Hydrogenation effects on the lithium ion battery performance of TiOF_2

Min He^{a,b}, Zhihui Wang^c, Xiaodong Yan^a, Lihong Tian^{a,d}, Gao Liu^{c*} and Xiaobo

Chen^{a*}

*a. Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO
64110, USA*

*b. Department of Applied Physical, College of Science, Wuhan University of Science
& Technology, Wuhan, Hubei 430065, China*

*c. Advanced Energy Technologies Department, Lawrence Berkeley National
Laboratory, Berkeley, CA 94720, USA*

*d. Hubei Collaborative Innovation Center for Advanced Organochemical Materials,
Hubei University, Wuhan, 430062, China*

Corresponding authors.

E-mail address: Chenxiaobo@umkc.edu (X. Chen), Tel.: +1 510 486 7202;

GLiu@lbl.gov (G. Liu), Tel.: +1 816 235 6420.

Abstract

Hydrogenated titanium oxyfluorides (TiOF_2) nanoparticles were synthesized via one-pot hydrothermal method and subsequent hydrogenation treatment. As anode materials for lithium ion batteries, the hydrogenated TiOF_2 showed a superior rate performance compared to the pristine TiOF_2 . A charge capacity of $118.4 \text{ mA h g}^{-1}$ was achieved at the current density of 1053 mA g^{-1} upon 150 cycles, which was 4 times higher than that of the pristine TiOF_2 . The rate performance of the hydrogenated TiOF_2 at different current density of 42, 210, 1053, 2106, 5265, 10530, 21060 and 52650 mA g^{-1} was 2.8, 6.0, 13.2, 14.7, 21.5, 30.6, 67.9 and 483.3 times higher than those of the pristine TiOF_2 electrode at the corresponding rates, respectively. The remarkable improvement of the electrochemical performance was likely related to the size breakdown in the (001) direction after hydrogenation, instead of oxygen vacancies induced better charge transfer properties.

Keywords: titanium oxyfluorides; hydrogenation; rate performance; lithium ion battery

1. Introduction

Lithium ion batteries (LIBs) have become an essential part of various portable electronic devices such as mobile phones, laptops, digital cameras and e-bikes, and also been considered as a potential power source for electric vehicles (EVs) and hybrid electric vehicles (HEVs) due to their high specific energy, good cycle-ability and safety. The growing demands of LIBs have encouraged great efforts to develop a cheap and high-performance electrode material ^[1-2]. Recently, titanium oxide has attracted extensive attention as an anode material for LIBs due to its low cost, good stability, low toxicity and low volume expansion compared to other transition-metal oxides ^[3-4]. However, the low electrical conductivity ($\sim 10^{-13}$ S cm⁻¹) of TiO₂ leads to a poor rate performance with a limited capacity, hindering its large-scale application ^[5-6]. Therefore, it is imperative to develop better anode materials for LIBs.

Some recent studies suggested that titanium oxyfluorides (TiOF₂) was a promising material for LIBs due to its higher theoretical specific capacity (1053 mAh g⁻¹) and lower polarization than titanium oxides ^[7]. TiOF₂ is an air stable compound and can be easily obtained by hydrolysis of titanium tetrafluoride. TiOF₂ possesses a cubic ReO₃-type structure (space group *Pm $\bar{3}$ m*, perovskite structure) at room temperature based from the corner sharing TiO₂F₄ octahedra with random distribution of O and F anions. Since the 12-fold O-coordinated site is empty and can accommodate other ions, thus, lithium ions could be inserted into the vacant octahedral sites ^[8, 9]. It was proved that TiOF₂ could be chemically or electrochemically lithiated using *n*-butyl lithium (*n*-BuLi) ^[10-12]. Recent researches

