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Electronic Supplementary Information

Understanding $Na_2Ti_3O_7$ as an ultra-low voltage anode material for Na-ion battery

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Experimental Details

Material Synthesis and Characterization: Pure $Na_2Ti_3O_7$ was prepared from anatase TiO_2 (>99.8%, Aldrich) and anhydrous Na_2CO_3 (>99.995%, Aldrich) mixtures with 10% excess of the latter based on stoichiometric amounts. These mixtures were milled and calcinated at 800℃ for 40h. The carbon coating was applied according to previous report:[1] $Na_2Ti_3O_7$ particles was dispersed in distilled water and ethanol solution, and mixed with sucrose solution. Then, a heat treatment at 600℃ was conducted after drying. The as-synthesized materials were characterized by a Philips XL30 environmental scanning electron microscope (ESEM) operating at 10 kV, and an FEI Tecnai G2 Sphera transmission electron microscopy (TEM) operating at 200 kV. XRD patterns were collected at ambient temperature on a Bruker D8 Advance diffractometer, using a LynxEye detector at 40 kV and 40 mA. Cu-anode ($K\alpha$, $\lambda = 1.5418$ Å) was used, with a scan speed 60 of 1 s/step, a step size of 0.02° in 2θ, and a 2θ range of 10−70°. XRD data analysis was carried out by utilizing Rietveld refinement using the FullProf software package. X-ray absorption spectroscopy measurements were performed at 20-BM-B beamline of Applied Photon Source (APS) at Argonne National Laboratory. Customized coin cells were used to prevent the sample contamination. Measurements at the Ti K-edge were performed under transmission mode using gas ionization chamber to monitor the incident and transmitted X-ray intensities. A third ionization chamber was used in conjunction with a Ti-foil standard to provide internal calibration for the alignment of the edge positions. The incident beam was monochromatized using a Si (111) double-crystal fixed exit monochromator. Harmonic rejection was accomplished using a rhodium-coated mirror. The reference standard, Ti_2O_3, was prepared by spreading uniform layer of powders on Kapton. Each spectrum was normalized using data processing software package IFEFFIT.[1]

Electrochemical tests: Electrodes were prepared by mixing 70 wt% active material, 10 wt% polyvinylidene fluoride (PVdF), and 20 wt% Super P carbon black. For the electrodes fabricated with bare $Na_2Ti_3O_7$ and carbon coated $Na_2Ti_3O_7$, same amount of external Super P carbon black (20 wt%) were added. A glass fiber GF/F (Whatman) filter was used as separator. 1 M NaPF6 in a 1:1 (v/v) mixture of ethylene carbonate (EC) and diethylene carbonate (DEC) solution was used as electrolyte. For half-cell test, the counter electrode was sodium metal foil (Sigma-Aldrich). For full cell tests, the counter electrode was $Na_{0.80}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$, reported in our previous work.[2] The cathode to anode weight ratio was around 2.36 : 1 in full cell. Both electrodes were directly assembled into the full cell without a pre-cycle with Na metal. All batteries were assembled in an MBraun glovebox (H_2O < 0.1ppm). Galvanostatic discharge and charge at various current densities were performed on an Arbin BT2000 battery cycler. The voltage windows for half cell and full cell were 0.01 - 2.5 V and 2.0 - 4.2 V respectively.

DFT Calculation: Density functional theory (DFT) calculations were performed in the spin-polarized GGA + U approximations to the Density Functional Theory (DFT). Core electron states were represented by the projector augmented-wave method[3] as implemented in the Vienna ab initio simulation package (VASP).[4]

The Perdew-Burke-Ernzerhof exchange correlation[5] and a plane wave representation for the wave function with a cutoff energy of 400 eV were used. The Brillouin zone was sampled with a dense k-points mesh by Gamma packing. The supercell was composed of two formula units of $Na_2Ti_3O_7$. The atomic positions and cell parameters were fully relaxed to obtain total energy and optimized cell structure. The Hubbard U correction was introduced to describe the effect of localized d electrons of transition metal ions. Each transition metal ion has a unique effective U value applied in the rotationally invariant GGA + U approach. The applied effective U value given to Ti-ion was 3 eV, consistent with early work.[6]

