

## Near-dimensionally invariable high-capacity positive electrode material

The development of high-capacity and long-life batteries is a key challenge for attaining a sustainable energy society. Lithium insertion materials are used as electrode materials in lithium-ion batteries. Reversible lithium extraction/re-insertion reactions with topotactic phase transitions have been achieved, coupled with cationic redox reactions of 3d-transition metal ions for these electrode materials [1]. Electrochemical lithium insertion/extraction generally alters the crystal structures of electrode materials, including volume changes, which induce strain. This leads to mechanical fractures, including the formation of cracks inside the particles. The fracture of lithium insertion materials due to mechanical strain results in the loss of electrical contacts in composite electrodes, and thus, a reduction in the reversible capacity during electrochemical cycles. Moreover, the electrode materials cannot be isolated in composite electrodes, which can be difficult to control, especially in the all-solid-state batteries that are currently being developed for advanced battery systems. Therefore, the discovery of materials that can reversibly insert/extract large quantities of charge carriers ( $\text{Li}^+$ ), that is, high capacity, with inherent dimensional stability during cycles is indispensable.

In this study, lithium-excess vanadium oxides with disordered rock salt structures are examined as high-capacity and long-life positive electrode materials. X-ray diffraction data of as-prepared  $\text{Li}_{8/7}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  are shown in Fig. 1(a). The crystal structure of the sample was defined as a typical layered structure (space group;  $R\bar{3}m$ ), which was isostructural with the  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  [2] used for practical lithium-ion batteries. However, the insufficient reversibility of the Li-storage properties in the as-prepared sample was noted; therefore, a nanosized material with a

shorter Li-migration path in the host structures was prepared by mechanical milling. Material synthesis via mechanical milling typically results in the formation of nanosized materials with high symmetry, and cation disordered rock salt oxides (space group;  $Fm\bar{3}m$ ) with low crystallinity can be obtained. In the case of  $\text{Li}_{8/7}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$ , the original layered structure was lost and a nanosized rock salt oxide with low crystallinity (<10 nm) was obtained after milling, as shown in Fig. 1(a). The nanosized sample showed a large reversible capacity of  $300 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  at room temperature (Fig. 1(b)) and delivered good capacity retention for the initial 20 cycles. However, an abrupt degradation in capacity retention was observed after 30 cycles (Fig. 1(c)) when 1 M  $\text{LiPF}_6$  in ethylene carbonate and dimethyl carbonate (EC/DMC), a conventional electrolyte used for practical battery applications, was used as the electrolyte. In contrast, excellent capacity retention was attained using a concentrated electrolyte solution of lithium bis(fluorosulfonyl)amide (LiFSA) and dimethyl carbonate (DMC), LiFSA:DMC = 1:1.1 in molar ratio [3]. Additionally, a reversible capacity of  $>260 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$  was achieved after the 100-cycle test at  $30 \text{ mA}\cdot\text{g}^{-1}$ , as shown in Figs. 1(b,c). The improved capacity retention with a concentrated electrolyte solution originated from the suppression of vanadium dissolution and deterioration of the metallic lithium electrode [4].

To further study the reaction mechanisms of nanosized  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$ , the structural changes during the electrochemical cycles were examined using *in situ* XRD studies. *In situ* XRD data and changes in the 200 peak profiles are shown in Fig. 2. Although the peak height systematically decreased with charging, the peak position remained invariable during electrochemical cycling.

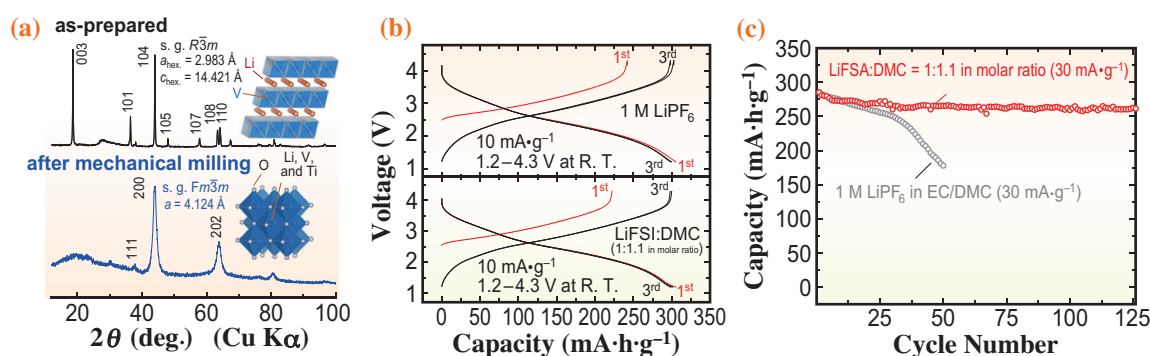


Fig.1. (a) XRD patterns of as-prepared and nanosized  $\text{Li}_{8/7}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$ . (b,c) Electrode performance of nanosized  $\text{Li}_{8/7}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  in different electrolyte solutions.

