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Supporting Information

## Stabilization of 4.5 V $Cr^{4+}/Cr^{3+}$ redox reaction in NASICON-type Na<sub>3</sub>Cr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> by Ti substitution

Kosuke Kawai,<sup>†</sup> Daisuke Asakura<sup>1</sup>, Shin-ichi Nishimura,<sup>†,‡,</sup> and Atsuo Yamada<sup>†,‡,\*</sup>

<sup>†</sup>Department of Chemical System Engineering, School of Engineering, The University of Tokyo,

Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

<sup>1</sup>Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and

Technology (AIST), Tsukuba, Ibaraki 305-8564, Japan

<sup>‡</sup>Elemental Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Nishikyo-ku,

Kyoto 615-8510, Japan

\*yamada@chemsys.t.u-tokyo.ac.jp

## **Experimental Details**

**Synthesis.** NCTP powder was synthesized through the classical solid-state method. Stoichiometric amount of  $Cr(OH)_3$  (Japan Pure Chemical Co., Ltd.), TiO<sub>2</sub> (anatase-type, first grade, Wako), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Wako) and NaHCO<sub>3</sub> (Wako) were mixed by planetary ball milling at 400 rpm for 12 hours. This mixture was formed to a pellet and sintered for 12 hours under argon flow three times at 850, 930 and 950 °C with two intermediate grindings. The final product was mixed with 5 wt% acetylene black (Li-400, DENKA) using the same instrument at 200 rpm for 4 hours. It was pelletized and then sintered under argon flow at 800 °C for 8 hours.

**SEM.** Resultant composite of NCTP and acetylene black (NCTP/C) was observed by a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI) with an acceleration voltage of 1 kV.

**Electrochemical Measurement.** For fabrication of working electrode, 80 wt% NCTP/C, additional 10 wt% acetylene black and 10 wt% poly(vinylidene difluoride) (KUREHA) were mixed in N-methyl pyrrolidone (Kanto Chemical Co., Inc., min. 99.0 %) overnight, and the slurry was spread on an Al foil as a current collector followed by drying at 65 °C overnight. 2032-type coin cells were assembled under an argon-filled grove box. Counter electrode was Na metal (Wako). Electrolyte was 1 M NaPF<sub>6</sub> PC (battery grade, Kishida Chemical). Separator was glass fibers (GB-100R, Advantec) dried at 180 °C under vacuum condition overnight. Galvanostatic charge/discharge measurements were performed by a potentiogalvanostat, TOSCAT (TOYO corporation). For *ex situ* analysis, cells were disassembled in the same grove box and collected electrodes were rinsed by dimethyl carbonate three times and dried there.

**XRD Analysis.** Powder X-ray diffraction (XRD) patterns were collected at the beamline 8B in Photon Factory (PF), High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The wavelength was calibrated to be 1.237088 Å by a standard reference material, Si (SRM640d. NIST). Borosilicate glass capillaries (Hilgenberg GmbH or Müller GmbH) were used as sample holders. The data were analyzed by Rietveld refinement program, Z-Rietveld (KEK).<sup>1</sup> The crystal structure was drawn by VESTA.<sup>2</sup>

For electrochemical *in situ* XRD measurement, we employed a two-axis powder diffractometer (Bruker-AXS D8 ADVANCE) in the Bragg-Brentano geometry equipped with a Co  $K\alpha$  radiation source (35 kV, 40 mA), a Fe foil as a  $K\beta$  filter, and a linear position-sensitive detector LYNX-EYE (Bruker-AXS). A modified Swagelok-type cell which has a beryllium X-ray window was used.<sup>3</sup> The *in situ* cell was operated by a potentiogalvanostat, VMP3 (Bio Logic). Working electrode for the *in situ* XRD was fabricated by forming a mixture of 90 wt% NCTP/C, additional 5 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) to be a circular sheet with a diameter of 12 mm.

