Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

The application of plasma treatment for Ti³⁺ modified TiO₂ nanowires film electrode with enhanced lithium-storage properties



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ARTICLE INFO

Article history: Received 3 February 2016 Received in revised form 11 April 2016 Accepted 28 May 2016 Available online 31 May 2016

Keywords: anatase TiO₂ nanowires lithium ion battery film electrodes hydrogen plasma

ABSTRACT

Hydrogen plasma processing offers improved thermodynamics, kinetics and optimal reductive environment over conventional, thermal processing. In the current work, we report the first demonstration of hydrogen plasma treatment as a simple and effective strategy to fundamentally improve the performance of TiO₂ nanowires for lithium storage. In comparison to pristine TiO₂ nanowires, the hydrogen plasma treated TiO₂ (H-TiO₂) samples show substantially enhanced electron conductivity due to Ti³⁺ introduction, which are successfully confirmed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and four-probe testing instrument. More importantly, the H-TiO₂ electrode exhibits a higher rate capability and better reversibility. At charge/discharge current of 200, 800, 1600 and 3350 mA/g (10C), the discharge capacity of the H-TiO₂ electrode is 200, 162, 144 and 130 mAhg⁻¹. After 200 cycles at current of 200 mA/g, its capacity retention was 99.8% with almost no capacity fading. The electrochemical impedance spectra analyses and theoretical energy calculations using density functional theory (DFT) finally suggest that the hydrogenation process not only improves electronic conductivity due to the formation of Ti³⁺ in the hydrogenation process but also dramatically augments lithium-ion mass transport within the crystalline lattice due to the introduction of Ti³⁺.

1. Introduction

Being inherently safe and chemically compatible with the electrolyte, titanium dioxide (TiO₂) is considered alternatives to carbonaceous anodes in Li-ion batteries. Compared with the commonly-used graphitic carbon anode materials, titanium dioxide is a high-capacity material with low cost, non-toxicity and environmental friendliness [1]. Moreover, anatase TiO₂ exhibits a relatively high lithium ion insertion/extraction voltage (>1.0 V vs. Li/Li⁺), which is obviously higher than the operating voltage of graphitic anodes, thereby the formation of SEI and electroplating of lithium can be avoided [2,3]. Besides, anatase TiO₂ possesses excellent reversibility and Li-ion mobility in the charge/ discharge process, which is attributed to its structural stability during the lithium ion insertion/extraction process [3]. These

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http://dx.doi.org/10.1016/j.electacta.2016.05.192 0013-4686/© 2016 Published by Elsevier Ltd. features make it a promising anode material for large-scale and long-life energy storage batteries.

However, titanium dioxide has a poor electronic conductivity, because of empty Ti 3d-states with a band gap energy of 2-3 eV [4,5], which may give a moderate rate performance for high power batteries. To date, the most common strategies for improving TiO₂ electrochemical performance are 1) particle size reduction to the nanometer scale to shorten the lithium ion diffusion length [6]; 2) structural doping with some defects [7]; and 3) surface modification with electronic conductive materials to reduce the resistance [8].

It is well-known that the hydrogenation process can produce abundant oxygen vacancy and Ti^{3+} that facilitate better electrical conductivity for lithium ion batteries [9,10]. Currently, most hydrogenation processes can be conducted either under pure hydrogen or mixture of hydrogen and inert atmosphere [11–13]. In contrast, the hydrogen plasma processing has not been reported for LIBs application up to now. Hydrogen plasma, in its most basic definition, is simply a highly ionized hydrogen gas. The high degree of ionization is produced and maintained by applying an



electromagnetic field (either AC or DC) to the hydrogen gas. It is worth noting that the plasma technique is well known as a powerful and versatile method for surface modification without the structural damage and the introduction of impurities. In addition, it is known that titanium is susceptible to hydrogen embrittlement [14]. Moreover, the hydrogen plasma technique can be conducted at low temperature with a short reaction time due to the production of extremely chemically reactive hydrogen radical.

In this work, hydrogen plasma processing as an enhanced hydrogenation is firstly used as a facile and effective strategy to hydrogenate the TiO_2 NWs. More importantly, the effect of hydrogen plasma on electrical conductivity and Li-ion mass transport of TiO_2 NWs for LIBs is also discussed in the present paper.