also showed that voltage window and synthesis method had an important influence on lithium storage capacity and mechanism. For example, Chowdari et al synthesized crystalline TiOF_2 by using Ti metal powder and a 1:1 mixture of HF and HNO_3 . They found that the crystal structure of TiOF_2 was destroyed during the first discharge reaction at voltage lower than 1 V in a TiOF_2/Li half-cell system ^[12]. TiOF_2 gave a capacity of $\sim 400 \text{ mAh g}^{-1}$ without noticeable capacity fading in a voltage window of 0.005-3.0 V at a current density of 65 mA g^{-1} during 5-100 cycles ^[12]. Dambournet et al found that the titanium-based anion nanocomposites demonstrated dual lithium insertion and conversion mechanisms between 0.05 and 3 V ^[13]. Louvain et al synthesized TiOF_2 by gas–solid fluorination of TiO_2 anatase nanocrystals, and a capacity of 220 mA h g^{-1} was achieved at the current density of 2.63 mA g^{-1} at the voltage ranges of 1.2-3.8 V ^[14]. Yan's et al synthesized single-crystalline TiOF_2 nanotubes via hydrothermal method, which showed a capacity of 391 mAh g^{-1} after 60 cycles at a current density of 400 mA g^{-1} within a charge-discharge range of 0.001-3 V ^[15]. Myung et al produced TiOF_2 by a reaction of TiO_2 and hydrofluoric acid. The synthesized TiOF_2 delivered a charge capacity of 526 mA h g^{-1} between 0.01 and 3 V versus Li ^[16]. In spite of these progresses, the electrochemical performance of TiOF_2 is still unsatisfying. Novel approaches are urgent to improve its cyclability and rate performance.

Very recently, hydrogenation has been attracting great interests in improving the electrochemical performance of anode materials ^[17-20]. Hydrogenation can change the arrangement of the atoms, form oxygen vacancies on the surface, and lead to

surface-disordered structure^[17, 21-23]. The surface-disordered layer is beneficial to the charge transfer and lithium ion transport, resulting in a significant improvement in capacity, cyclability and rate performance^[18, 21-22]. Meanwhile, hydrogenation can also reduce the particle size and increase interface area, triggering the enhancement of the electrochemical reactions and reactivity^[24-25]. Herein, we first reported TiOF₂ treated by hydrogenation and its performance as anode material for LIBs. Compared with the pristine TiOF₂, the hydrogenated TiOF₂ with small particle size, surface-disordered structure and oxygen deficiency, was more favorable to quicken lithium ion transport and facilitate electronic transfer. Accordingly, remarkably enhanced lithium storage capacity, cyclability and rate performance were achieved.

2. Experimental

2.1 Synthesis of hydrogenated TiOF₂

Hydrogenated TiOF₂ was fabricated by a modified one-pot hydrothermal method^[26-28] and subsequent hydrogenation treatment. Typically, Titanium butoxide (Ti(OC₄H₉)₄, 5 mL) and hydrofluoric acid solution (0.6 mL, 48 wt %) were mixed in a Teflon-lined stainless steel autoclave and then kept at 200 °C for about 24 h. After cooling down naturally, the obtained precipitates were centrifuged, washed with deionized water and ethanol several times, and finally dried at 80 °C overnight. For hydrogenation, the as-prepared products were calcinated at 250 °C for 3 h under flowing hydrogen. The sample was denoted as H-TiOF₂. For comparison, the hydrothermal products were also treated in a furnace at 250 °C for 3 h under flowing

air, signed to be TiOF_2 .

2.2 Materials characterization

The X-ray diffraction patterns were checked using a Panalytical X'pert Pro diffractometer with high intensity $\text{Cu K}\alpha$ irradiation. Transmission electron microscopy (TEM) observations were carried out on a Philips CM 200 microscopy. Raman spectra was recorded using EZRaman-N Raman spectrometer equipped with a 300 mW diode laser (Enwave Optronics, Inc.) and the excitation wavelength was 785 nm. The FTIR spectra were collected using a Thermo-Nicolet iS10 FT-IR spectrometer with an attenuated total reflectance unit. The X-ray photoelectron spectra were measured on a PHI Versaprobe 5000 Scanning X-Ray Photoelectron Spectrometer (XPS). The samples were pasted on a conductive carbon tape. The electrical conductivity was measured with a Biologic potentiostat/electrochemical impedance spectroscopy instrument. The samples were pressed into small disks with diameter of 10.0 mm, and thickness of 1.0 mm. The pellets were sandwiched between two stainless steel disks for the conductivity measurements. The Mott-Schottky plots were collected with a scan rate of 10 mV/s in 0.5 M H_2SO_4 electrolyte at a frequency of 10 kHz in a typical three-electrode system with Pt and Ag/AgCl electrodes as the counter and reference electrodes, respectively ^[29,30]. The electrochemically active surface areas (ECSAs) of the catalysts were estimated from the double layer capacitance (C_{dl}), as C_{dl} was linearly proportional to the effective active surface area. The linear slope of the capacitive current against scan rate was used to represent the ECSA. The C_{dl} was measured using a simple cyclic voltammetry method. The voltage

