Amorphous Vanadium Titanates as a Negative Electrode for Lithium-ion Batteries

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ABSTRACT

Amorphous vanadium titanates (*a*VTOs) are examined for use as a negative electrode in lithium-ion batteries. These amorphous mixed oxides are synthesized in nanosized particles (<100 nm) and flocculated to form secondary particles. The V⁵⁺ ions in *a*VTO are found to occupy tetrahedral sites, whereas the Ti⁴⁺ ions show fivefold coordination. Both are uniformly dispersed at the atomic scale in the amorphous oxide matrix, which has abundant structural defects. The first reversible capacity of an *a*VTO electrode (295 mA h g⁻¹) is larger than that observed for a physically mixed electrode (1:2 *a*V₂O₅ | *a*TiO₂, 245 mA h g⁻¹). The discrepancy seems to be due to the unique four-coordinated V⁵⁺ ions in *a*VTO, which either are more electron-accepting or generate more structural defects that serve as Li⁺ storage sites. Coin-type Li/*a*VTO cells show a large irreversible capacity in the first cycle. When they are prepared under nitrogen (*a*VTO-N), the population of surface hydroxyl groups is greatly reduced. These groups irreversibly produce highly resistive inorganic compounds (LiOH and Li₂O), leading to increased irreversible capacity and electrode resistance. As a result, the material prepared under nitrogen shows higher Coulombic efficiency and rate capability.

Keywords : Amorphous metal oxides, Lithium-ion batteries, X-ray absorption fine structure (XAFS), Surface hydroxyl groups, Electrochemistry

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1. Introduction

Since lithium-ion batteries (LIBs) were first commercialized in 1991, the market for their use in portable electronic devices and electric vehicles (EVs) has grown steadily [1,2]. The market could be further expanded if the cell performance is improved in terms of capacity, power, safety, and cycle life [3]. Unfortunately, current LIBs cannot fully satisfy the high-power demand of EVs. One reason for this limitation is the use of graphite negative electrodes; the working potential of graphite is so close to that of Li metal that Li plating is highly probable under high-

rate charging and frequently leads to severe safety problems such as internal shorting by dendritic Li metal.

Ti-based oxides such as lithium titanate (Li₄Ti₅O₁₂, LTO) [4-7] and titanium oxides (TiO₂) [8-10] have emerged as alternatives to graphite for negative electrode materials in high-power applications. Here, Li plating is unlikely even under high-current charging because their working potential (1.5-1.8 V vs. Li/Li⁺) is much higher than that of Li metal. The high-current performance of TiO₂ is, however, largely offset by the limited specific capacity (<200 mA h g⁻¹). Their latent specific capacity cannot be fully utilized because of irreversible changes to inactive phases upon deep charging [11]. To prevent or mitigate the irreversible phase transitions, TiO₂

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has been prepared in nanostructured forms or amorphous phases. It is intuitive that phase transitions can be suppressed by introducing disorder, for instance, structural defects such as vacancies and void spaces on the surface of nanostructured materials or in the bulk of amorphous materials [12]. Moreover, nanostructuring of electrode materials is expected to be a promising strategy to increase the power density of cells by shortening the Li^+ diffusion path within the bulk materials [13-17]. In addition to suppressing unwanted phase transitions, amorphization of electrode materials has also been proven effective for increasing the number of Li^+ storage sites and facilitating solid-state Li^+ diffusion through the abundant void spaces [18-21]. The reason is very likely that the structural defects (vacancies and void spaces) can serve as Li^+ storage sites, as is well-known for hard carbons [22,23]. Recent studies have demonstrated that several amorphous materials can be successfully applied in Na^+ ion batteries because the amorphous framework provides Na^+ storage sites and ion diffusion channels [24,25].