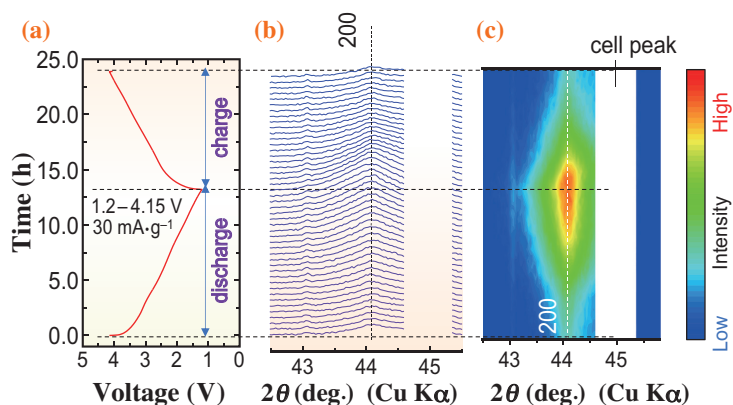


Fig. 2. (a) Charge/discharge curves of nanosized  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  during *in situ* XRD measurement, (b) corresponding *in situ* XRD patterns for the 200 diffraction lines, and (c) a contour plot of XRD patterns.

Bulk and local structural changes in the nanosized  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  during electrochemical cycling were also studied using high-energy X-ray total scattering (Fig. 3). The findings can be summarized as follows: (1) reversible V migration between octahedral and tetrahedral sites with cycling and (2) partial formation of the amorphous phase upon charging. Although V ions migrated into neighboring face-shared tetrahedral sites upon charging, these processes were reversible, and destruction of the phase was not observed [4].

In general, the unit cell volume of Li-insertion materials decreased upon charging because of the oxidation of transition-metal ions coupled with an increase in effective nuclear charge. The enrichment of vacant sites (an increase in free volume) also resulted in lattice contraction. However, the migration of cations, as observed in Fig. 3, strongly influenced the volume-change trend. The migration of V ions

into smaller tetrahedral sites inevitably increased the repulsive interactions between V and O ions, resulting in the expansion of the crystal lattice. Such an expansion of the lattice would be partially canceled out by the volume decrease associated with the increase in the free volume by Li extraction as two competing factors. When shrinkage and expansion were well balanced, dimensional stability was retained, leading to a near-dimensionally invariable character, as observed in  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$ . Furthermore, highly reversible Li storage for  $\text{Li}_{8/7}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  with no capacity fading over 400 cycles was achieved using a sulfide-based solid electrolyte [4]. This study demonstrates an example of an electrode/electrolyte couple that produces high-capacity and long-life batteries, including operation with solid electrolytes, associated with a unique structural phase transition, that is, invariant volume change during cycling.

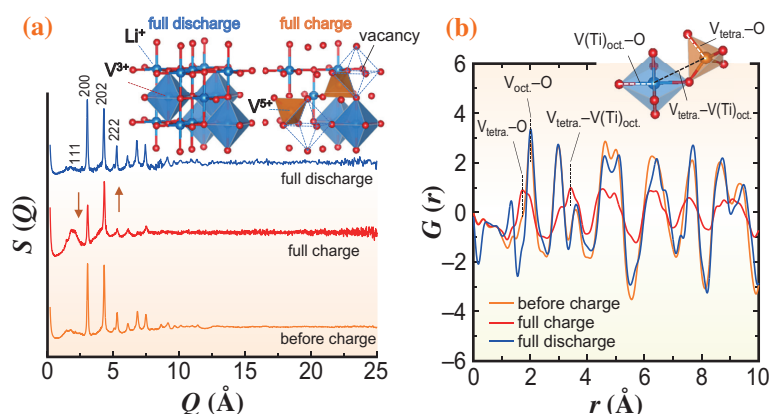


Fig. 3. (a) Structure factors of nanosized  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  with different charging conditions using high-energy X-ray ( $E = 61.4$  keV) at room temperature, from which (b) X-ray pair distribution functions were obtained. Schematic illustrations of crystal structures for charged and discharged  $\text{Li}_{8/7-x}\text{Ti}_{2/7}\text{V}_{4/7}\text{O}_2$  are also shown. The synchrotron radiation experiments were performed at SPring-8 BL04B2.

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## References

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