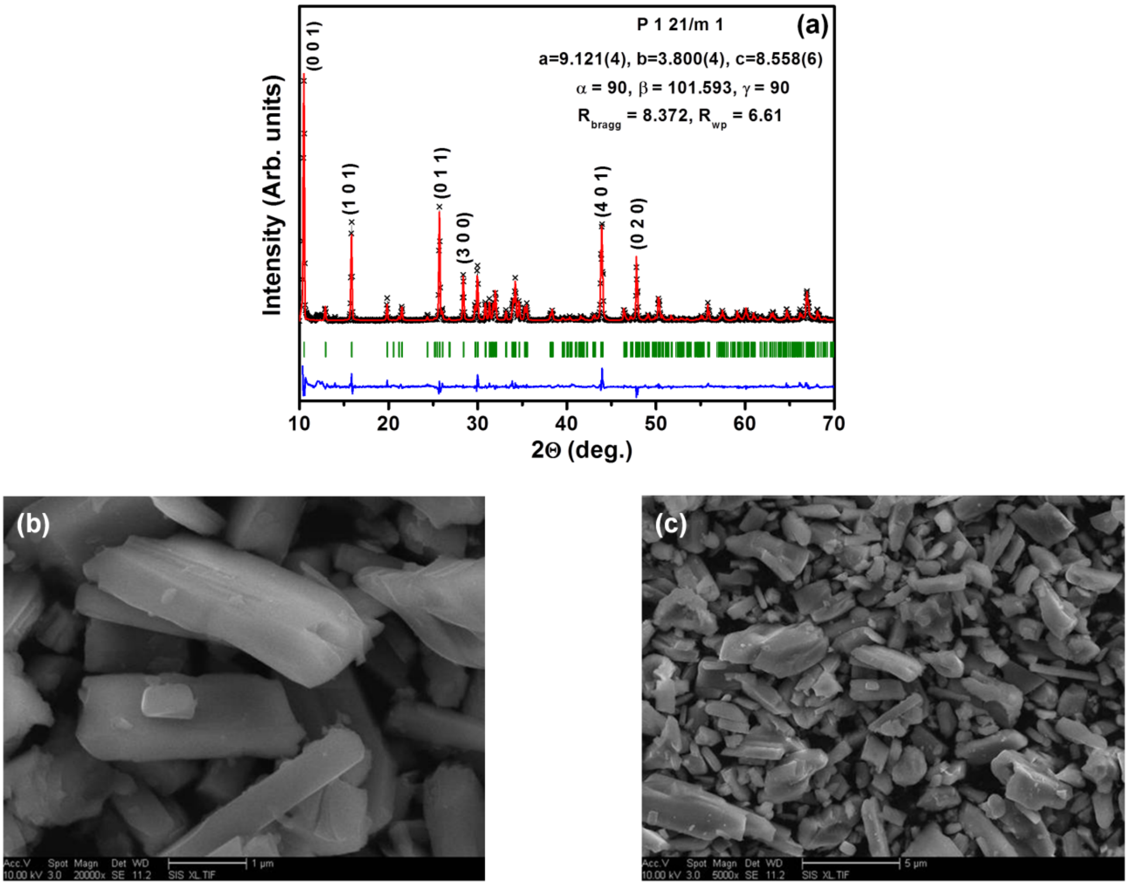

Figure S1. The (a) XRD and (b) (c) SEM images of as-synthesized $Na_2Ti_3O_7$ powder.

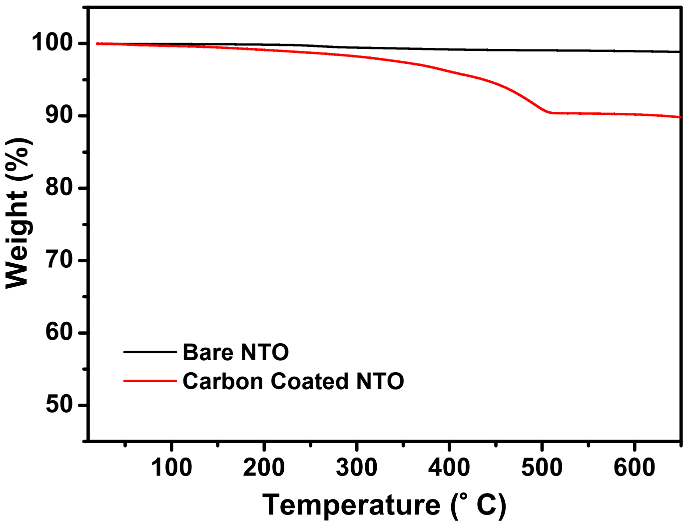

Figure S2. Thermogravimetric analysis for bare (black) and carbon coated (red) $Na_2Ti_3O_7$ powder.