2. Experiment

2.1. Preparation of TiO₂-NWs electrode on Ti substrates

In a typical hydrothermal procedure, a piece of commercial Ti substrates (99.5% in purity) with the thickness of 0.05 mm was used as the Ti source and the substrate, which is ultrasonically washed with ethanol and acetone for 30 min in sequence. The dried Ti substrate was transferred into the 100 mL Teflon-lined stainless steel autoclave and was kept vertical. Then 10 mL ethanol and 80 mL of 0.5 M NaOH solution were added into the autoclave, respectively. The sealed autoclave was heated to 220 °C with a heating rate of 3 °C/min and maintained at 220 °C for 16 h. After the autoclave was cooled naturally to room temperature, the obtained precursor was taken out. At this point, the precursor had lost its metallic luster and turned to be light blue. After washing with deionized water several times, the precursor was immersed into 100 mL of 0.1 M HCl for 6 h to achieve ion exchange of Na⁺ into H⁺, followed by washing several times and dried in air at room temperature. Finally, the as-prepared hydrogen titanate was placed into a muffle furnace, heated to 400 °C with a temperature ramp of 3 °C/min and calcined in air atmosphere at 400 °C for 4 h. When the sample cools to room temperature, the pristine TiO₂-NWs electrode grown on Ti substrates was obtained.

3. Preparation of H-TiO₂-NWs film electrode

The above obtained pristine TiO₂-NWs were placed into a quartz glass chamber and annealed to 400 °C with a temperature ramp of 6 °C/min. As the temperature reached at 400 °C, the films were treated from hydrogen-argon mixtures by radio-frequency discharge (power supply = 10 W, frequency = 13.56 MHz), under the following conditions, at a pressure of 177 Pa, a plasma treating time of 30 min, and the flow rates of H₂ and Ar were 3% and 97%, respectively. When the samples cool to room temperature, the hydrogenated plasma-treated TiO₂-NWs electrodes (H-TiO₂ NWs) were obtained.

4. Materials characterizations

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku MiniFlex600 X'pert (D8 Advance, Japan) diffractometer using Cu Kα radiation (λ = 1.5405 Å). Morphologies and structure of the samples were examined with a field emission scanning electron microcopy (SEM, LEO 1530, HITACHI S-4800) and high resolution transmission electron microcopy (HRTEM, JEM-2100). For TEM, TiO₂ and H-TiO₂ materials from the Ti substrate were redispersed ultrasonically in ethanol solution and then dropped onto the surface of bronze nets. No metal coating treatment was performed on the samples before characterization by electron microscopy. The X-ray photoelectron spectroscopy (XPS) analysis

was performed with a QUANTUM 2000 SCANNING ESCA MICRO-PROBE spectrometer using a focused monochromatized Al K α radiation (1486.6 eV). The pass energy was 60 eV for the survey spectra and 20 eV for particular elements. Raman spectra (JOBIN Yvon Horiba Raman Spectrometer model HR800) were collected by a 10 mW helium/neon laser at 514.5 nm excitation.

5. Electrochemical performance characterization

The TiO₂-NWs and H-TiO₂ –NWs grown on Ti substrates were directly used as film electrodes for electrochemical characterization. CR2016-type coin cells for lithium battery were assembled in an argon-filled glove box with Li metal foil (China Energy Lithium CO., LTD.) as the counter and reference electrode, one layer of Celgard 2400 (Celgard, Inc., USA) as the separator, and LiPF₆ (1 mol/L) dissolved in a 1:1:1 (V:V:V) mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and (DEC) as the electrolyte. Galvanostatic charge/discharge experiments were performed at different current densities between 1.0 and 3.0 V (vs. Li/Li⁺) using an Arbin cell test instrument (BT2000, College Station, Texas, USA) at room temperature. The electrochemical impedance spectra (EIS) of the unmodified and hydrogen-modified TiO₂-NWs film electrodes at an open-circuit potential (OCP) of ${\sim}3.0$ V and the discharge plateau voltage of ${\sim}1.75$ V were measured in the frequency range of 10 mHz-100 kHz using two-electrode coin cells with Li metal as the counter electrode via an Autolab PGSTAT 101 cell test instrument. A four-point probe meter (SX1934 (SZ-82) digital four-probe testing instrument) was also used to investigate the sheet resistances of TiO₂ and H-TiO₂ film electrodes in this work.

