Although lithium-ion batteries that run on the conversion reaction have high capacity, their cyclability remains problematic due to large volume changes and material pulverization. Dimensional confinement, such as 2D thin film or nanodots in a conductive matrix, is proposed as a way of improving the cyclic stability, but the lithiation mechanism of such dimensionally controlled materials remains largely unknown. Here, by in situ transmission electron microscopy, lithiation of thin RuO$_2$ films with different thicknesses and directions of lithium-ion diffusion are observed at atomic resolution to monitor the reactions. From the side-wall diffusion in ≈4 nm RuO$_2$ film, the ion-diffusion and reaction are fast, called “interface-dominant” mode. In contrast, in ≈12 nm film, the ion diffusion–reaction only occurs at the interface where there is a high density of defects due to misfits between the film and substrate, called the “interface-to-film” mode. Compared to the side-wall diffusion, the reaction along the normal direction of the thin film are found to be sluggish (“layer-to-layer” mode). Once lithiation speed is higher, the volume expansion is larger and the intercalation stage becomes shorter. Such observation of preferential lithiation direction in 2D-like RuO$_2$ thin film provides useful insights to develop dimensionally confined electrodes for lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) are spreading in the secondary rechargeable battery market in devices from portable electronics to large-scale electric vehicles and power tools that require large capacity, fast charge/discharge, and high stability.$^{[1–4]}$ The commercialized electrode materials for these batteries are mainly run on the intercalation mechanism, e.g., graphite with an interlayer spacing of 0.34 nm as anode of LIBs with stable and reversible cyclability.$^{[5–7]}$ In particular, Li$_4$Ti$_5$O$_12$ has been reported to have excellent operating stabilities due to its zero-strain characteristic during electrochemical reactions and high potential above 1.5 V versus Li.$^{[8,9]}$ However, these commercialized anode materials based solely on intercalation reaction have limitations in their large-scale device applications, due to the theoretical capacity limit (graphite: 372 mAh g$^{-1}$, Li$_4$Ti$_5$O$_12$: 175 mAh g$^{-1}$). There have been many research efforts to develop electrodes with various structure and compositions for LIBs with high capacity and cyclability.$^{[10–14]}$

Among them, development of an electrode based on the conversion reaction is promising, as the capacity of a conversion reaction electrode is normally much higher than that based solely on an intercalation reaction. However, unlike the intercalation reaction, the structure framework of the host material collapses in a conversion reaction, causing not only large volume change but also phase transformation and separation. There are thus many problems in a conversion reaction–based electrode, such as large overpotential, sluggish kinetics, and large volume change. Each of these will lead to a low cyclic stability. Dimensional confinement such as 2D thin film or quantum dots within a conductive matrix have been proposed as a way of improving the cyclic stability of the conversion reaction electrodes.$^{[15–17]}$ This approach could enable conversion-based materials to serve as practical electrodes for LIBs. In a dimensionally confined and low-dimensional material, it is expected that reaction products can be accommodated to maintain contact with an electric collector, where the volume change hopefully can be suppressed and the new phase nucleation and growth ideally can be controlled.$^{[18–20]}$ The actual mechanism of lithiation in such a dimensional confined electrode, however, remains largely unknown.
The transition metal oxide, RuO$_2$, is one of the anode materials for full-cell LIBs based on a conversion reaction with a high theoretical capacity, metallic conductivity, high chemical/thermal stability, and electrochemical redox properties. As reported, RuO$_2$ is an ideal material for theoretical study, with which the understanding can be transferred to other battery systems.$^{[23–29]}$ Here, we used RuO$_2$ as a testing electrode material run on the conversion reaction to study the effects of dimensional confinement. RuO$_2$ thin films at different thickness were grown first by pulsed laser deposition (PLD). With an electric biasing transmission electron microscopy (TEM) holder with a movable probe, a small prototype all solid lithium-ion battery half-cell can be built inside the TEM.$^{[30–34]}$ In the half cell, RuO$_2$ thin film was used as cathode, the Li$_2$O as solid electrolyte and Li as anode. We then studied the morphological and structural evolutions of the RuO$_2$ thin films’ lithiation. We designed three types of in situ TEM experiments: RuO$_2$ film of 4.1 nm (Type I) and 12.4 nm (Type II) in thickness with Li-ion diffusion along the side-wall direction of the film, and RuO$_2$ film of 12.4 nm with Li-ion diffusion along the vertical direction (direction perpendicular to the film) as Type III (Figure S1, Supporting Information).