From the TGA curve, the major weight loss from 450 to 600 °Cis due to the removal of coated carbon by the oxidation process, and it can be calculated that the coated material contains 9 % carbon.

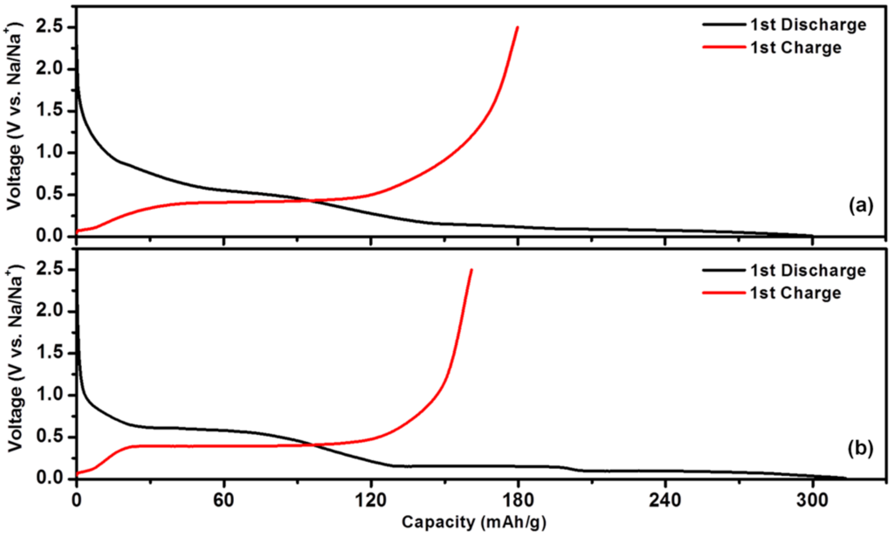

Figure S3. Electrochemical profiles at of (a) carbon-coated and (b) bare $Na_2Ti_3O_7$ at C/25

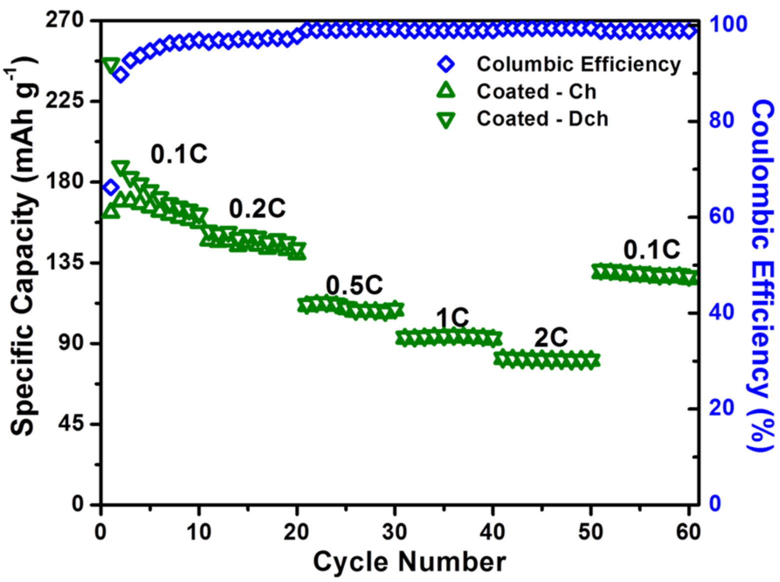

Figure S4. Rate performance of carbon-coated $Na_2Ti_3O_7$ electrode.