6. Calculation detail

All calculations were performed using the plane-wave pseudopotential based on the density functional theory (DFT), as implemented in the CASTEP code [15]. The electronic exchange correlation energy was modeled using the Perdew–Burke– Ernzerhof (PBE) function within the generalized gradient approx-imation (GGA) [16,17]. The wave functions were expanded in plan-wave basis up to a kinetic energy cutoff of 340 eV or higher. To obtain the equilibrium geometries, the structural relaxations were performed until the total energy was converged to $5 \times 10-6$ eV in the self-consistent loop and the force on each



Fig. 1. The XRD patterns of the hydrogen-modified and pristine TiO_2 electrodes.

Table 1	
Impact of hydrogen modification on the cell parameter.	

TiO ₂ 3.77 9.	ll parameter c (Å)
H-TiO ₂ 3.78 9.	41 47

atom was smaller than 0.01 eV/Å. Throughout this work, $(2 \times 3 \times 1)$ k-point meshes were used to sample the reciprocal space.

Also, (101) surfaces are modeled by 2×2 slabs with 12 atomic layers, with a vacuum of 15 Å between neighboring slabs. In our slab model, three upper layers of the slab were allowed to relax during geometry optimization while the other remaining layers at the bottom side were kept fix as its initial bulk position.

7. Results and discussion

The crystal structure of the hydrogen-modified (named H-TiO₂ hereafter) and as-prepared TiO₂ electrodes were characterized by X-ray diffraction as shown in Fig. 1. For the unmodified TiO₂ electrode, all the diffraction peaks position at $2\theta = 25.4^{\circ}$, 37.8° , 48.1°, 62.8°, 76.2° are well indexed to the anatase phase of TiO_2 (JCPDS No. 89-4921) [18,19]. It's obvious that there is neither huge change in the crystallinity nor any negative impact on the crystal phase during the hydrogen plasma treatment. After the hydrogen plasma treatment, all the Bragg reflections of the TiO₂ phase remain intact without any impurity peaks. However, it's obvious as shown in Table 1 that there is little increase on the lattice constant and volume. And this can be beneficial for the Li mass migration and electrochemical reaction activity.

After hydrogen modification, the pearl blue for TiO₂ film deepens into dark blue and the uneven white dot also disappears (Fig. 2a, 2b). This discoloration is one of the direct indications that the homogenous film with Ti³⁺ doped can be simply obtain by the hydrogen plasma treatment [20]. SEM images of the pristine TiO₂ and hydrogen-modified TiO₂ electrodes are shown in Fig. 2. All the samples show a 3D nano-network structure, composed of lots of non-directional, homogeneous 1D nanowire with a column diameter of $50 \sim 60 \text{ nm}$ and length of several micrometers. The special 3D nano-network structure could be expected to provide short pathways for Li⁺ diffusion, large specific space to facilitate the fast transfer of Li⁺ and the facile electrolyte infiltration throughout the thin film electrode. After the hydrogen plasma treatment, we



Fig. 3. Bright-filed TEM images of a single (a) TiO₂ nanowire and (c) H-TiO₂ nanowire. The corresponding HRTEM images and SAED pattern from selected area in (b) TiO₂ nanowire and (d) H-TiO₂ nanowire.

can clearly see that 3D nano-network structure can keep in the primary shape (Fig. $2e \sim f$), which is well consistent with the XRD data as above.

Further morphological and structural characterizations of the TiO₂ NW and H-TiO₂ NW are performed using transmission electron microscopy (TEM). Fig. 3(a) and Fig. 3(b) are typical TEM images of a single TiO₂ NW and H-TiO₂ NW with about 50 nm in diameter which agrees with the SEM observation. HRTEM (Fig. 3b) together with SAED (inset in Fig. 3b) further show that the TiO₂ nanowire is single crystalline across its entire length and grows along the [100] direction. The interplanar space of d₁₀₁ = 0.35 nm is in excellent agreement with the d-spacing of the anatase (101) planes. Furthermore, from a statistically significant number of measurements, an average angle of 71.5° was found between the (101) planes and the axis of nanowires, which is in agreement with the results of Aydil and Liao et al. [21–23]. After the hydrogen modification, the H-TiO₂ NW keeps the similar single crystal structure with the exposed anatase (101) planes.