The pristine RuO$_2$ film is uniformly formed on the Al$_2$O$_3$ substrate (Figure 1a and Figure S2 (Supporting Information)). Figure 1a shows the cross-sectional TEM image of RuO$_2$ films on Al$_2$O$_3$ substrate. A thin layer of Pt was deposited on top of RuO$_2$ as the protecting layer. From selected-area electron diffraction (SAED) patterns in Figure 1b,c, the RuO$_2$ film with tetragonal structure was epitaxially grown on the single-crystalline Al$_2$O$_3$ substrate (RuO$_2$ (101)//Al$_2$O$_3$ (1̅2̅)). The lattice mismatch in the [1̅0̅1]$_{RuO_2}$ direction between RuO$_2$ and Al$_2$O$_3$ is about 6.4% and thus there is misfit strain in the interface due to the lattice mismatch (Figure S3, Supporting Information)$^{[35]}$. When the RuO$_2$ electrode is exposed to the electrolyte, the top surface provides a large area into which the Li-ion can diffuse, which has been marked as Diffusion Path 1 (Figure 1d). Meanwhile, there is also an opportunity for Li-ions to diffuse along the side-wall of the thin film, labeled Diffusion Path 2. In general, 2D-like thin films or plate-shaped materials have two Li-diffusion paths: a large top-bottom surface and ultrathin side wall. We thus designed in situ TEM experiments to investigate the electrochemical reaction of RuO$_2$ thin films with Li-ions by the two Li-ion diffusing routes (Figure 1f and Figure S1, Supporting Information).

The focused ion beam (FIB)-cleaved RuO$_2$ sample was mounted on the TEM grid as a cathode, and the Li$_2$O solid electrolyte with Li metal (as anode) was selectively connected by STM control system to build a half-cell battery inside the TEM. The diffusion of Li-ions along the RuO$_2$ films is controlled by potentiostatic bias between the two electrodes. By positioning the Li$_2$O/Li probe in different orientations along the RuO$_2$ thin sections prepared by FIB, the diffusing path of Li-ions can be directed either along the top surface or along the side-wall of the thin film. The interface between an Al$_2$O$_3$ substrate and the RuO$_2$ film can be identified due to the lattice mismatch (Figure 1e).

The Li-ion diffusion along the side-wall direction in an ultrathin RuO$_2$ films is fast, as the entire film is under the direct influence of the interface. We fabricated 4.1 nm RuO$_2$ films onto Al$_2$O$_3$ substrate to study electrochemical behavior of ultrathin RuO$_2$ films (diffusion path 2), as shown in Figure 2a. The pristine RuO$_2$ film is uniformly formed on the Al$_2$O$_3$ substrate, showing atomic mismatch in the interface region and the film (Figure 2b). The counter electrode composed of Li metal and Li$_2$O electrolyte is then directly connected to the edge of RuO$_2$ (prepared by FIB technique, as shown in Figure S1a, Supporting Information), enabling only Li-ion diffusion along the side-wall direction. Meanwhile, the other side of the RuO$_2$ film is connected to the Pt electrode as the electric collector of the electrochemical battery. The Li$_2$O/Li probe is connected to the left side of the film, and the Li-ion diffusion is from the left to right side. From the time-lapsed TEM images of RuO$_2$ films during lithiation process (Figure 2c and Video S1, Supporting Information), a gradual transformation in the RuO$_2$ film is observed from the left to the right side. For most metal oxides in lithiation, the electrochemical reaction consists of two steps: intercalation reaction followed by conversion reaction. In the intercalation reaction, the volume expansion is normally quite small with formation of Li$_x$M$_2$O$_3$ (where M = metal) type phase. Sequentially, large volume expansion and morphological changes are normally observed during the conversion stage, due to the formation of Li$_2$O and phase separation (i.e., island-like structure of mixture of metal and Li$_2$O). Here in the film of 4.1 nm, it is, however, hard to distinguish the two types of reactions in lithiation as the reaction interface moved from left to the right. When the reaction occurred very quickly, it seemed that the intercalation reaction (Li$_x$RuO$_2$) has been bypassed, as the single-crystalline RuO$_2$ film converted to nanostructured material with a mixture of Ru and Li$_2$O nanoparticles instantly. The thickness of RuO$_2$ film increased by 124.4% after full lithiation (Figure 2d).