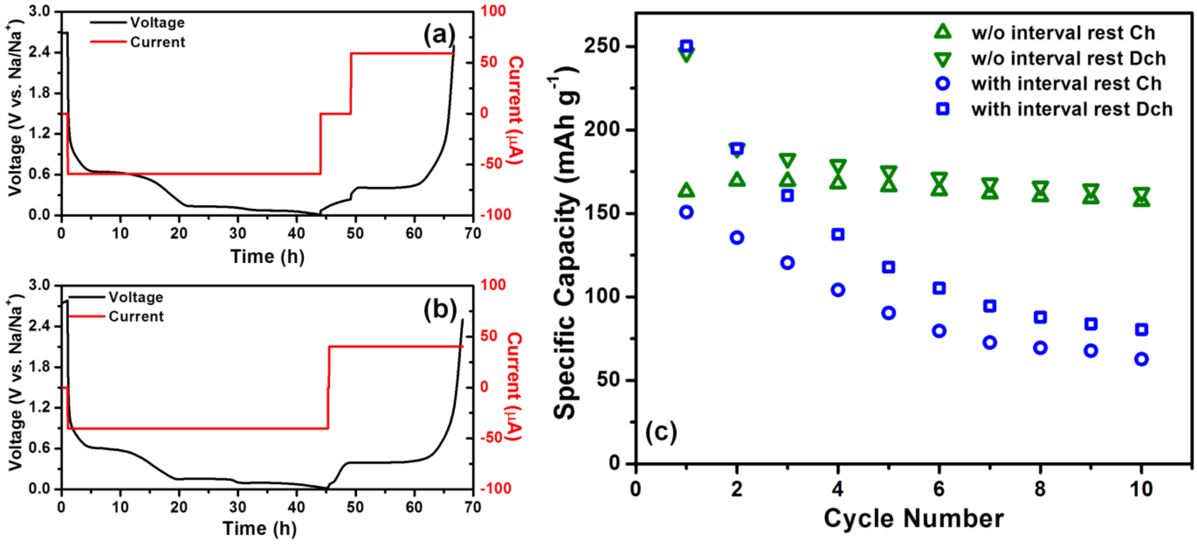

Figure. S5 Voltage profiles for electrodes under cycling (a) with and (b) without interval rest (5 hour between charge and discharge). (c) Cycling performance for cell with (blue) and without (green) interval rest.

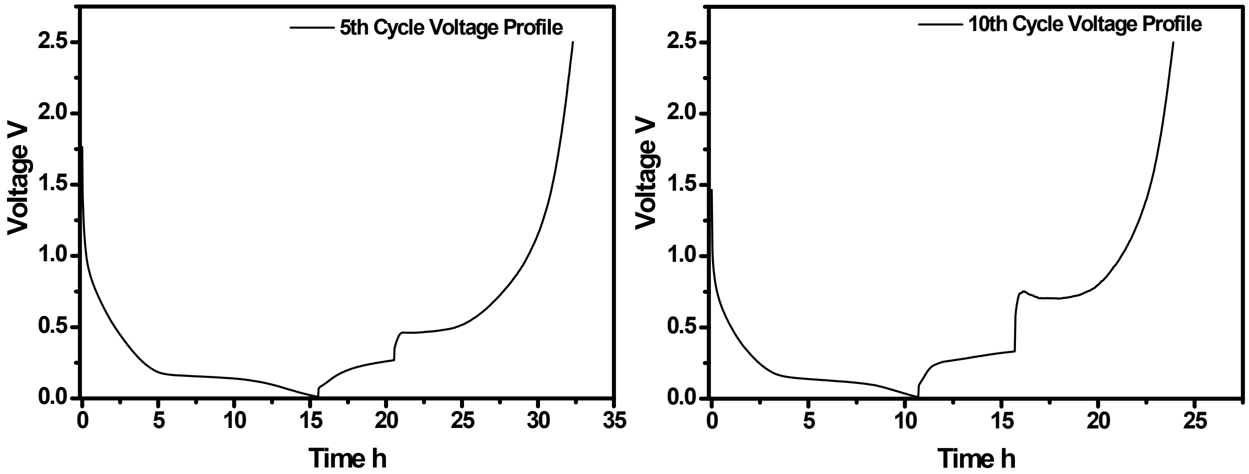

Figure. S6 5th and 10th Voltage profiles for electrodes with interval rest (5 hour between charge and discharge).

Reference

1 B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, 2005, **12**, 537.

2 J. Xu, D. H. Lee, R. J. Clement, X. Q. Yu, M. Leskes, A. J. Pell, G. Pintacuda, X. Q. Yang, C. P. Grey and Y. S. Meng, *Chemistry of Materials*, 2014, **26**, 1260.

3 G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758.

4 G. Kresse and J. Furthmuller, *Computational Materials Science*, 1996, **6**, 15; *Physical Review B*, 1996, **54**, 11169; G. Kresse, J. Furthmuller and J. Hafner, *Physical Review B*, 1994, **50**, 13181.

5 J. P. Perdew, K. Burke and Y. Wang, *Physical Review B*, 1996, **54**, 16533.

6 S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. H. Ma and G. Ceder, *Energy & Environmental Science*, 2011, **4**, 3680; A. I. Liechtenstein, V. I. Anisimov and J. Zaanen, *Physical Review B*, 1995, **52**, R5467; L. Wang, T. Maxisch and G. Ceder, *Physical Review B*, 2006, **73**.