A literature survey reveals that the rate performance of TiO_2 electrodes can be improved somewhat by amorphization, but their specific capacity cannot be increased [18,26,27]. The capacity limitation can be understood by considering that lithiation proceeds via co-injection of Li^+ ions and the equivalent quantity of electrons. Electrode materials should carry both Li^+ storage sites and electron storage sites (redox centers). Even if the number of Li^+ storage sites (vacancies and void spaces) can be increased by amorphization of TiO_2 , the electron-accepting ability cannot be enlarged by amorphization because the redox centers are the metal (Ti) ions in TiO_2 . In this work, to increase the specific capacity of amorphous TiO_2 ($a\text{TiO}_2$), a mixed oxide containing Ti and V ions was prepared on the basis of information in previous reports. As reported in a previous study, V^{5+} ions in amorphous V_2O_5 ($a\text{V}_2\text{O}_5$) have better electron uptake than Ti^{4+} in $a\text{TiO}_2$ at >1.0 V [28-31]. If this is the case in the mixed oxide prepared in this work, V^{5+} ions can show a higher electron-accepting ability as a redox center than Ti^{4+} ions; the net result will be an increase in the specific capacity. A further role of V^{5+} ions is that homogeneous mixing of V^{5+} and Ti^{4+} ions in the oxide matrix can produce a larger number of structural disorders that can act as Li^+ storage sites [32,33].

As a way to introduce V^{5+} ions into $a\text{TiO}_2$, amorphous vanadium titanate ($a\text{VTO}$) was synthesized using a simple precipitation method. The following features of the synthesized $a\text{VTO}$ were examined: (i) whether the V and Ti ions in $a\text{VTO}$ are homogeneously mixed at an atomic scale instead of existing in a physical mixture of $a\text{V}_2\text{O}_5$ and $a\text{TiO}_2$, (ii) how the oxidation state of the V and Ti ions and the surrounding local structure in $a\text{VTO}$ differ from those in their respective oxides ($a\text{V}_2\text{O}_5$ and $a\text{TiO}_2$), and (iii) how the Li^+ storage sites and redox centers in $a\text{VTO}$ differ from those in their respective oxides. Another objective of this work was to decrease the quantity of surface impurities such as surface hydroxyl groups and residual water, which are known to cause side reactions that lower the Coulombic efficiency and increase the electrode resistance [20,34,35]. In this work, the amorphous materials were synthesized by a precipitation method without heat treatment; a high population of surface hydroxyl groups and residual water was unavoidable. The effects of these impurities on the electrode performance of $a\text{VTO}$ were examined. To avoid these impurities, the synthetic atmosphere was changed from air to nitrogen, and the effect of this change on the impurity levels and electrochemical performance was also examined.

2. Experimental Section

Amorphous vanadium titanates ($a\text{VTOs}$) were synthesized by a precipitation method. Vanadium oxide sulfate hydrate (2.5 g, $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, Alfa Aesar) and titanium oxide sulfate sulfuric acid hydrate (2.5 g, $\text{TiOSO}_4 \cdot x\text{H}_2\text{O} + \text{H}_2\text{SO}_4$, Alfa Aesar) were dissolved in 250 mL of distilled water. Then, the precursor solution was dropped into a gas (air or nitrogen)-purged urea solution to obtain precipitates [36]. The reaction temperature was fixed at 60°C , and an ammonia solution was added dropwise to the solution to maintain the solution pH at 7. The precipitates obtained under air and nitrogen atmospheres are denoted $a\text{VTO}$ and $a\text{VTO-N}$, respectively. The resulting precipitates were centrifuged and washed with distilled water; this was followed by drying at 80°C overnight and additional drying at 300°C under vacuum for 2 h. For comparison, amorphous vanadium pentoxide ($a\text{V}_2\text{O}_5$) and titanium oxide ($a\text{TiO}_2$) were also synthesized using the same procedure.