We fabricated a thin RuO$_2$ film with the increased thickness of 12.4 nm and used it as the cathode in the half-cell miniature battery to monitor the effects of film thickness to electrochemical reactions. Figure 3a–d show time-lapsed cross-sectional TEM and corresponding high-resolution TEM (HRTEM)
images of the RuO<sub>2</sub> film during lithiation process. Interestingly, we found that Li-ion was selectively intercalated along the interface region at the early stage. Along the interface, the morphological and volumetric changes are obvious, while in the upper area of the film the original structure of RuO<sub>2</sub> maintains well without noticeable changes (15 s). In about 25 s lithiation after the RuO<sub>2</sub> in the interface has been completely lithiated, the reaction front moved upward indicating Li-ion diffusion from the interface region (with high Li-ion concentration) to upper RuO<sub>2</sub> film (with low Li-ion concentration). After the whole film has been lithiated, there is a 99.2% expansion in thickness (Figure S4a, Supporting Information). The observation shows that diffusion of Li-ion along the interface is much faster than that inside the film (Figure 3f). The enhancement of Li-ion diffusion along the interface region can be also identified in a thin film with ≈4 nm thickness under specific conditions (Figure S6 and Video S2, Supporting Information), in which the Li–Li₂O probe was connected far away from the edge of RuO<sub>2</sub> film thus Li-ions’ diffusion was reduced. Based on the previous studies, the lithiation behaviors can be classified according to the shape of RuO<sub>2</sub>. Nanowire normally shows “edge-to-edge” behavior which the lithiation starts from the contacted Li-metal.

Figure 1. a) Cross-sectional TEM image of RuO<sub>2</sub> thin film grown onto Al₂O₃ substrate. SAED patterns obtained from b) Al₂O₃ substrate and c) RuO<sub>2</sub> film including the substrate. d) Illustration of the diffusion paths that Li-ions can penetrate into RuO<sub>2</sub> thin film–based structure. e) Cross-sectional HRTEM image of RuO<sub>2</sub> film and Al₂O₃ substrate including the interface region between them. Each inset shows FFT patterns converted from RuO<sub>2</sub> film and the substrate, respectively. f) Schematic illustration of in situ experimental set up inside a TEM. RuO<sub>2</sub>-based electrode is prepared by FIB technique, and Li-metal electrode is controlled by STM system.
part to the other part\cite{26,29} while nanoparticle has a “shrinking-core" model in which reactions occur from the surface to the core. Here, we showed the interface formed in thin-film structure provides a fast ion-diffusion path for lithiation, which can be termed as “interface-to-film" process. The interface has a low activation barrier for diffusion and reaction, possibly due to the high strain existing in the interface. For dimensionally confined nanostructures, many interfaces are naturally created, which will alter the lithiation mechanism.

