Atomic resolution observation of conversion-type anode RuO₂ during the first electrochemical lithiation

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RuO₂ is a model transition metal oxide for promising conversion-type electrodes. Here we use *in-situ* transmission electron microscopy (TEM) to investigate the lithiation mechanism of RuO₂ nanowire grown by chemical vapor deposition (CVD) method on Si substrate. We show that the phase evolution of RuO₂ nanowire during first electrochemical lithiation. The constitution and distribution of the resultant products are shown in a single nanowire with the reaction front. Near the reaction front, a step-like surface with atomic-scale rough ledges are formed at the phase boundary. At early stage lithiation, lattice distorted nano-areas and a high density of lattice dislocations with large strain surrounded are observed due to lithium insertion behavior during electrochemical lithiation.

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1.Introduction

Transition metal oxides have drawn intense research for alternative anode materials of rechargeable lithium-ion batteries (LIBs), due to their higher capacity two to three times as much as those of current commercial carbon anode materials.¹⁻⁵ They lead to a new Li storage mechanism different from classical lithiation/delithiation process, based on the reversible formation and decomposition of Li₂O for the transition metal oxide referred as “conversion reaction” described as follows:

where M represents transition metal.⁶⁻⁷ Moreover, the reaction potential depending on the M-O bond can be tuned by selecting an appropriate transition metal for the application requirement.⁸⁻⁹ Therefore, transition metal oxides have been proposed to be a promising candidate for designing next generation LIBs. However, the practical use of these materials is still impeded by their generally rather poor cyclability.^{3, 10-14} Huge volume expansion leads to significant morphology change in the transition metal oxide anodes, such as pulverization and cracking, which cause loss of electrical contact and eventually capacity fading. Despite the effect of the solid electrolyte interphase (SEI), the problems are suggested to be significant volume changes leading to induced mechanical stresses large enough to fracture, which eventually make the system becoming electrically disconnected and possibly inactive.¹⁵⁻¹⁷ Meanwhile, the Coulomb efficiency of the first cycle is of critical importance to most anode materials and determines the cycling behavior afterwards.^{18,19} Therefore, it is crucial to uncover what exactly happens in the first lithiation.

Among various transition metal oxide materials, RuO₂ is considered to be a prototype material that exhibits a high measured capacity of 1130 mAhg⁻¹ and a

metallic conductivity.²⁰⁻²² It also suffers from the volume expansion once upon lithiation and thus capacity dropping.^{20,23-25} The lithiation reaction follows as

This makes it a model material to study the conversion reaction mechanism of transition metal oxides. Interestingly, SnO_2 as well as TiO_2 with the same tetragonal rutile structure has been intensively investigated as important anode materials. Huang *et. al.*²⁶ revealed the lithiation mechanism of SnO_2 using *in-situ* TEM study by observing the reaction front. Further investigations²⁷ provided the atomic-scale observation of lithiation reaction front to better understand the lithiation nature in rutile SnO_2 nanowire. However, there is still a lack of atomistic understanding of the lithiation mechanism of a transition metal oxide.

In the present work, we carried out *in-situ* TEM study on the first lithiation for RuO_2 to reveal the lithiation mechanism underlying the conversion reaction and electrochemical behavior at atomic scale. These findings show that the lattice dislocations accompanied by lattice distortion and expansion generated near the reaction front upon lithiation. The induced high density of lattice dislocations with large strain surrounded should be attributed to lithium insertion behavior during electrochemical lithiation. A step-like surface with atomic-scale rough ledges appeared at the phase interface due to the non-uniform lithiation. And not fully lithiated segments nearby left embedded in the $\text{Ru}/\text{Li}_2\text{O}$ network. The above results provide a better understanding of the electrochemical lithiation behavior of conversion-type materials.