The particle morphology was examined using

field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). Energy-dispersive X-ray spectroscopy (EDS) mapping was performed using a scanning transmission electron microscope (STEM, Tecnai F20). The surface area was measured from the nitrogen adsorption isotherm using a Micromeritics ASAP 2010 instrument. The X-ray diffraction (XRD) patterns were obtained using a Bruker D8 diffractometer equipped with Cu K α radiation (1.54056 Å). The atomic ratio of titanium and vanadium in *a*VTO was measured by the inductively coupled plasma (ICP) technique using the Optima-4300 DV installed at the National Center for Inter-University Research Facilities at Seoul National University. X-ray absorption spectroscopy data for the titanium K-edge ($E_0 = 4966$ eV) and vanadium K-edge ($E_0 = 5465.1$ eV) were obtained using transmission mode with a ring current of 320-400 mA at 3.0 GeV at the Pohang Light Source. A Si (111) monochromator crystal was used with detuning to 70% in intensity to eliminate the high-order harmonics. Energy calibration for the titanium and vanadium K-edges was conducted using titanium and vanadium metal foil. Fourier transform infrared (FTIR) transmission spectra for *a*VTO and the reference oxides were measured using a Bruker Vertex 80V IR spectrometer in vacuum. The samples for the transmission spectra were pelletized with potassium bromide (KBr).

To prepare the composite electrodes, the synthesized metal oxides, Super-P, styrene-butadiene rubber (SBR), and carboxymethyl cellulose (CMC) (80:10:5:5 in weight ratio) were mixed in an agate mortar and dispersed in distilled water. The slurry was then coated on copper foil (LS wire, thickness 20 μm) with a doctor blade in a drying room. The composite electrodes were punched and dried at 120°C overnight in vacuum. The mass loading of active material in the electrodes was 1.6-2.0 mg cm^{-2} . Coin cells (2032-type) were fabricated in an argon-filled dry box. Lithium foil and a trilayered polypropylene-polyethylene membrane (PP-PE-PP, Celgard 2320) were used as the counter electrode and separator, respectively. LiPF_6 (1.0 M) dissolved in ethylene carbonate and dimethyl carbonate (DMC) (1:2 in volume ratio) was used as the electrolyte. Galvanostatic charge/discharge measurements were performed at a current density of 100 mA g^{-1} over the potential range of 0.8-3.0 V (vs. Li/Li^+). X-ray photoelectron spectroscopy (XPS) data were collected in an ultrahigh-vacuum

multipurpose surface analysis system (Sigma Probe, Thermo Scientific, UK) operating at a base pressure of $<10^{-10}$ mbar. The photoelectrons were excited by an Al K α (1486.6 eV) anode operating at a constant power of 100 W (15 kV and 10 mA). For ex situ XPS analysis, *a*VTO and *a*VTO-N electrodes were prepared by embedding the powder in a copper foil to eliminate interference coming from the conductive carbon (Super-P) and the polymer binder (SBR-CMC). The cycled cells were disassembled, and the electrode samples were washed with DMC in an argon-filled glove box. They were then transferred to the XPS instrument without air exposure. The binding energy was calibrated from the hydrocarbon contamination using the C 1s peak at 285.0 eV.

3. Results and Discussion

Fig. 1a and 1b show FE-SEM images of the synthesized *a*VTO powder. Its size was approximately

Fig. 1. (a) and (b) FE-SEM images of *a*VTO, (c) STEM image of *a*VTO, (d) and (e) EDS mappings of vanadium and titanium, and (f) XRD patterns of *a*VTO powder and *a*V₂O₅ + *a*TiO₂ (1:2 in mole ratio) powder dried at 300°C under vacuum.

several microns, and it consisted of small primary particles <100 nm in size, resulting in a large surface area of $54.39 \text{ m}^2 \text{ g}^{-1}$. The morphology of *a*VTO powder is advantageous in high-power applications because it provides a short Li^+ diffusion path and a larger contact area with the electrolyte solution [13-17]. Fig. 1c-e show the STEM image and EDS mappings, which demonstrate that titanium and vanadium are homogeneously dispersed within the nanosized primary particles. The ICP measurement reveals that the atomic ratio of titanium and vanadium is close to 1:1. The XRD pattern obtained from the *a*VTO pow-

der was featureless, indicating the amorphous nature of the synthesized powder (Fig. 1f).