The phase transformation of RuO\textsubscript{2} thin film of 12.4 nm in lithiation are identified by HRTEM images and SAED patterns. Figure 4a shows SAED patterns of hetero-epitaxial grown RuO\textsubscript{2} film and Al\textsubscript{2}O\textsubscript{3} substrate, showing pristine RuO\textsubscript{2} film has a single-crystalline structure. As we confirmed from HRTEM observation and energy dispersive spectroscopy (EDS) map (Figure S7, Supporting Information), RuO\textsubscript{2} structure is converted into the expanded matrix with bright contrast and nanoparticles with the dark contrast after lithiation process. From SAED patterns and intensity profiles in Figure 4b,c, phases formed after lithiation can be identified as Li\textsubscript{2}O and metal Ru nanoparticles.

We then studied the Li-ion diffusion along the top surface direction of the RuO\textsubscript{2} thin film to investigate its effects to lithiation (diffusion path 1). The top surface will be fully exposed to electrolyte in a real battery, thus the behavior of Li-ion diffusion along this direction is important to understand the electrochemical behavior. To study the electrochemical diffusion of Li-ions in RuO\textsubscript{2} thin film by in situ TEM, a Li metal electrode is connected to a Pt top layer which located far enough from the edge of RuO\textsubscript{2} film. In contrast to the rapid diffusion of Li-ion along the interface region, Li-ions diffused slowly along the film-growing direction at the early stage (Figure 5 and Video S3, Supporting Information). We did not observe any diffusion and phase transformation along the interface, thus we termed this lithiation a “layer-to-layer" lithiation mode from

**Figure 2.** a) Cross-sectional TEM image of the Type I battery cell with 4.1 nm RuO\textsubscript{2} film. The inset shows FFT pattern obtained from Al\textsubscript{2}O\textsubscript{3} substrate. b) HRTEM image of the interface region between RuO\textsubscript{2} film and Al\textsubscript{2}O\textsubscript{3} substrate. c) Time lapse TEM images of RuO\textsubscript{2} thin film–based battery cell during the first lithiation process. Li-ions are diffused from the left side of TEM images marked by the arrow. d) Plot of the thickness and thickness expansion are based on the pristine value of RuO\textsubscript{2} film as a function of reaction time.
the top surface down to the whole film. This is similar to what previously reported in NiO thin film electrodes where conversion reaction started from the interfacial regions and propagated into the matrix. [17,36] Meanwhile, the electrochemical reaction occurred in the “layer-to-layer” type is much slower than the “interface-to-film” type. The film thickness increased from 12.0 to 16.0 nm after lithiation, given a 33.6% expansion (Figure S4b, Supporting Information). As the reaction Li-diffusion/reaction speed is relatively slow, there is an obvious stage of intercalation which could provide stable electrochemical properties (Figure S8, Supporting Information).

From the three in situ TEM observations performed in this work, we find that a fast Li-ion diffusion and reaction lead to a shortened intercalation stage and a large volume expansion. When the RuO2 thin film is only \( \approx 4 \) nm and the Li-ions are mainly diffused along the side-wall direction, its lithiation is dominated by interface effects and has a very high speed of lithiation. The reaction product showed, however, the largest volume expansion. When the film thickness increased to \( \approx 12 \) nm (while the lithium-ion diffuses still along the side-wall direction), the interface effect remained at the interface area which led to a medium lithiation speed. The reaction product also showed medium volume expansion. When the lithium-ion diffusion direction is controlled to mainly along the top surface to inner film direction, the lithiation/diffusion speed is slow. There is then an obvious and longer intercalation stage leading to the smallest volume expansion among the three observations.

Strain and defects-induced fast ion diffusion could be the underlying cause of the three lithiation modes. A recent DFT calculation shows that interfacial strain can strongly affect ionic conductivities and enhance lithium transport.[37] Our GPA analysis shows that the strain at the RuO2/Al2O3 interface has been released in the lithiated RuO2 thin film as shown in Figure S12 (Supporting Information). When lithium-ions diffuse from the side of the films, the interface where the strain is highest becomes the path of fast diffusion. This is the cause of the “interface-dominant” and “interface-to-film” lithiation modes.

