Intercalation $Na_2Ti_3O_7$ Anode for Na-ion Batteries with Ultra Low Voltage

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Rechargeable lithium-ion batteries, used extensively in power sources for potable electronics are now being considered for electric vehicles and smart grid applications. However, high cost and limited availability of lithium would be a possible constraint if they are applied to large scale energy storages. Therefore Na-ion batteries have re-captured the attentions of the scientific communities as an alternative due to the natural abundance and broad distribution of sodium reserve. A study by Palacín et. al.[1] demonstrated that the layered oxide $Na_2Ti_3O_7$ could reversibly exchange Na-ions in the Na cells with the lowest voltage ever reported for oxide insertion electrode.[1] More recently, the same compound was studied by Balaya et. al, and their Na-ion battery exhibited 100 mAh/g of specific capacity with acceptable cycling properties up to 90 cycles.[2] However, the working mechanism for such a low voltage oxide material is still unknown. In addition, the structure of the end member phase after fully discharge is not clearly identified and explained. Considering that the Ti^{3+}/Ti^{4+} redox reaction in $Li_4Ti_5O_{12}$ is happened at 1.5 V[3] in the lithium ion batteries, it is quite intriguing that the same redox demonstrates just 0.3 V voltage plateau in $Na_4Ti_3O_7$ as anode materials in the Na-ion batteries.

In this work, we report our in-depth investigation on $Na_2Ti_3O_7$, as an anode material in Na-ion batteries. Combined work of computational and experimental methods is being conducted to investigate the working mechanisms. Pristine $Na_2Ti_3O_7$ has been synthesized by solid state method, and the crystallinity and phase purity are studied by X-ray diffraction (XRD). Its electrochemical profiles are in a good accordance with the literature[1], as shown in Fig 1 (a). *Ex-situ* X-ray absorption spectroscopy (XAS) has been performed on $Na_2Ti_3O_7$ electrodes to investigate the changes in the oxidation state so as to reveal electronic structural information. According to the normalized X-ray absorption near edge spectroscopy (XANES), which is shown in Fig 1 (b), no obvious Ti K-edge shift was observed for the $Na_2Ti_3O_7$ electrodes at different state of charge. Meanwhile, the first principles calculation results also show that the charge density change due to the reduction of Ti^{4+} to Ti^{3+} is too slight after Na-ions are intercalated into the structure. These results suggest the possibility that oxygen may get involved into the redox reaction, leading to such low voltage plateau. X-ray photoelectron spectroscopy (XPS) as well as first principles calculation is performed to investigate the oxygen changes during the Na-ions intercalation. The electrochemistry is further studied by galvanostatic intermittent titration technique (GITT) method. Detailed mechanism for this low voltage oxide anode is proposed.

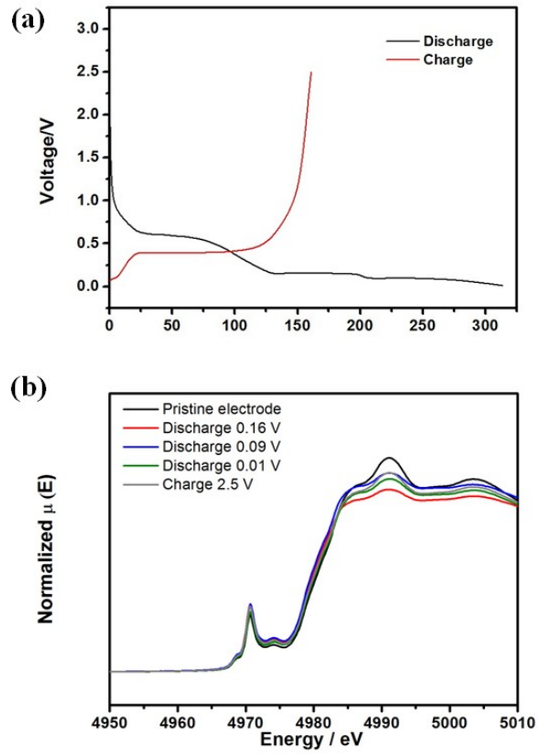

Fig. 1. (a) The electrochemical profile of $Na_4Ti_3O_7$ half cell, using sodium as the anode (b) XANES spectra of Ti K-edge for the $Na_4Ti_3O_7$ electrode electrochemically charged and discharged to certain states.

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