The metal valence and local structure of metal ions in *a*VTO, *a*V₂O₅, and *a*TiO₂ were examined using X-ray absorption near-edge structure (XANES) spectra (Fig. 2a and 2b) and extended X-ray absorption fine structure (EXAFS) spectra (Fig. 2c and 2d). The appearance of the main edge of vanadium, which is a common feature of crystalline vanadium pentoxide (*c*V₂O₅) [37], indicates that the vanadium valence is 5+ for both *a*VTO and *a*V₂O₅ (Fig. 2a). The titanium valence is 4+ in both *a*VTO and *a*TiO₂ because the

Fig. 2. XANES data for *a*VTO and some reference oxides: (a) vanadium K-edge and (b) titanium K-edge. XANES data for *a*VTO and *a*TiO₂ are taken from a physically mixed *a*TiO₂ + *a*V₂O₅ electrode. Fourier transformed EXAFS data: (c) vanadium and (d) titanium K-edge for *a*VTO and reference oxides. EXAFS data for amorphous V₂O₅ and TiO₂ are taken from a physically mixed *a*V₂O₅ + *a*TiO₂ electrode. (e) FTIR spectra measured in vacuum for KBr-pelletized *a*VTO, *c*V₂O₅, *c*TiO₂, and a physical mixture of *a*V₂O₅ + *a*TiO₂ (1:2 mol ratio).

main edge appears as it does for crystalline titanium oxide ($c\text{TiO}_2$), which also has a Ti valence of 4+. The local structure of V^{5+} in $a\text{VTO}$ and $a\text{V}_2\text{O}_5$ was analyzed using the data shown in Fig. 2a and 2c. The pre-edge of the vanadium K-edge does not appear if the local symmetry of V^{5+} is octahedral. With a decrease in the local symmetry from an octahedral geometry, the pre-edge of the vanadium K-edge becomes stronger owing to a formally forbidden dipole transition from the vanadium 1s orbital to oxygen 2p states hybridized with 3d orbitals [22]. As shown in Fig. 2a, the orthorhombic V_2O_5 ($c\text{V}_2\text{O}_5$) shows a strong pre-edge because vanadium ions are located at the five-coordinate (VO_5) square pyramidal sites [29], which exhibit much lower symmetry than the six-coordinate octahedral structure. This strong pre-edge peak is also observed in both $a\text{V}_2\text{O}_5$ and $a\text{VTO}$, implying that the local structure of V^{5+} is not octahedral. The detailed local structure can be estimated from the V-O shell depicted in Fig. 2c. The V-O peak of orthorhombic V_2O_5 ($c\text{V}_2\text{O}_5$) has low intensity and is divided into two (black line), which must be due to the fact that the V-O shell is composed of one short V = O bond (1.07 Å) and four long V-O bonds (1.53 Å) (five-coordinate square pyramidal sites, as shown in Fig. 2a). $a\text{V}_2\text{O}_5$ also shows a similar V-O shell comprising a short V = O bond and long V-O bonds, although the former is more intense than the latter (blue line), illustrating that the local structure of V^{5+} in $a\text{V}_2\text{O}_5$ does not differ greatly from that in $c\text{V}_2\text{O}_5$ (five-coordinate). However, the local structure of V^{5+} in $a\text{VTO}$ is not five-coordinate, as demonstrated by the EXAFS data in Fig. 2c. Namely, the V-O shell produces an intensified single peak (red) at 1.20 Å, which corresponds to a tetrahedral structure around the V^{5+} ions [38]. The difference in V^{5+} local structure between $a\text{VTO}$ (four-coordinate) and $a\text{V}_2\text{O}_5$ (five-coordinate) indicates that $a\text{VTO}$ is not a physical mixture of $a\text{V}_2\text{O}_5$ and $a\text{TiO}_2$; rather, the V^{5+} and Ti^{4+} ions are homogeneously mixed at the atomic scale. The local structure modification and homogeneous atomic scale mixing of V^{5+} can also be observed in the FTIR spectrum of $a\text{VTO}$ (Fig. 2e). A sharp peak at about 995-1028 cm^{-1} , indicative of a V = O bond, was significantly reduced. A broad shoulder between 950 and 980 cm^{-1} , which is known to indicate the Ti-O-V bond, strongly implies chemical interaction between V^{5+} and Ti^{4+} [39].