window of cyclic voltammograms was 0.2 – 0.3 V vs Ag/AgCl. The scan rates were 10, 20, 40, 60, and 80 mV s⁻¹ in 1.0 M H₂SO₄. C_{dl} was estimated by plotting the Δj ($j_a - j_c$) at 0.25 V vs Ag/AgCl against the scan rate, where the slope was twice as the C_{dl} [29].

2.3 Coin cell preparation and electrochemical measurement

The standard 2325 coin cells were assembled in an argon-filled glove box where moisture and oxygen concentrations were strictly limited to below 1 ppm. The working electrode was fabricated by 82 wt% active materials, 8 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF). The mixture was well dispersed in N-methylpyrrolidone (NMP) using a Polytron PT10-35 homogenizer at 2700 rpm for 30 min, and then the slurry was cast on a battery-grade copper foil using a doctor blade. After being dried overnight in an oven, the electrodes were cut into 12.7 mm-diameter discs and dried again before being assembled into cell. Lithium foil was used as the counter electrode, a Celgard 2400 membrane was used as the separator and 1 M lithium hexafluorophosphate (LiPF₆) in ethylenecarbonate (EC): diethylcarbonate (DEC) (1:2 weight ratio) was used as the electrolyte.

Cells were tested between 1.0 and 3.0 V (vs. Li/Li⁺) using a Maccor battery cycler at 30 °C. The first discharge and charge cycle were tested at a current density of 42 mA g⁻¹ (where C was calculated from a specific capacity value of 1053 mAh g⁻¹), and the second one was at a current density of 210 mA g⁻¹. Then the cell were cycled at a current density of 1053 mA g⁻¹. For the rate performance test, the charge and discharge rates were changed symmetrically.

3. Results and discussions

The phase and crystallinity of pristine and hydrogenated TiOF₂ were tested by power XRD. As shown in Fig. 1a, the strong diffraction peaks indicated high crystallinity and could be identified to be cubic TiOF₂ (JCPDS No. 77-0132, Pm-3m, a=b=c=3.780 Å). No impurity was found in both pristine and hydrogenated TiOF₂. The average crystalline size of the pristine TiOF₂ and hydrogenated TiOF₂ were evaluated using the Scherrer formula: $\tau = k\lambda/(\beta \cos\theta)$, where τ, k, λ, β and θ are the mean size of the ordered (crystalline) domains, the shape factor with a typical value of 0.9, the X-ray wavelength (0.15418 nm for Cu-K α), the line broadening full width at half maximum (FWHM) of the diffraction peak height in radians, and the Bragg diffraction angle, respectively [31]. The crystalline size of the original TiOF₂ is 39.4, 34.9, 29.6, 28.6 and 23.6 nm along (100), (110), (200), (210) and (211) direction, respectively, while the size of crystalline phase of H-TiOF₂ change into 35.9, 33.6, 31.2, 31.9 and 27.9 nm along the corresponding directions. This suggested that the size of crystalline phase of hydrogenated TiOF₂ shrunk 8.88% (3.5 nm) and 3.72% (1.3 nm) along (100) and (110). However, a slightly increase in (200), (210) and (211) directions was observed.