Figure 3. a) Time lapse cross-sectional TEM images of 12.4 nm RuO2 thin film battery cell (Type II) during lithiation process. Li-metal electrode is connected to the right side of RuO2 film, and Li-ions are diffused along the blue arrows. HRTEM images of RuO2 film obtained from areas illustrated by squares at lithiation time of b) 0 s, c) 15 s, and d) 55 s lithiation time. e) FFT patterns converted from HRTEM image of (d). f) Cross-sectional TEM image of the boundary formed before/after conversion reaction of RuO2 film.

Figure 4. SAED patterns of RuO2 film of 12.4 nm on Al2O3 substrate obtained from the same region a) at the pristine state and b) after lithiation process, respectively. Single crystalline RuO2 film changes into Li2O and Ru phases after conversion process. c) Intensity profiles are based on the SAED patterns of Al2O3 substrate (Figure 1b) and RuO2 film onto substrate before/after lithiation process as a function of the distance.
When the film thickness is thin (such as \( \approx 4 \) nm), the enhancement of ionic diffusion in up and down interfaces becomes dominant which leads to a fast lithiation. Thus the “interface-dominant” mode happens only in very thin films in which film thickness is also an important factor. When Li-ions diffuse from the top of the films, lithiation occurs in “layer-to-layer” mode as there is no variation in strain and microstructure along this direction.

3. Conclusions

In summary, we studied the lithiation mechanism of RuO\(_2\) thin films by in situ TEM technique. Three types of miniature half-cells were designed and applied inside a TEM to characterize the electrochemical behavior and Li-diffusion pathway. The fast Li-diffusion and phase transformation occurred along the side-wall direction are observed in the ultrathin RuO\(_2\) film (\( \approx 4 \) nm), termed as “interface-dominant lithiation” mode. In the \( \approx 12 \) nm RuO\(_2\) film, the fast intercalation and conversion process are observed along the interface region, and the reaction is propagated into the entire film, termed as “interface-to-film” mode. When the lithium-ion diffusion is along the top-surface to inner film direction, the diffusion and lithiation are slow compared to the ones where interfaces are involved, the described “layer-to-layer” mode. Different diffusion and reaction mechanisms lead to different speeds of lithiation. Based on the current observations of lithiation in films with \( \approx 4 \) and \( \approx 12 \) nm, we found that the higher the lithiation speed, the shorter the intercalation stage and the larger the volume expansion. We believe our findings will provide insights to understand electrochemical mechanism of dimensionally confined nanostructures and pave ways to designing nanostructured thin film–based electrodes for high performance lithium-ion battery.

4. Experimental Section

**Thin Film Fabrication**: Crystalline RuO\(_2\) films were grown on sapphire (1\(\text{TO}_2\)) substrates. For the films grown at 350 °C, X-ray diffraction (XRD) established an alignment of RuO\(_2\) (101)/Al\(_2\)O\(_3\)(1\(\text{TO}_1\)). Grazing incidence X-ray measurements provide strong evidence that the same in-plane epitaxial relationship existed [\(\text{TO}_1\)]\(\text{RuO}_2\)//[\(\text{TO}_1\)]\(\text{Al}_2\)O\(_3\) and [\(\text{TO}_0\)]\(\text{RuO}_2\)//[\(\text{TO}_2\)]\(\text{Al}_2\)O\(_3\).\(^{35}\) The \(d\)-spacing of the (101) plane was measured to be 2.52 Å, which compared with the bulk value of 2.56 Å. The model suggested