The local structure of Ti^{4+} in $a\text{VTO}$ and $a\text{TiO}_2$ was

also analyzed. The titanium pre-edge peaks from crystalline (anatase) TiO_2 ($c\text{TiO}_2$) appear at 4969.2, 4970.8, 4972.0, and 4974.4 eV and are labeled A_1 , A_2 , A_3 , and B, respectively, as shown in the inset of Fig. 2b [40]. The first three (A_1 , A_2 , and A_3) are due to dipole transitions to titanium 4p states hybridized with titanium 3d orbitals that are split into the t_{2g} and e_g bands, respectively [40]. As shown in Fig. 2b, the A_2 and A_3 peaks of $a\text{TiO}_2$ and $a\text{VTO}$ are much stronger than those of $c\text{TiO}_2$, implying that the regular TiO_6 octahedron, which is dominant in anatase TiO_2 , is distorted to form an irregular fivefold coordination (TiO_5) structure in both $a\text{TiO}_2$ and $a\text{VTO}$ [18,41,42]. This feature can be ascertained from the radial distribution obtained from the Fourier transformation of the EXAFS spectra shown in Fig. 2d. The Ti-O bond in $c\text{TiO}_2$ is located at 1.41 Å, but this peak is shifted to 1.35 Å for $a\text{TiO}_2$ and $a\text{VTO}$. This observation agrees with the XANES spectra, which suggest irregular fivefold coordination of Ti^{4+} in $a\text{TiO}_2$ and $a\text{VTO}$ (Fig. 2b). That is, the Ti-O bond length is shorter for five-coordinate structures ($a\text{TiO}_2$ and $a\text{VTO}$) than for the six-coordinate structure ($c\text{TiO}_2$). In short, it is found that $a\text{VTO}$ is composed of homogeneous mixing of irregular TiO_5 and tetrahedral VO_4 at the atomic scale rather than a physical mixture of the two separate oxides.

The galvanostatic lithiation and delithiation voltage profiles of the Li/ $a\text{VTO}$ cell are shown in Fig. 3a. The $a\text{VTO}$ electrode shows a sloping voltage profile, which is a characteristic feature of amorphous electrodes, and exhibits a reversible capacity of 295 mA h g^{-1} in the first cycle. Note that this value is much larger than those of LTO (175 mA h g^{-1}), anatase TiO_2 (168 mA h g^{-1}), and even amorphous TiO_2 , which shows a slightly larger capacity than anatase TiO_2 (Fig. 3d) [7,43]. The electrode consisting of mechanically mixed $a\text{V}_2\text{O}_5$ and $a\text{TiO}_2$, which were mixed in a 1:2 mole ratio to simulate the atomic ratio (1:1) in $a\text{VTO}$, delivers a reversible capacity of 245 mA h g^{-1} in the first cycle (Fig. 3c). Note that the reversible capacity of the $a\text{VTO}$ electrode is larger than that of the mixed electrode, and the voltage profiles of the two are different in the first lithiation.

The redox behaviors of the two redox centers (V and Ti) in the $a\text{VTO}$ and $a\text{V}_2\text{O}_5 + a\text{TiO}_2$ electrodes were compared using ex situ XANES spectra (Fig. 4a and 4b). To obtain the relationship between the metal valence and absorption energy, XANES data were obtained from some reference oxides, namely, crys-

Fig. 3. (a) Lithiation/delithiation voltage profile obtained from Li/aVTO cell, (b) differential capacity plot derived from (a), (c) lithiation/delithiation voltage profile obtained from Li/aV₂O₅ + aTiO₂ (physical mixture in 1:2 mole ratio) cell, and (d) cycle performance of Li/aVTO, Li/aTiO₂, and Li/aV₂O₅ + aTiO₂ cells.