**X-ray Absorption Spectroscopy.** *Ex situ* soft X-ray absorption spectroscopy (XAS) were conducted at BL-7A of the Photon Factory, KEK. Electrodes were attached with carbon tapes on the sample holders in an Ar-filled glovebox and were transferred to a vacuum chamber using a transfer vessel without air exposure. Bulk-sensitive partial-fluorescence-yield (PFY) mode was adopted for O *K*-edge and Ti  $L_{2,3}$ -edge and inverse PFY (IPFY) mode for Cr  $L_{2,3}$ -edge XAS. IPFY spectra were calculated from inverse of integrated O *K*-edge emission and free from self-absorption and saturation effects.<sup>4-6</sup> Surface-sensitive total-electron-yield (TEY) mode was also employed. Simulation of Cr and Ti  $L_{2,3}$ -edge XAS was performed in the charge-transfer multiplet (CTM) approach with the CTM4XAS program based on Cowan code.<sup>7</sup> This method uses some adjustable parameters to imitate the ground and excited states of transition metals surrounded by ligands representing orbital interactions empirically.

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Fig. S1 Secondary electron micrograph of the as synthesized NCTP/C powder.



**Fig. S2** Galvanostatic charge-discharge curves of NCTP/C electrode in Na half-cell at a rate of 0.1 C between 1.5 and 4.7 V vs. Na/Na<sup>+</sup>.



**Fig. S3** *Ex situ* Cr  $L_{2,3}$ -edge absorption spectra of NCTP/C electrode at pristine, 1st full-charged and full-discharged states obtained in surface-sensitive total electron yield (TEY) mode. Enlarged view in the excitation photon energy range between 575 and 584 eV are shown on the right side.



**Fig. S4** *Ex situ* O *K*-edge absorption spectra of NCTP/C electrode at pristine, 1st full-charged and full-discharged states obtained in surface-sensitive partial fluorescence yield (PFY) mode.



**Fig. S5** *Ex situ* Ti  $L_{2,3}$ -edge absorption spectra of NCTP/C electrode at pristine, 1st full-charged and full-discharged states obtained in (a) bulk-sensitive partial fluorescence yield (PFY) and (b) surface-sensitive total electron yield (TEY) mode.



**Fig. S6** Experimental Ti  $L_{2,3}$ -edge X-ray absorption spectrum of pristine NCTP/C electrode (solid black line) and calculated one for Ti<sup>4+</sup> in  $O_h$  symmetry (red dashed line). Parameters used for these simulations are listed in Table S5.



**Fig. S7** The comparison of the calculated spectrum for  $Cr^{4+}$  in  $O_h$  symmetry with the original Cr  $L_{2,3}$ -edge X-ray absorption spectrum of 1st full-charged NCTP and the difference spectra obtained by subtracting the 0.3- or 0.5-multipled spectrum of 1st full-discharged NCTP from the original one of 1st full-charged NCTP.

Table S1. Structural	l parameters from Rietveld refinement of synchr	otron powder X-ray diffraction
for pristine NCTP/C	C electrode.	

Chemical formula : Na <sub>2</sub> CrTi(PO <sub>4</sub> ) <sub>3</sub>							
Space group : R	3 <i>c</i> , Formula weight	z = 430.7567, Z = 6					
<i>a</i> = 8.56002(5) Å	A, c = 21.7267(3)  Å,	V = 1378.71 Å <sup>3</sup>					
$R_{\rm Bragg} = 3.57 \%,$	$R_{\rm wp} = 2.08 \%, R_{\rm p} =$	1.51 %, $R_{wp}/R_e = 1$	1.53				
Atomic coordinate	ates						
Atom	Wyckoff site	x	У	z	Occupancy	$B_{ m eq}~or~B_{ m iso}$ / ${ m \AA}^2$	
Na(1)	6 <i>b</i>	0	0	0	1	4.57(13)	
Na(2)	18e	0.6329(7)	0	0.25	0.33	3.23(3)	
Cr	12 <i>c</i>	0	0	0.14573(4)	0.5	0.28(3)	
Ti	12 <i>c</i>	0	0	0.14573(4)	0.5	0.28(3)	
Р	18 <i>e</i>	0.28821(14)	0	0.25	1	0.59(3)	
<b>O</b> (1)	36 <i>f</i>	0.1763(3)	-0.0259(3)	0.19380(9)	1	1.13(5)	
O(2)	36 <i>f</i>	0.3066(2)	0.8304(2)	0.25589(9)	1	0.35(5)	
Site	U <sub>11</sub> / Å	U22 / Å	U <sub>33</sub> / Å	$U_{12}$ / Å	U <sub>13</sub> / Å	U <sub>23</sub> / Å	
Na(1)	0.079(2)	0.079(2)	0.016(2)	0.0394(12)	0	0	
Na(2)	0.025(5)	0.027(5)	0.071(6)	0.014(3)	0.0102(19)	0.020(4)	

**Table S2**. Structural parameters from Rietveld refinement of synchrotron powder X-ray diffraction

 for 2nd full-charged NCTP/C electrode.

