO_2)_4(OH)_2$. It was a supercell with two layers of TiO_6 octahedra sandwiching the ions. In the second step, a simulated oxygen vacancy generating (SOVG) process began to introduced oxygen vacancy and $K_4(TiO_{1.75})_4(OH)_2$ was formed. The structure at this point contained excess of potassium. Therefore, in the next step, one potassium atom was removed to make $K_3(TiO_{1.75})_4(OH)_2$. The XRD patterns had not deviated from the original one so far. To shift the (020) peak to the right (decreasing the d-spacing/interlayer spacing of the structure), one OH molecule was removed and resulted in the c axis to dramatically decrease from 21.79 Å to 18.56 Å. Since it was still potassium in excess, one potassium atom was further removed to make $K_2(TiO_{1.75})_4OH$. In the next step, the supercell size was doubled the to 2 x 1 x 1 with one more potassium atom removed but all the oxygen atoms inserted back (to prevent the structure collapsing during refinement) to construct $K(TiO_2)_4OH$, as illustrated in Fig. S4C. To finally obtain structures for LL-KTO and KTO, two oxygen atoms, circled in orange and brown were removed separately via SOVG. By removing the oxygen atom circled in orange, $K(TiO_{1.875})_4OH$ that closely matched experimental data of LL-KTO was obtained; on the other hand, by removing the oxygen atom circled in brown, $K(TiO_2)_4 \cdot 0.5H_2O$ that closely matched experimental data of KTO was obtained.

Note S2 Calculating capacity of LL-KTO and KTO. In this work, the active material for LL-KTO is $(TiO_{1.875})_4$ ·OH based on Equation 3. At the point of electrochemistry data collection, the results were based on the weight of $K(TiO_{1.875})_4$ OH, the pristine LL-KTO. $(TiO_{1.875})_4$ ·OH and $K(TiO_{1.875})_4$ OH have a molar mass of 328.3 and 367.2 g mol⁻¹. The actual specific capacities were then converted by dividing the collected specific capacities with 0.9 (328.2/367.2 \approx 0.9).

For KTO, there is no difference in actual and collected specific capacities since the active material is KTO itself.

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