In order to further reveal the structural evolution and surface functional groups in the TiOF₂ nanocrystals during hydrogenation process, Raman spectra of the original TiOF₂ and hydrogenated TiOF₂ were collected. For TiOF₂, there were five active bands with wavenumber at 248 (B_{1g}), 394 (B_{1g}), 530, 634 (E_g), 760 cm⁻¹, respectively (Fig. 1b), which corresponded to the typical Raman spectra of TiOF₂

except a slight shift ($\sim 14\text{ cm}^{-1}$) toward higher wavenumber of some peaks ^[22, 28]. Interestingly, two frequency bands at 248 and 760 cm^{-1} were observed, which were also detected in another study ^[32]. After hydrogenation, these active bands disappeared, which indicated oxygen deficiency and the appearance of some disorder by the hydrogen treatment ^[17, 21, 33].

Morphologies and microstructure of original TiOF_2 and hydrogenated TiOF_2 were checked by TEM characterization. Fig. 2a-2c displayed a typical TEM image of TiOF_2 nanocubes with a size of $300\text{-}500\text{ nm}$. HRTEM analyses (Fig. 2c) showed the distinct lattice fringes, indicating good crystallinity. However, after hydrogenation, the morphology of TiOF_2 were greatly changed from cube to nanosheets with smaller thickness (Fig. 2d and 2e). These TiOF_2 nanosheets were similar in morphology to the TiO_2 nanosheets formed in the preparation of the large TiOF_2 cubes ^[26-28]. HRTEM image in Fig. 2f showed some amorphous phase in the hydrogenated TiOF_2 , these amorphous phase is favorable to transport of ion. Meanwhile, it showed layered structures of smaller nanosheets. The layered structure was very similar to the TiOF_2 cubes formed due to the (001) stacking of the TiO_2 nanosheets during the hydrothermal synthesis ^[28]. Thus, it seemed that during the hydrogenation reaction, large TiOF_2 cubes reconstructed into smaller TiOF_2 nanosheets which were stacked with (001)-faceted TiOF_2 nanosheets. (001)-faceted TiO_2 has shown better lithium ion battery performance than spherical TiO_2 nanoparticles due to preferential charge transfer across the (001) facet ^[34]. Thus, it is expected that hydrogenated TiOF_2 will have similar enhancement.

Fig. 3a and 3b demonstrated the charge-discharge curves of the original TiOF₂ and hydrogenated TiOF₂ at different cycles. It can be seen that there was a substantial difference between the first cycle and subsequent cycles. The original TiOF₂ electrode displayed two distinct voltage plateaus at about 1.8 and 2.6 V in the initial discharge process, corresponding to a chemical lithiation process [13, 16, 35]. After the second cycle, the charge/discharge voltage plateaus located at 1.9/1.7-1.8V. The Li ion intercalation/deintercalation reaction in TiOF₂-Li system was similar to that of TiO₂-Li system, which followed a reversible reaction: $\text{TiO}_2 + x\text{Li} + x\text{e}^- \rightarrow \text{Li}_x\text{TiO}_2$, indicating the good lithium insertion/desertion and the good reversibility of the Li-TiOF₂ system [7, 12]. Interestingly, the hydrogenated TiOF₂ electrode displayed an additional lithium insertion plateau at about 1.2 V (Fig. 3b), which meant lithium ions might insert into cubic/rhombohedral phase boundary and induced the transition between cubic and rhombohedral for ReO₃ phase due to the decrease of particle size and the increase of amorphous phase after hydrogenation [13, 21, 35]. Meanwhile, the potential difference of the hydrogenated TiOF₂ electrode was smaller than that of the original TiOF₂ electrode between the charge and discharge cycles, which implied smaller charge transfer resistance and faster lithium ion transport after hydrogenation treatment. Recent researches indicated that interface lithium storage might occur according to the slope of the discharge curves, which enhanced capacity and rate performance [21, 35].