It is well known that Raman spectroscopy, is a simple, efficient, well-established technique and accurate alternative approach to study the significant structural changes in titanium dioxide [24,25]. In Fig. 4, four Raman-active modes of anatase phase can be found at 142 cm^{-1} (Eg), 403 cm^{-1} (B_{1g}), 521 cm^{-1} (A_{1g}), and 639 cm^{-1} (Eg) for TiO₂ and H-TiO₂, which shows a good agreement with that reported in the literature [26–28]. These results confirm that the H-TiO₂ sample is composed of the anatase phase similar with the TiO₂ sample, consistent with the XRD and SEM results.

The major difference between the two samples is that the E_g mode of the H-TiO₂ sample shifts to a higher frequency (150 cm⁻¹). This is attributed to the presence of lattice disorder resulting from non-stoichiometric H-TiO₂ as a result of oxygen vacancies and Ti³⁺ doped [29]. The other difference is the intensity of the H-TiO₂ is weaker than the pristine TiO₂. A similar phenomenon has been reported [29], but the specific reason for the changes is still not clear.

To investigate the elemental compositions and the binding states of derived H-TiO₂ sample, high-resolution XPS was used to detect the surface Ti2p and O1 s core levels (Fig. 5). The XPS Ti2p peaks corresponding to H-TiO₂ show a unique doublet at 458.8-464.4 eV, associated with tetravalent Ti based on TiO₂ [29]. Compared with the pristine TiO₂, we observe a new Ti2p doublet at lower binding energies (455.8-461.9 eV) in the H-TiO₂ material after the hydrogen treatment, which is assigned to the presence of trivalent Ti [30,31,22]. It also can be clearly observed that a new peak at approximately 532 eV, ascribed to water adsorbed on the TiO₂ surface, appears in the H-TiO₂ sample [32]. The above results clearly show that the Ti³⁺ modification of TiO₂ materials via the hydrogen plasma treatment can be successfully carried out.

The specific discharge capacity and coulombic efficiency with respect to cycle number for the TiO_2 and H- TiO_2 electrodes at a current density of 200 mA/g in a half cell are shown in Fig. 6(a). In terms of TiO_2 electrode, the second discharge capacity is 246 mAh/g and decreases to 199 mAh/g after 200 cycles with capacity retention of 80.8%. However, for H- TiO_2 electrode, it delivers 225.6



Fig. 4. Raman spectra of (a) the pristine TiO₂ and (b) H-TiO₂.

mAh/g with high capacity retention of 99.8% after 200 cycles, indicating the remarkable cycling stability. Fig. 6(b) shows the comparison of the rate capabilities between unmodified and hydrogen-modified TiO₂ electrodes at different current rates range from 50 mA/g to 3350 mA/g (10C). It can be clearly found that the capacity of TiO₂ electrode decreases rapidly with the cycles and the increase of current density, but H-TiO₂ electrode obviously exhibits a much higher storage capacity and much better rate capability than TiO₂ electrode at the higher current rates. For example, at a current rate of 3350 mA/g, the specific capacity of H-TiO₂ electrode is around 129.5 mA h/g, which is remarkably higher than the same rate capacity (87.6 mAh/g) of TiO₂ electrode. (The detailed comparison of each rate capacities of TiO₂ and H-TiO₂ electrodes are summarized in Table S1.)

A comparison of the voltage profiles for the prepared TiO₂ and H-TiO₂ electrodes are shown in Fig. 7 There are distinct potential plateaus observed at \approx 1.75 and 2.0 V (vs. Li/Li⁺) during discharging (Li⁺ insertion) and charging (Li⁺ extraction) for the TiO₂ and H-TiO₂ electrodes. The discharge curves of TiO₂-NWs, corresponding to Li⁺ insertion process, can be divided into three consecutive potential regions [33,34]. The first potential region is marked by a steep voltage decrease from the open-circuit potential (OCP) to 1.75 V (vs. Li/Li⁺) forming a solid solution phase, which is attributed to Li insertion into the $l4_1/amd$ tetragonal anatase lattice (Li_xTiO₂) without the nucleation of other phases [34,35]. The second potential region is the discharge plateau region at \approx 1.75 V (vs. Li/Li⁺), indicating a two-phase reaction between the Li-poor