Fig. 4. Ex situ XANES spectra of (a) Ti K-edge and (b) V K-edge for aVTO, aTiO₂, and aV₂O₅ electrodes, which were obtained in the fully lithiated state (0.8 V vs. Li/Li⁺) and fully delithiated state (3.0 V) in the first cycle. Metal valence changes for (c) Ti and (d) V upon the first lithiation, which were estimated from (a) and (b), respectively.

talline titanium oxides (*c*TiO₂ and *c*Ti₂O₃) and vanadium oxides (*c*V₂O₅, *c*VO₂, and *c*V₂O₃), the metal valence of which has a formal value (for example, 4+ for *c*TiO₂ and *c*VO₂). The valence of the transition

metal ions was calculated assuming that the metal valence is linearly related to the position of the main absorption edge. The electron energy at the half-height of the main absorption edge was taken and

plotted, along with the estimated metal valences of the reference oxides. Note that the shape and position of the main edge depend on not only the metal valence but also the local structure and coordination of metal ions, such that the calculated values carry an appreciable uncertainty. As shown in Fig. 4c, the Ti valence in *a*VTO changes from 3.58+ to 3.74+. A comparable change is observed for *a*TiO₂ (from 3.61+ to 3.81+), illustrating that the electron-accepting ability of Ti ions is comparable for *a*VTO and *a*TiO₂. The redox behavior of V ions in *a*VTO and *a*V₂O₅ was also examined. As shown in Fig. 4d, the V valence in *a*VTO changes from 2.7+ to 4.6+, whereas it changes from 3.6+ to 4.7+ in *a*V₂O₅. Clearly, the oxidation state of V ions in *a*VTO is lower (2.7+) than that in *a*V₂O₅ (3.6+) upon lithiation, illustrating that the electron-accepting ability of V⁵⁺ ions as a redox center is greater in *a*VTO. As shown in Fig. 3a and 3c, the first reversible specific capacity of *a*VTO (295 mA h g⁻¹) is larger than that of the physically mixed oxide (*a*V₂O₅ + *a*TiO₂) (245 mA h g⁻¹). Hence, the extra capacity (ca. 50 mA h g⁻¹) delivered by *a*VTO can be attributed to the higher electron-accepting ability of the V⁵⁺ ions in *a*VTO. The apparent difference between *a*VTO and *a*V₂O₅ is due to the local structure; the V⁵⁺ ions in *a*VTO are four-coordinate, but those in *a*V₂O₅ are five-coordinate. The experimental data suggest that the difference in the local structure of the V⁵⁺ ions can cause different redox behavior.

The extra capacity delivered by *a*VTO can also be explained in another way. Namely, *a*VTO should carry both Li⁺ storage sites and redox centers for lithiation. Two possibilities exist. First, if *a*VTO has abundant Li⁺ storage sites (structural defects), which is likely because it is amorphous, the number of redox centers (number of electrons to be stored) determines the overall Li storage capacity. If this is the case, the changes in the electronic structure of *a*VTO, which can be caused by modification of the local geometry by homogeneous mixing of cations, can change the Li storage capacity. One example is the Co³⁺ ions in the spinel-structured LiMn_{2-x}Co_xO₄ and layered LiCoO₂. Both the redox potential and redox capacity of Co³⁺ ions are different in the two oxides [44]. Considering that Ti substitution in V₂O₅ can alter the electronic structure of its original framework [45,46], it is very likely that the V ions in the V-Ti-O structure have a different redox behavior

from those in V₂O₅. However, because it is difficult to analyze the band structure of amorphous materials, it is still unclear why the V ions in *a*VTO show a higher electron-accepting ability. The second possibility is the reverse case. Here, if the number of Li⁺ storage sites is smaller than that of redox centers, the overall capacity is determined by the former. If this is the case in *a*VTO, the larger specific capacity of *a*VTO over the mixed electrode (*a*V₂O₅ + *a*TiO₂) can be accounted for by the generation of extra Li⁺ storage sites (structural defects) resulting from the addition of V⁵⁺ ions to the *a*TiO₂ matrix. This possibility has been proposed in previous studies [32,33].