Indeed, it can be observed from Fig. 3a–d that the charge-discharge capacity, cycle stability and columbic efficiency of hydrogenated TiOF₂ showed obvious

improvement compared with those of the original TiOF₂. In detail, the original TiOF₂ delivered the initial charge and discharge capacities of 101.8 and 145.3 mA h g⁻¹ at a current density of 42 mA g⁻¹, respectively, corresponding to an initial coulombic efficiency of 53.0%. The initial capacity loss might result from irreversible lithium insertion due to possible phase transition. The charge capacity and coulombic efficiency for the original TiOF₂ maintained 39.1 mA h g⁻¹ and 56.7% at the second cycle at a current density of 210 mA g⁻¹, and around 22 mA h g⁻¹ and above 75% after the third cycle at a current density of 1053 mA g⁻¹, then the capacity kept slight increase and reached 29.8 mA h g⁻¹ after 150 cycles from Fig. 3c. The specific capacity reduced with increase of current density that indicated the kinetics was limited by slow electronic and ion diffusion. Compared to the large theoretical capacity of TiOF₂, the small capacity obtained here could be related to the poor usage of the actual TiOF₂ volume during charge/discharge process due to the limited diffusion length within certain charge/discharge time, as the size of the TiOF₂ crystals was on the order of a few hundreds of nanometers and the charge diffusion coefficients in oxides were very small. However, after hydrogenation, the first charge and discharge capacity increased to 254.8 and 338.1 mA h g⁻¹ at a current density of 42 mA g⁻¹, respectively, resulting in an initial coulombic efficiency of 75.4%, which was 42% higher than that of the original TiOF₂. During the second cycle, the charge-discharge capacity of the hydrogenated TiOF₂ (170.5 and 196.9 mA h g⁻¹) were much higher than that of the original TiOF₂ (39.1 and 69.1 mA h g⁻¹) at a current density of 210 mA g⁻¹. From the third cycle to 150th cycle at a current density of 1053

mA g⁻¹, the capacity of the hydrogenated TiOF₂ electrode remained relatively stable in the range from 110.7 to 124.9 mA h g⁻¹, and the specific charge capacity was maintained at 118.4 mA h g⁻¹ after 150 cycles, which was 4 times higher than that of the original TiOF₂ from Fig. 3c. As shown in Fig. 3d, the coulombic efficiency of the hydrogenated TiOF₂ samples reached above 90% after the third cycle, and stabilized above 98% after the fifth cycle. By contrast, the original TiOF₂ product only showed the coulombic efficiency of 90% after the tenth cycle, and slowly increased to above 98% after 30 cycles. Apparently, the electrochemical performance of the hydrogenated TiOF₂ was superior to that of the original TiOF₂ and much better than the previous reported the TiOF₂ electrodes [12, 14-16].

The improvement of the cycle performance and coulombic efficiency for the hydrogenated TiOF₂ electrode can be attributed to the following reasons: on the one hand, the hydrogenation process decreased the grain size, increased the disorder layer and interface area, which lowered the lithium ion transport resistance, and allowed better adsorption of electrolyte and easier lithium ion insertion-desertion within interface transfer compared to the crystalline TiOF₂, resulting in higher electrochemical activity and more interface lithium storage compared with the original TiOF₂, thus improving lithium storage capacity [14, 18]; on the other hand, the hydrogenation treatment could help to quicken transfer of electron and transport of lithium ion due to the possible formation of oxygen vacancy from Raman spectrum [21, 22].

In order to further evaluate influence of hydrogenation on lithium storage, the

rate capability of the original TiOF_2 and hydrogenated TiOF_2 at different current density were examined (Fig. 4). The hydrogenated TiOF_2 electrode exhibited the average specific charge capacity of 293.9, 208.3, 163.2, 143.9, 115.4, 93.7, 70.6 and 40.6 mA h g^{-1} at the current density of 42, 210, 1053, 2106, 5265, 10530, 21060 and 52650 mA g^{-1} , respectively. The specific charge capacity bounced back to 165.2 mA h g^{-1} when the current density returned to 1050 mA g^{-1} . By contrast, the original TiOF_2 electrode only showed a negligible specific charge capacity ($< 10 \text{ mA h g}^{-1}$) when the current density exceeded 1053 mA g^{-1} . The enhancement of the specific charge capacity at different current density was displayed in Fig. 4 (b). The rate performance of the hydrogenated TiOF_2 at different current densities of 42, 210, 1053, 2106, 5263, 10530, 21060 and 52650 mA g^{-1} was 2.8, 6.0, 13.2, 14.7, 21.5, 30.6, 67.9 and 483.3 times higher than those of the original TiOF_2 electrode at the corresponding rate, respectively. The remarkably improving rate performance is likely related to the preferential charge transfer across the (001) facet, the unique amorphous or disordered layer, oxygen deficiency and small grain size of H- TiOF_2 , which induced the fast transport of lithium ion, the convenient accessibility of electrolyte and the easy transfer of electron [18, 21-22].