2. Experimental section

RuO_2 nanowires preparation:

The single-crystal RuO₂ nanowires were synthesized by chemical vapor deposition (CVD) method as a result of the thermal conversion from supercooled liquid nanodroplets^{28,29}. The growth of RuO₂ nanowires was carried out in the easy-developed CVD system (Fig. S1). First, RuO₂ powder (99.9%, Aldrich) was loaded in the alumina boat and was further introduced at the center of a quartz tube furnace. A piece of (001) Si substrate of 1 cm × 4 cm was cleaned with acetone and distilled water. After that, the substrate was dried with N₂ gas flow and placed over the alumina boat at a point ~3 cm downstream of the RuO₂ powder source. He (99.999%) carrier gas was used to flow for about 10 min with a flow rate of 300 sccm before heating and the pressure of the quartz tube furnace was kept about 0.5 atm with pumping system. The furnace was then heated to the temperature of 950 °C at the rate of 100 °C/min with flowing He (99.999%, 300 sccm) and O₂ (99.9%, 10 sccm). The RuO₂ nanowire growth proceeded for 2h in the heating furnace. The furnace was then cooled to room temperature under the flowing He.

In-situ TEM setup:

In order to investigate the lithiation mechanism of RuO₂ nanowire, a nanoscale battery^{30,31} was built for TEM study. The nanoscale battery was established in a Nanofactory TEM scanning tunnelling microscope (STM) holder (Fig. S2). First, RuO₂ nanowires were scratched off from the Si substrate and transformed onto the Au tip with conductive epoxy. Good electrical contact was checked. Then Li metal was scratched off from a Li metal foil with W tip mounted onto the conductive hat. The holder was quickly inserted into TEM microscope. The Li₂O was formed to serve as a solid-state electrolyte. The experiments were performed using a high resolution TEM (TITAN 80-300, FEI). Li/Li₂O end was driven to touch the other end of RuO₂

nanowires by using Nanofactory system. A bias voltage of -2V to -4V was applied by the Nanofactory system to conduct the lithiation process.

2. Results and Discussion

Fig. 1a and b illustrate the scanning electron microscope (SEM) images of as-grown RuO₂ nanowires on the Si substrate. The nanowires were mostly distributed with 100-200 nm in diameter and 2-8 μ m in length (Fig. 1b). The TEM image of the nanowire taken along $[\bar{1}10]$ (Fig. 1c) indicated clearly a $[001]$ growth direction with side wall and tip facets terminated by $\{110\}$ and $\{111\}$ planes respectively, compared similarly with previous results.^{32,33} These crystalline characteristics were dependent on the surface energies of the crystal planes, i.e., $(001) > \{111\} > \{110\}$.²⁸ The TEM image taken along another zone axis of $[\bar{1}\bar{1}2]$ and the corresponding selected area electron diffraction (SAED) pattern (inset) further indicated the crystallographic features of RuO₂ nanowires (Fig. 1d).

The evolution of SAED patterns taken along $[\bar{1}\bar{1}0]$ zone axis at the same area of the RuO₂ nanowire during the whole lithiation process is recorded in Fig. 2a-d. The pristine RuO₂ nanowire has a single crystal rutile structure with (110), (111), (001) and (002) indexed in Fig. 2a. As the lithiation process took place (Fig. 2b), the sharp diffraction spots were coarsened and extended into short curves. The red arrows referring to Ru (100), (101) and (110), while very weak diffuse diffraction rings appeared as Li₂O (200) and (311). Besides, some weak diffraction spots (green arrows) appeared in the vicinity of the spots for RuO₂ (001), (110), (002), (111), but with a larger length-width ratio along $[001]$ direction. They can be identified to an intermediate phase Li_xRuO₂ with certain Li insertion into RuO₂, an intercalation

structure analogue to that of LiRuO_2 .^{20,34,35} As the lithiation process continued (Fig. 2c), RuO_2 diffraction spots disappeared, leaving Ru and Li_2O diffraction features. However, the diffraction spots for Li_xRuO_2 cannot be seen clearly for it should decompose into Ru and Li_2O almost completely. At the final stage (Fig. 2d), the only left diffraction patterns were for Ru and Li_2O , which is in accordance with the final resultants of the lithiation process. The corresponding schematics of reaction stage are shown in Figures 2e-h.