Fig. 5. X-ray Photoelectron Spectra of Ti2p(a), O1s(b) in H-TiO₂.

tetragonal anatase $\text{Li}_x \text{TiO}_2$ and orthorhombic $\text{Li}_{0.5}\text{TiO}_2$ phases [36–38]. A long slope-like potential region is observed from 1.75 V to 1.0 V (vs. Li/Li^+), which represents the non-faradaic process in which the interfacial Li^+ insertion storage is similar to the capacitive behavior of nanomaterial [36].

This interfacial Li⁺ insertion storage contributes to the additional pseudocapacitive lithium inserted into the surface layer of the TiO₂, forming the Li-rich $l4_1/amd$ tetragonal lattice (Li_{0.5} +_xTiO₂), as observed in many other nano-TiO₂ materials [37,38]. It is clearly seen that the capacity of the long slope-like region is the main contribution to the capacity of TiO₂-NWs and is also larger than that reported by other research groups, which is probably due to its improved conductivity. As shown in Fig. 7(b), the discharge/charge curves of hydrogen-modified TiO₂ are similar to unmodified TiO₂ without any other charge/discharge plateaus occurred. Compared with the TiO₂, the capacity retention of the hydrogen-modified TiO₂ is higher, suggesting that the H-TiO₂ electrodes can exhibit higher reversibility towards lithium ion insertion and enhanced electrochemical storage of lithium than the TiO₂ electrode.

Fig. 8a~b compares the representative cyclic voltammograms for unmodified TiO_2 and H- TiO_2 film electrodes at a scan rate of 0.1 mV/s. The area under the curves represents the total stored charges which arise from both faradaic and nonfaradaic processes [38]. It can be found that two couples of oxidation-reduction peaks appear when the electrode potential scans from 1.0 to 3.0 V (vs. Li/ Li⁺). The cathodic/anodic peaks (named A-peaks), usually occurred at ca. 1.75 and 2.0 V (vs. Li/Li⁺), respectively, represent the solid-



Fig. 6. (a) Cycle performances for TiO_2 and H- TiO_2 electrodes at a current density of 200 mA/g. (b) Rate capabilities of TiO_2 and H- TiO_2 electrodes at different current densities.

state lithium ion insertion/extraction behavior in the anatase TiO_2 lattice. And the other cathodic/anodic peaks (named S-peaks) occurred at ca. 1.55 and 1.65 V (vs. Li/Li⁺), respectively, represent the pseudocapacitive lithium ion insertion/extraction process in the anatase TiO_2 lattice, which are consistent with previous reports [39,40]. This lithium ion insertion process can be written as the follow equation:

$$\text{TiO}_2 + x\text{Li}^+ + \frac{\text{Discharge}}{\text{charge}} \rightleftharpoons \text{Li}_x\text{TiO}_2 \tag{1}$$

The lithium ion insertion coefficient, *x*, is normally found to be close to 0.5 for the anatase structure when it is at maximum accommodation [21] and corresponds to a specific capacity of 168 mA h/g. In comparison, both of the A-peaks shapes and current densities are similar, whereas, the S-peaks of H-TiO₂ material are sharper and higher than TiO₂ material, indicating that the Ti³⁺ modification can significantly improve the kinetics of TiO₂ toward fast lithium ion insertion/extraction and the specific capacity followed by the hydrogen plasma processing.