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Figure 5. Time-lapse cross-sectional HRTEM images of RuO\(_2\) film with 12.0 nm thickness (Type III) during the first lithiation process. Li-metal is connected to the top Pt electrode, and Li-ions are diffused into RuO\(_2\) matrix through the top surface. The phase transformation of RuO\(_2\) film occurs via three steps: First, the intercalation process of vertical (120 s) and horizontal (124 s) direction. After inserting sufficient Li-ions into RuO\(_2\) film, it shows an amorphous-like structure (140 s). Finally, Li\(_2\)O phase and Ru nanoparticles with the dark contrast are formed during the conversion step (200 s).
the lattice mismatch is 6.4% in the \([101]_{\text{RuO}_2}\) direction and –3.5% in the \([010]_{\text{RuO}_2}\) direction. Before film deposition, the substrates were cleaned in acetone and isopropanol. The Pt/RuO2 multilayers were grown on the substrates by PLD using a PVD Products nanoPLD 1000. The laser was a 248 nm KrF excimer laser with 25 ns duration. The system had a background pressure of \(4 \times 10^{-8}\) Torr. The beam was focused onto a 1.5 × 3.5 mm spot on the targets. The targets were rotated at 15 rpm to prevent localized heating, and the laser pulses were swept across the target radius to additionally prevent localized heating. The target-substrate separation was fixed at 8 cm. The RuO2 layer was deposited using a dense hot-pressed RuO2 target, ~25 mm in diameter. A laser pulse energy of 200 mJ per pulse and a repetition rate of 5 Hz was used (This is the energy as measured at the laser; there is ~30% energy loss along the optical train between the laser and the target). The RuO2 films were deposited in a 10 mTorr argon ambient and a temperature of 350 °C. The substrates with the RuO2 films were removed to atmosphere and masked so as to cover the RuO2 film from both edges inward for 3 mm along the long axis of the substrate. The masked substrates were returned to the deposition chamber and pumped down to the background pressure. The Pt layer was deposited using a metallic Pt target, ~25 mm in diameter. A laser pulse energy of 250 mJ per pulse and a repetition rate 5 Hz was used. The Pt films were deposited in a 10 mTorr argon ambient and a temperature of 25 °C. X-ray reflectivity data (Figure S9, Supporting Information) show that the growing films have 40.9 and 112.5 Å thicknesses with surface roughness of 5–5.5 Å. XRR analysis used Motofit with a model that includes a sapphire substrate and RuO2 layer.38 XRD measurements confirm an alignment of RuO2 (101) in perpendicular direction to substrate with domain sizes, which are corresponded to the film thicknesses (Figure S10a, Supporting Information). Horizontal domain size calculated from the rocking curves (Figure S10b, Supporting Information) is about 530 nm for both films. The films deposited on sapphire (1T02) exhibit the epitaxial growth of RuO2 (Figure S11, Supporting Information).

**Battery Test:** To conduct cyclic voltammetry measurements of RuO2 thin film, RuO2 films of similar thicknesses were deposited in the same PLD conditions but without Pt top layer. Each sample was fully immersed in an electrochemical cell.39 The electrochemical cell had separate lithium metal counter and reference electrodes and was fully immersed in a 1 m solution of LiClO4 in a 1:1 ratio of ethylene carbonate and dimethyl carbonate by volume. A CH17600 electrochemical workstation was used for electrochemical control of lithiation. The first cycle voltammograms between the open circuit potentials of the pristine films (3.46 V for 40.9 Å and 3.67 V for 112.5 Å films) and 0.05 V (with respect to Li/Li+) with the sweep rate of 0.2 mV s⁻¹ was conducted.

**TEM Characterization:** FIB-cleaved RuO2 thin film sample was mounted to a TEM grid using Pt, and this grid was connected with a Nanofactory TEM-STM holder. Li metal with Li2O solid electrolyte was connected a piezo-driven metal probe in an Ar-filled glovebox and was assembled with a TEM holder. The in situ electrochemical reaction inside the TEM, constant potential were maintained to RuO2 film against Li metal part. The in situ lithiation of RuO2 film along each direction was performed on a JEOL ARM 300CF operated at 300 kV, and TEM images were recorded using GATAN OneView camera with 4k × 4k resolution.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

in situ transmission electron microscopy (TEM), interface diffusion, lithium-ion batteries, ruthenium oxide, thin film electrodes

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