In order to improve our understanding of why H- TiOF_2 showed a better performance than the pristine TiOF_2 crystals, we performed a series of analysis. It is suggested by the Raman measurements and TEM analysis that H- TiOF_2 might have oxygen deficiency and the appearance of some disorder by hydrogen treatment. Fig. 5A shows the global survey spectra of TiOF_2 and H- TiOF_2 with the major difference

in the F 1s signal. All the spectra were calibrated to the carbon signal from the carbon tape at 284.6 eV. Fig. 5B shows the core-level Ti 2p XPS spectra, which suggested Ti^{4+} ions for both samples with the Ti 2p_{3/2} peak at 458.8 eV and the Ti 2p_{1/2} peak at 464.6 eV. Fig. 5C shows the core-level O 1s XPS spectra. Both TiOF_2 and H-TiOF_2 had a major O1s peak at 530.0 eV from the O^{2-} ions in the lattice. TiOF_2 had two shoulder peaks around 531.9 eV and near 533.3 eV, which matched well with the oxygen in the adsorbed water and hydroxyl groups on the surface. While H-TiOF_2 only had a small shoulder peak around 531.9 eV. This peak was likely from oxygen vacancy instead of hydroxyl groups as suggested later from FTIR spectrum. Fig. 5D shows the core-level F 1s XPS spectra. TiOF_2 had a peak at 684.7 eV while this peak decreased for H-TiOF_2 , indicating that the hydrogenation treatment likely removed some of the surface fluorine ions.

Fig. 6A shows the FTIR spectra of TiOF_2 and H-TiOF_2 . For the TiOF_2 , the broad band centered at 3460 cm^{-1} and the peak at 1645 cm^{-1} were due to O-H stretching and bending of strongly adsorbed H_2O , respectively. The peaks at 986 cm^{-1} and 903 cm^{-1} was due to the Ti-F and Ti-O vibrations in the TiOF_2 , respectively^[26-28]. These fine IR characteristics were almost disappeared for H-TiOF_2 . Instead an increased featureless broad band whose intensity increased as the wavenumber decreased was observed across the entire IR region for H-TiOF_2 , indicating the existence of oxygen vacancy defects with various energies. Fig. 6B shows the I-V curves of TiOF_2 and H-TiOF_2 . The resistivity of TiOF_2 ($1.91 \times 10^{12}\ \Omega / \text{m}$) was smaller than that of H-TiOF_2 ($2.74 \times 10^{12}\ \Omega / \text{m}$). Fig. 6C shows the Mott-Schottky plots of TiOF_2 and H-TiOF_2 . As both