As shown in Fig. 3a and 3b, the Li/*a*VTO cell shows a large irreversible capacity in the first cycle, which diminishes in subsequent cycles. The major irreversible reactions occur at <2.0 V, as indicated by an arrow in Fig. 3b. Two possibilities exist for the irreversible reactions: electrolyte decomposition and Li reaction with residual water or surface hydroxyl groups. The former possibility is discarded because electrolyte decomposition is commonly observed at 0.7-0.8 V (vs. Li/Li⁺). The latter possibility seems more probable because the amorphous samples can carry residual water and surface hydroxyl groups, as they were prepared by drying at 300°C under vacuum. Two irreversible reactions (Eqns. 1 and 2) can be assumed [34,35]:

This is validated by the XPS spectra obtained from the *a*VTO electrode before and after lithiation (Fig. 5a and 5b). The O 1s spectra obtained before lithiation were deconvoluted into three peaks. The peak at 530.7 eV corresponds to the bulk oxygen in amorphous metal oxides. The O 1s photoelectrons at 532.7 and 534.0 eV come from the oxygen in hydroxyl groups and adsorbed water on the metal oxide surface, respectively [47]. As shown in Fig. 5a, the surface of *a*VTO is covered with hydroxyl groups. The four peaks in the O 1s spectra obtained after lithiation were assigned according to the reported binding energies: Li₂O at 528.5 eV, LiOH at 531.5 eV, Li₂CO₃ and

oxygen atoms doubly bound to carbon atoms at 532 eV, and oxygen bound to carbon with a single bond at 533.5 eV [48,49]. A large amount of Li_2O and LiOH is found on the surface of lithiated $a\text{VTO}$. Clearly, the surface hydroxyl groups and residual water in $a\text{VTO}$ are converted into Li_2O and LiOH according to Eqns. 1 and 2, which appear as the irreversible capacity in Fig. 3a and 3b.

Fig. 5. O 1s XPS spectra: (a) $a\text{VTO}$ in the initial open-circuit voltage (OCV) state, (b) $a\text{VTO}$ after lithiation down to 0.8 V, (c) $a\text{VTO-N}$ in the initial OCV state, and (d) $a\text{VTO-N}$ after lithiation down to 0.8 V.

Fig. 5c displays the O 1s XPS spectra obtained from the pristine $a\text{VTO-N}$ electrode. The major O 1s photoelectrons are emitted from the lattice (bulk) oxygen. The population of surface hydroxyl groups and adsorbed water is much smaller than that in $a\text{VTO}$. The only difference between the two samples is the synthetic atmosphere (air and nitrogen). It is curious that more surface hydroxyl groups form in the presence of excess oxygen. The following reaction is proposed. Molecular oxygen can be converted into lattice oxygen, accompanied by generation of metal vacancies and holes as described by Eqn. 3. In the presence of water, the lattice oxygen and holes react further with water to generate surface hydroxyl groups as shown in Eqn. 4 [50].

If this is the case, the reduced population of surface hydroxyl groups on $a\text{VTO-N}$ can be rationalized.