Fig. 3a shows a lithiated RuO_2 nanowire with reaction front. The SAED pattern in Fig. 3b indicates a rather well single crystallinity with some blurring diffraction spots and diffuse rings. It suggests that the nanowire beyond the reaction front still remain RuO_2 crystal structure though minor lithiation takes place near the outer surface layer. On the other side of the reaction front, the SAED patterns in Fig. 3c indicated that RuO_2 phase completely changes into the final resultant phases of Li_2O and Ru. A great many nano-particles of Ru are embedded in the Li_2O matrix. A high resolution TEM image of area (marked 1) shows that the Ru nanocrystals with (101) interplaner spacing of $2.1\text{\AA}$ are visible within the matrix (Fig. S3).

The detail of the reaction front is illustrated in Figure 4. The HAADF images (Fig. 4a) gives the Z contrast information of the neighborhood area at the reaction front. The trace of lithium can be detected across the reaction front. The shape of the reaction front is not imaginary smooth. Two stripes with darker contrast compared to surrounded area appear from the final resultant phase of Li_2O and Ru due to lithium invasion. Fig. 4b shows the magnified image of rectangular area with the stripe below in Fig. 4a. The stripe contrast should be related to three different area denoted by I, II, and III. Area II consists of Ru nano-sized particles embedded in Li_2O matrix, while Area I and III consist of initially lithiated RuO_2 and not fully lithiated segment left respectively. It

may indicate that the lithiation reaction is not proceeded uniformly. The existence of not fully lithiated segment in area III may lead to a possible capacity loss. A close-up look was taken from the rectangular area marked 2 (Fig. 4c). The HRTEM image shows that the atomic arrangement at the two phase interface. A step-like surface consists of several $(01\bar{1})$ facets with rough atomic-scale ledges between adjacent facets, which is probably due to the non-uniform lithiation. Meanwhile, it is easy to observe initially lithiated lattice distorted nano-areas nearby. Fig. 4d shows another area (white rectangle marked 3) with a heavier lattice distorted nano-areas. Besides, some dislocations can be found in the above lattice distorted areas.

In order to further investigate the lattice distorted nano-areas with dislocations to gain deeper insights into Li insertion in RuO_2 , the atomic scale imaging of initial lithiation was applied. As shown in Fig. 5a, Li insertion into RuO_2 crystal leads to the distortion in the host structure, emerging with nano-sized lattice distorted areas, where the lattice fringes became indiscernible. The HRTEM image taken along $[1\bar{1}\bar{1}]$ zone axis illustrated a high density of dislocations located at nano-sized areas, which is estimated to be about 10^{13} cm^{-2} according to several HRTEM images. The dislocations in the white square are analyzed by transferring to inverse fast Fourier transformed (IFFT) image (Fig. 5b). By using Burgers loops, the dislocation on the upper side was determined to be $b=[101]$, while interestingly the dislocation on the underside only a few atoms distance nearby was determined to be $b=[\bar{1}0\bar{1}]$ with the opposite sign. Meanwhile, the same type of dislocations can be found in other nano-sized areas around. These dislocations can glide on $\{011\}$ planes in the $\langle 101 \rangle$ directions, which were clarified as the most active slip system in rutile structure crystals.^{36,37} However, the generation of dislocations in RuO_2 accompanied with locally severe lattice distortions