In order to further understand how the Ti^{3+} modification improve the kinetics of TiO_2 toward fast lithium ion insertion/ extraction and the specific capacity, CV measurements at different scan rates were also tested. Fig. 7c~d summarizes the specific capacitance calculated from the integration of the CV curves at different scan rates. It can be found that the total amount of the stored charge in the TiO_2 and H- TiO_2 are strongly dependent on the sweep rate in the range between 0.1 and 10 mV/s. As the sweep rate decreases, the total amount of stored charge increases. This



Fig. 7. Charge and discharge curves of (a)TiO₂ and (b)H-TiO₂ electrodes at a current density of 200 mA/g.

indicates that the full storage capacity has not been reached at the given sweep rates because of kinetic limitations associated with the diffusion of Li⁺ through the TiO₂ [40]. In addition, all A-peaks of TiO₂ and H-TiO₂ gradually disappear with the sweep rate increase, and all H-TiO₂ S-peaks shapes are sharper than TiO₂ material, further indicating the Ti³⁺ are beneficial to improve the rate performance of TiO₂. To obtain more information about capacitive contributions to overall charge of Li-storage, cyclic voltammograms of the Li⁺ insertion into TiO₂ and H-TiO₂ were analyzed in detail according to the mathematical deconvolution of cyclic voltammograms recently reported by Yan, Zhu, Laskova and Dunn et al. [41–44]. According to the discussion as shown above, both of the A-peaks shapes and current densities of TiO₂ and H-TiO₂ electrodes are similar. So in this part, we just analyze the CV parameters of S peak in detail.

The S peak current response at a fixed potential can be expressed by:

$$i(\nu) = k_1 \cdot \nu + k_2 \cdot \nu^{1/2}$$
(2)

where $k_1\nu$ corresponds to the capacitive current contribution associated with the storage of Li⁺ at the TiO₂ surface and also to the bulk faradaic pseudocapacitance. The second term $k_2\nu^{1/2}$ corresponds to the diffusion-controlled current, which is attributed to the insertion of Li⁺ in the bulk of anatase TiO₂ lattice. According to the CV measurements at different scan rates shown in Fig. 8, we



Fig. 8. CV measurements of (a) TiO₂ and (b) H-TiO₂ at a scan rate of 0.1 mV/s. CV measurements of (c) TiO₂ and (d) H-TiO₂ at different scan rates.

randomly chose four groups data (Table S2) to calculate the coefficients k_1 and k_2 (Table S3). It can be clearly seen that the average value of k_1 and k_2 for H-TiO₂ is much greater than that of TiO₂, conforming that plasma hydrogen modification is beneficial to improve the Li-storage of TiO₂, which is corresponding to the improved electronic conductivity and the fast lithium ion insertion.

To further understand the distinctions of the TiO_2 and $H-TiO_2$ electrodes on the electrochemical performance, all the film electrodes were investigated by electrochemical impedance

spectroscopy (EIS) and four-point probe meter. EIS may be considered as one of the most powerful tools to study the kinetic parameters of the electrode process [34]. Fig. 9 shows the obtained EIS data of TiO₂ and H-TiO₂ film electrodes, which were measured at the open circuit potential (OCP) of \approx 3.0 V and the discharge plateau voltage of \approx 1.75 V. The AC impedance parameters of TiO₂-NWs and H-TiO₂-NWs electrodes are shown in Table 2. The high-frequency semicircle is related to the charge transfer resistance, while the low frequency region of the straight line is attributed to the Warburg impedance of long-range lithium ion diffusion [31].



Fig. 9. (a). AC impedance measurements of TiO₂ and H-TiO₂ electrodes at open-circuit potential of \approx 3.0 V (vs. Li/Li⁺). (b) AC impedance measurements of TiO₂ and H-TiO₂ electrodes at discharge plateau of \approx 1.75 V (vs. Li/Li⁺).

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Table 2
AC impedance parameters of TiO ₂ -NWs and H-TiO ₂ -NWs electrodes

Sample	Rs (Ω)	Error%	Rct (Ω)	Error%
TiO ₂ -NWs (OCP)	7.81	2.87	326.8	1.25
H-TiO ₂ -NWs (OCP)	4.00	1.51	91.7	0.23
TiO ₂ -NWs (1.75 V)	2.95	1.00	175.0	0.62
H-TiO ₂ -NWs (1.75 V)	2.30	0.76	33.2	0.46

Table 3

Sheet resistances of TiO_2 NWs and H- TiO_2 NWs electrodes measured by the fourpoint probe testing method.