Chemical formula : NaCrTi(PO <sub>4</sub> ) <sub>3</sub>							
Space group : R	3 <i>c</i> , Formula weight	z = 407.7670, Z = 6					
a = 8.42637(6) Å	Å, <i>c</i> = 21.6801(3) Å,	V = 1333.13 Å <sup>3</sup>					
$R_{\rm Bragg} = 3.84 \%,$	$R_{\rm wp} = 2.08 \%, R_{\rm p} =$	1.49 %, $R_{\rm wp}/R_{\rm e} = 1$	1.53				
Atomic coordin	ates						
Atom	Wyckoff site	x	у	z	Occupancy	$B_{ m eq} \ or \ B_{ m iso}$ / ${ m \AA}^2$	
Na	6 <i>b</i>	0	0	0	1	2.07(8)	
Cr	12 <i>c</i>	0	0	0.14500(4)	0.5	0.32(3)	
Ti	12 <i>c</i>	0	0	0.14500(4)	0.5	0.32(3)	
Р	18 <i>e</i>	0.28618(15)	0	0.25	1	0.89(4)	
<b>O</b> (1)	36 <i>f</i>	0.1724(2)	-0.0266(3)	0.19212(10)	1	0.96(4)	
O(2)	36 <i>f</i>	0.3063(3)	0.8304(2)	0.25527(10)	1	0.96(4)	
Site	<i>U</i> <sub>11</sub> / Å	$U_{22}$ / Å	U <sub>33</sub> / Å	$U_{12}$ / Å	$U_{13}$ / Å	$U_{23}$ / Å	
Na	0.0366(16)	0.0366(16)	0.005(2)	0.0183(8)	0	0	

	$Na_2CrTi(PO_4)_3$	$NaCrTi(PO_4)_3$	Difference
Unit cell volume / Å <sup>3</sup>	1378.71	1333.13	-45.58 (-3.306 %)
Average <i>TM</i> -O bond length / Å	1.949(2)	1.909(2)	-0.040
Quadratic elongation of [ <i>TM</i> O <sub>6</sub> ] octahedron	1.0031	1.0035	0.0004
Bond angle variance of [ <i>TM</i> O <sub>6</sub> ] octahedron / deg. <sup>2</sup>	10.8464	11.6036	0.7572
Effective coordination number of [ <i>TM</i> O <sub>6</sub> ] octahedron	5.9921	5.9423	-0.0498

**Table S3** Change of structural parameters obtained from Rietveld refinement. (TM = Cr or Ti)Relative difference of unit cell volume was defined as  $\Delta V = (V_{2nd charged} - V_{pristine})/V_{pristine}$ .

**Table S4**. Electronic structure parameters used for the CTM calculations in Figure 5. 10Dq,  $\Delta$ , U and Q are crystal field splitting, charge-transfer energy, intra-atomic coulombic interaction for d electron and core-hole potential, respectively. Spin-orbital coupling was reduced to 97 % for only  $Cr^{4+}$ .

	Symmetry	10 <i>Dq</i> / eV	⊿ / eV	U/eV	<i>Q</i> / eV
Cr <sup>3+</sup>	$O_h$	1.0	1.0	5.0	6.0
Cr <sup>4+</sup>	$O_h$	1.6	0.5	5.0	6.0

**Table S5**. Electronic structure parameters used for the CTM calculations in Figure S7. 10Dq,  $\Delta$ , U and Q are crystal field splitting, charge-transfer energy, intra-atomic coulombic interaction for d electron and core-hole potential, respectively. Spin-orbital coupling was reduced to 94 %.

	Symmetry	10 <i>Dq</i> / eV	⊿ / eV	U / eV	<i>Q</i> / eV
Ti <sup>4+</sup>	$O_h$	1.9	3.0	5.0	6.0