is different from that leading long stripes in the case of SnO_2 ²⁷ (see Fig. S4). According to the energetically calculation for rutile structure crystals including TiO_2 , SnO_2 and RuO_2 , $\langle 001 \rangle$ crystallographic direction with the lowest energy cost is the most favorable lithium diffusion pathway.^{27,38-41} But the energy difference for Li ion arrangement along c axis and a or b axis is much lower in RuO_2 than that in TiO_2 or SnO_2 .^{39,41-43} As a result, the negative effect of low diffusivity in ab planes on the migration of Li along c direction in RuO_2 is not as pronounced as in TiO_2 or SnO_2 . Therefore, it should lead to different lithiation induced features in RuO_2 . Strain mapping (Fig. 5c) calculated by geometrical phase analysis (GPA) indicates a $\sim 10\%$ lattice expansion in RuO_2 due to Li intercalation. The core of the dislocation is just located at the intersection of compression and tension field (Fig. 5d). The large lattice expansion and such a high density dislocations should result in stress concentration and in turn facilitate the diffusion of lithium ions into RuO_2 crystal. The attraction and repulsion between the dislocations can promote the movement, reaction and generation of dislocations and thus further facilitate the diffusion of lithium ions. On the other hand, it would deteriorate mechanical stability and may be a reason for the possible mechanical failure during lithiation.

3. Conclusions

In-situ TEM study shows the lithiation behavior of RuO_2 nanowire at atomic resolution during the first lithiation. During the lithiation process, an intermediate phase of Li_xRuO_2 is formed due to partial lithium ions intercalated into RuO_2 host structure. The fully lithiated mixed phase of $\text{Ru/Li}_2\text{O}$ is finally formed behind the reaction front, while un-lithiated part far beyond the reaction front almost stays pristine RuO_2 structure. A step-like surface with atomic-scale rough ledges appears at

the phase boundary. Below the surface, initially inserted lithium ions make a great deal of lattice distorted nano-areas. A high density of dislocations are also generated in the nano-sized areas, which causes a heterogeneous strain distribution in the local areas. Stress concentration will possibly occur during lithiation process and it may be a reason for the mechanical degradation of RuO₂ nanowire. However, the interaction and movement of the dislocations would further facilitate the diffusion of lithium ions. This could provide a better understanding of electrochemical lithiation behavior of transition metal oxide electrode and it might pave the way for further improving the performance.

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List of Figure Captions

Fig.1 SEM image of RuO₂ nanowires grown on (001) Si substrate, showing tetragonal structure grown: (a) low-magnification, (b) high-magnification. (c) TEM image of a [001] direction grown RuO₂ nanowire taken along the zone axis of $[\bar{1}10]$. The inset shows the high resolution TEM (HRTEM) image of the tip of the nanowire. (d) TEM image of another zone axis of $[\bar{1}\bar{1}2]$. The insets are the corresponding SAED patterns and HRTEM image.

Fig.2 a)-d) The evolution of SAED patterns of RuO₂ nanowire along $[1\bar{1}0]$ zone axis during lithiation and e)-h) corresponding schematic of reaction stages.

Fig.3 a)TEM image of lithiated RuO_2 nanowire with reaction front. b) SAED pattern of rectangular area behind reaction front, c) SAED pattern of rectangular area behind reaction front.

Fig.4 a) High angle annular dark field (HAADF) image of the reaction front. b) magnified TEM image of rectangular area. c) HRTEM image of area 2 and d) HRTEM image of area 3.

Fig.5 a) HRTEM image of initially lithiated RuO_2 , b) Inverse Fast Fourier transformed (IFFT) image of the square. c) corresponding strain mapping of a) by GPA, d) magnified image of the square.

Figures of supporting information:

Fig. S1 Schematic view of the easy-developed CVD system for RuO₂ nanowires growth.

Fig. S2 Nanoscale battery setup for in-situ TEM in the Nanofactory STM holder.

Fig. S3 HRTEM image of Ru nanoparticles embedded in the matrix.

Fig. S4 a) lithium insertion induced stripe in SnO_2 nanowire; b) lithium insertion induced lattice distorted nano-areas in RuO_2 nanowire.