showed positive slopes, they were n-type semiconductors with electrons as majority carriers. The carrier density N_D were calculated from the slope with $N_d = (2/e\epsilon\epsilon_0)/[d(1/C^2)/dV]$, where C is the interfacial capacitance, V is the applied voltage, e is the electronic charge, and ϵ is the dielectric constant^[36]. The H-TiOF₂ had a lower carrier density than TiOF₂, as the carrier density N_D is inversely proportional to the slope. Fig. 6D shows the ECSAs of TiOF₂ and H-TiOF₂. The electrochemically active surface areas (ECSAs) of the catalysts were estimated from the double layer capacitance (C_{dl}), as C_{dl} was linearly proportional to the effective active surface area^[29]. The linear slope of the capacitive current against scan rate was used to represent the ECSA. C_{dl} was estimated by plotting the Δj ($j_a - j_c$) at 0.25 V vs Ag/AgCl against the scan rate, where the slope was twice as the C_{dl} ^[29]. H-TiOF₂ had a 12-fold increase in ECSA compared with TiOF₂. Based on the above results, the enhanced LIB performance of the H-TiOF₂ over TiOF₂ was most likely due to the enhancement of the ECSA as a result of the size shrinkage after hydrogenation, instead of the changes of electrical conductivity or carrier density. This is different from previous studies that hydrogenation induced the improvement of electrical conductivity and carrier density of TiO₂ nanomaterials through the creation of oxygen vacancies to improve their LIB performance^[18,21]. The difference might be related to the existence of the fluorine in the TiOF₂. Nevertheless, hydrogenation did improve the LIB performance of TiOF₂, but through the break-down of the particle size of TiOF₂, thus providing additional channel in improving the performance of LIB materials.

4. Conclusions

In conclusion, we have successfully synthesized hydrogenated titanium oxyfluoride by one-pot hydrothermal treatment combined with a simple hydrogenation process. As anode material for LIBs, the hydrogenated TiOF_2 electrode exhibited much higher lithium storage capacity and rate performance than the original TiOF_2 electrode. The high electrochemical performance made such hydrogenated titanium oxyfluoride an attractive anode material for LIBs.

Acknowledgments

X. C. thanks the support from College of Arts and Sciences, University of Missouri - Kansas City and the University of Missouri Research Board. G. L. thanks the fund by the Assistant Secretary for Energy Efficiency, Office of Vehicle Technologies of the United State Department of Energy under Contract No. DE-AC03-76SF00098. M. H. thanks the fund from China Scholarship Council for its financial support. L. T. thanks China Scholarship Council for it financial support.

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Figure captions

Fig. 1. XRD patterns (a) and Raman spectra (b) of as-synthesized TiOF₂ and H-TiOF₂

Fig. 2. TEM and HRTEM images of the original TiOF₂ (a-c) and hydrogenated TiOF₂ (d-f)

Fig. 3. Galvanostatic charge/discharge profiles at the first cycle at a current density of 42 mA g⁻¹, the second cycle at a current density of 210 mA g⁻¹, and then other cycles at a current density of 1053 mA g⁻¹ for the original TiOF₂ (a) and hydrogenated TiOF₂ (b). The cycle performance (c) and Coulombic efficiency curves (d) of the original TiOF₂ and hydrogenated TiOF₂ at the first cycle at a current density of 42 mA g⁻¹, the second cycle at a current density of 210 mA g⁻¹, and then other cycle at a current density of 1053 mA g⁻¹ in voltage ranges 1.0-3.0 V.

Fig. 4. Rate performance (a, unit: mA g⁻¹) and comparison of the average charge capacities (b) of TiOF₂ and H-TiOF₂ at various current density.

Fig. 5 XPS spectra of TiOF₂ and H-TiOF₂: (A) global survey, (B) Ti 2p core-level, (C) O 1s core-level, and (D) F 1s core-level.

Fig. 6 (A) FTIR spectra, (B) I-V curves, (C) M-S plots, and (D) the ECSAs of TiOF₂ and H-TiOF₂.

Fig. 1. XRD patterns (a) and Raman spectra of as-synthesized TiOF_2 and H-TiOF_2

Fig. 2. TEM and HRTEM images of the original TiOF_2 (a-c) and hydrogenated TiOF_2 (d-f)

Fig. 3. Galvanostatic charge/discharge profiles at the first cycle at a current density of 42 mA g^{-1} , the second cycle at a current density of 210 mA g^{-1} , and then other cycles at a current density of 1053 mA g^{-1} for the original TiOF_2 (a) and hydrogenated TiOF_2 (b). The cycle performance (c) and Coulombic efficiency curves (d) of the original TiOF_2 and hydrogenated TiOF_2 at the first cycle at a current density of 42 mA g^{-1} , the second cycle at a current density of 210 mA g^{-1} , and then other cycle at a current density of 1053 mA g^{-1} in voltage ranges 1.0-3.0 V.

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