The morphology and bulk properties of $a\text{VTO-N}$ are very similar to those of $a\text{VTO}$ even though $a\text{VTO-N}$ has a larger surface area ($62.77 \text{ m}^2 \text{ g}^{-1}$). The

Fig. 6. (a) Lithiation/delithiation voltage profile obtained from the $\text{Li}/a\text{VTO-N}$ cell, (b) differential capacity plot derived from (a), (c) comparison of the cycle data and Coulombic efficiency of $a\text{VTO}$ and $a\text{VTO-N}$, and (d) rate performance of $a\text{VTO}$ and $a\text{VTO-N}$ electrodes.

metal valence is not changed even when the reaction atmosphere is changed from air to nitrogen. As shown in Fig. 6a, the electrode performance of the Li/*a*VTO-N cell, including the reversible capacity and cycling ability, is also comparable to that of Li/*a*VTO. The notable difference is the irreversible capacity in the first cycle. The irreversible capacity observed at <2.0 V in the *a*VTO electrode (Fig. 3b) is notably diminished in the *a*VTO-N electrode (Fig. 6b). As a result, the initial Coulombic efficiency increases in the Li/*a*VTO-N cell, as shown in Fig. 6c. Furthermore, the Li/*a*VTO-N cell shows higher Coulombic efficiency during cycling, indicating that the decreased quantity of surface hydroxyl groups positively affects the side reactions even after the first cycle.

The Li/*a*VTO-N cell outperforms the Li/*a*VTO cell with respect to the rate capability (Fig. 6d). As pointed out above, the only difference between the two electrodes is the quantity of surface hydroxyl groups; thus, the difference in rate capability should be explained on the basis of the quantity of surface hydroxyl groups. As shown in Fig. 5d, the quantity of inorganic components such as Li₂O and LiOH, which are known to impede Li⁺ diffusion [51], is greatly diminished on the *a*VTO-N electrode. This must be due to the lower quantity of surface hydroxyl groups on *a*VTO-N. As a result, the formation of highly resistive inorganic compounds (Li₂O and LiOH) is greatly suppressed during cell cycling. In short, a lower population of surface hydroxyl groups on *a*VTO-N is responsible for the decrease in irreversible capacity and the enhanced rate capability of the Li/*a*VTO-N cell.

4. Conclusions

To increase the specific capacity of amorphous titanium dioxide (*a*TiO₂) electrodes, which are known to exhibit a reasonable rate capability, V⁵⁺ ions were incorporated into the *a*TiO₂ matrix. The physico-chemical properties and electrode performance of the resulting amorphous vanadium titanates (*a*VTOs) are summarized as follows.

(i) The prepared samples were not a physical mixture of *a*V₂O₅ and *a*TiO₂. The V⁵⁺ and Ti⁴⁺ ions were homogeneously dispersed in the amorphous oxide matrix at the atomic scale.

(ii) The V⁵⁺ ions in *a*VTO were at four-coordinate sites, in contrast to the five-coordinate V⁵⁺ ions in

*a*V₂O₅. However, fivefold coordination of Ti⁴⁺ ions appeared for *a*TiO₂ and *a*VTO.

(iii) The oxide electrodes showed a sloping charge/discharge voltage profile, which is a characteristic feature of amorphous electrodes. Li⁺ storage in structural defects (vacancies, void spaces, cluster gaps, or interstitial sites) can thus be assumed.

(iv) The reversible specific capacity of *a*VTO was larger than that of the physically mixed (*a*V₂O₅ and *a*TiO₂ in stoichiometric ratio) electrode. The extra capacity delivered by *a*VTO was thus attributed to contributions from the fourfold-coordinated V⁵⁺ ions in *a*VTO. Two possibilities were proposed for this contribution. One is the modification of the electronic structure by a local geometric change of V ions in *a*VTO. The other is the creation of extra Li⁺ storage sites (structural defects) by the incorporation of V⁵⁺ ions into the *a*TiO₂ matrix.

(v) The surface hydroxyl groups and residual water in *a*VTO caused a serious irreversible reaction and formation of highly resistive inorganic species. The impurity population was, however, greatly reduced by changing the synthetic atmosphere from air to nitrogen. The amorphous vanadium titanate prepared under nitrogen (*a*VTO-N) outperformed that prepared under air in terms of the Coulombic efficiency and rate capability.

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