	TiO ₂	H-TiO ₂
Sheet resistance (Ω / \Box)	>1.0 × 10 ⁵	$(3.2\pm0.6)\times10^2$



defection	free	2c-0	3c-0
Ti-O/Å	1.968	1.972	1.969

Table	6	
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Electrostatic charge distribution of TiO₂ NWs and H-TiO₂ NWs electrodes.

defection	2c-0	3c-0	5c-Ti	3c-Ti
free	-0.600	-0.730	1.360	1.320
2c-0	-0.600	-0.740	1.290	1.225
3c-0	-0.600	-0.720	1.140	1.195

2c-0	
3c-O 5c-Ti 6c-Ti	
A PRIMA	

Fig. 10. The crystal structure of TiO_2 (101) face with oxygen vacancy.

Obviously, hydrogen-modified TiO₂ electrode exhibits much lower charge-transfer resistance than that of unmodified TiO₂ electrode, meaning that the modification of hydrogen plasam on the surface of TiO₂ can effectively improve the electronic conductivity. Table 3 shows the four-point probe meter testing results. Clearly, the sheet resistance of H-TiO₂ electrode ($(3.2 \pm 0.6) \times 10^2 \Omega/\Box$) is eminently smaller than that of TiO₂ (>1.0 × 10⁵ Ω/\Box), further indicating that the modification of hydrogen plasam is beneficial to improve the electrical conductivity of TiO₂.

In this study, we also use DFT calculations to explain the experiments results. From the structure analysis, we know the main exposure faces of TiO_2 is (101) face. So we simulated oxygen vacancy for (101) face as shown in Fig. 10 If the oxygen vacancy appears, there are two kinds O and Ti on the surface, 2c-O stands for two coordination O on(101)surface layer, 3c-O stands four coordination O on the third layer, 5c-Ti stands for five coordination Ti on the second layer, 6c-Ti stands for six coordination on the forth layer. In order to calculate the oxygen vacancy state in our work, we used the equation of defect formation energy as followed.

$$E_f = E_{total}(D^q) - E_{total}(0) + \sum \Delta n_x \mu_x + q E_f$$
⁽²⁾

Table 4

Defect formation energy of TiO2 NWs and H-TiO2 NWs electrodes.

States	2c-0	3c-0
Ti-rich	-1.81ev	–1.02ev
O-rich	4.96ev	5.76ev

Table 7	
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Band energy of TiO₂ NWs and H-TiO₂ NWs electrodes.

defection	free	2c-0	3c-0
ev	3.019	2.829	2.805

According to the equation as shown above, we have found that 2c-O is more easily to form defection due to less coordination and exposure on the surface (Table 4). In addition, Ti-O bond length increases due to the defection formation, which will bring about easily Li ion insertion (Table 5). Moreover, charge transfer from O to Ti after the defection formation, which makes Ti electropositive and bring about more Ti³⁺ (Table 6). From the band energy results, we can see the band energy decreases followed by the defection formation (Table 7), which will improve the electronic conductivity. All the results discussed above indicate that hydrogen plasma treatment can improve the electronic conductivity and lithium insertion of TiO₂ to some degree.

8. Conclusion

An enhanced hydrogenation process via hydrogen plasma processing was used to prepare the Ti³⁺ doped TiO₂ as anode for LIBs for the first time. When being evaluated as an anode material for LIBs, the H-TiO₂ electrodes exhibit high rate capabilities and high stabilities for lithium storage. At a current rate of 3350 mA/g, the specific capacity of H-TiO₂ electrode is around 129.5 mA h/g, which is remarkably higher than the same rate capacity (87.6 mA h/ g) of TiO₂ electrode. In addition, after 200 cycles at 100 mA/g, it delivers 225.6 mA h/g with high capacity retention of 99.8% with nearly no capacity fading, indicating the remarkable cycling stability. The superior electrochemical performance of H-TiO₂ is attributed to the fast lithium – ion mass transport and electron transfer during the charge/discharge process. Generally speaking, this surface modification is relatively simple and effective and may be a helpful approach to solve the problems of poor electronic conductivity and rate performance. We believe that such a hydrogen surface modification method could be applied in a wide range of fields and that H-TiO₂ could be a promising anode material for high-rate lithium ion batteries.

Acknowledgements

The project was supported by the State Key Laboratory of Physical Chemistry of Solid Surfaces of Xiamen University (201506), National Natural Science Foundation of China (Nos. 51364021 and 51264016) and the Natural Science Foundation of Yunnan Province (2014FA025).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.05.192.

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