

Lithium Intercalation Properties of Octatitanate Synthesized through Exfoliation/Reassembly

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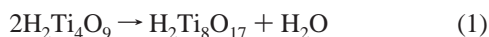
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Lithium intercalation properties of octatitanate synthesized through exfoliation/reassembly process, denoted reassembled-octatitanate, were examined for the first time and compared with those of octatitanate prepared without the exfoliation/reassembly process. Reassembled-octatitanate was prepared by the exfoliation of tetrabutylammonium-intercalated tetratitanate compound and the reassembly of the obtained nanosheets. The electrochemical activity was maintained in the reassembled-octatitanate. The overvoltage of reassembled-octatitanate was smaller than that of a conventional octatitanate. The reversible capacity and energy efficiency of reassembled-octatitanate were 170 (mA h)/g and 91%, respectively, larger than those of a conventional octatitanate. The exfoliation/reassembly process was found to be effective in improving the electrode performance.

Introduction

A lithium ion secondary battery is an energy storage device with a high-energy density and is used as a power source in mobile phones and other electronic devices. Many lithium intercalation host materials such as LiCoO_2 have been studied as cathode materials, since the energy density of the cell mainly depends on the properties of cathode materials.

We have reported the lithium intercalation properties of the fibrous octatitanate $\text{H}_2\text{Ti}_8\text{O}_{17}$.¹ The octatitanate is synthesized from the tetratitanate $\text{H}_2\text{Ti}_4\text{O}_9$ by heat treatment at a moderate temperature below 280 °C.^{2,3} The tetratitanate has a layer structure shown in Figure 1a, and one layer consists of linear groups of four TiO_6 octahedra with overlapping edges. The host layers in the tetratitanate are condensed in a topotactic manner through heat treatment via



resulting in one-dimensional tunnels in the octatitanate shown in Figure 1b. A fibrous tetratitanate was found to be thermally unstable and exhibit inferior electrode properties, such as capacity and cycling durability. The fibrous octatitanate shows a reversible capacity of 160 (mA h)/g, and discharge and charge potentials of approximately 1.55 and 1.95 V (vs Li^+/Li), respectively.¹

Sugimoto et al. reported the exfoliation of a tetratitanate.⁴ Dispersing a tetrabutylammonium-intercalated tetratitanate compound in a particular solvent leads to the delamination of layers into multilamellar or unilamellar sheets, called “nanosheets”. This formation of nanosheets in a colloidal suspension is called exfoliation. When a colloidal suspension is treated with an acid or a base, the nanosheets become stacked and form the tetratitanate again. This is called reassembly. A tetratitanate with a large surface area can be obtained by this exfoliation/reassembly process.⁵

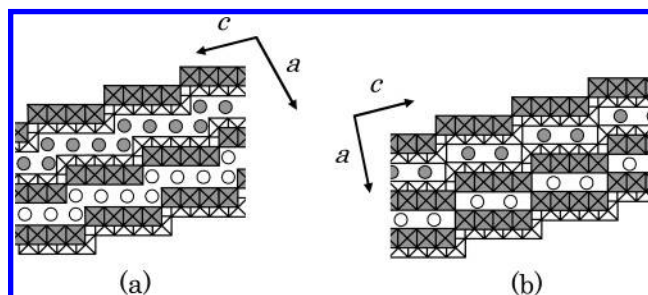


Figure 1. Crystal structures for (a) tetratitanate, $\text{H}_2\text{Ti}_4\text{O}_9$ and (b) octatitanate, $\text{H}_2\text{Ti}_8\text{O}_{17}$ projected in the ac plane. The unshaded, crisscrossed boxes and open symbols represent TiO_6 octahedron and proton, respectively.

The elements that limit the capacity of a lithium ion secondary battery have been reported by Fuller et al. using a mathematical model to describe the diffusion coefficient of lithium ion in the host material and the rate of the charge-transfer reaction.⁶ Since the interfacial kinetic resistance is due to the rate of the charge-transfer reaction, a host material with a large surface area is expected to have a small interfacial resistance. Materials synthesized through exfoliation/reassembly of nanosheets with a small interfacial kinetic resistance are promising for lithium intercalation host with high-energy density because of their large surface area. In addition, small particles of the host material, such as nanosheets, will contribute to the decrease in the diffusion period of lithium ions into the host material, and then to the increase in a rate capability.

Recently, the formation of MnO_2 nanosheets from a proton-exchanged form of layered $\text{K}_{0.45}\text{MnO}_2$ ⁷ and the synthesis of Li-Mn-oxide synthesized by the reassembly of MnO_2 nanosheets⁸ were reported. The Li-Mn-oxide synthesized by the reassembly of nanosheets was confirmed to work as a lithium intercalation host material. On exfoliation and reassembly of both $\text{K}_{0.45}\text{MnO}_2$ and tetratitanate, the interlayer guest cations are exchanged. The Li ions in the interlayer sites are able to be extracted electrochemically for the layered Li-Mn-oxide ; consequently the lithium intercalation properties would be

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changed by the state and degree of reassembly. On the contrary, the cations in the interlayer sites are not extracted electrochemically for an octatitanate, since Ti is a tetravalent state in an octatitanate and Ti cannot be oxidized further. Therefore an octatitanate is supposed to be more suitable for examining the effects of the exfoliation/reassembly process on the lithium intercalation properties. In this paper, we report the synthesis and lithium intercalation properties of an octatitanate through exfoliation/reassembly to confirm the possibility for the lithium intercalation host material with excellent electrode performance.

Experimental Section

The fibrous tetratitanate $\text{H}_2\text{Ti}_4\text{O}_9 \cdot 1.9\text{H}_2\text{O}$ (Otsuka Chemical) of 20 μm length and 300 nm diameter was used as the starting material. A weighed amount (1.0 g) of the fibrous tetratitanate powder was stirred in 200 cm^3 of aqueous solution of ethylamine for 24 h, and the ethylammonium-intercalated tetratitanate compound obtained was reacted with 200 cm^3 of aqueous solution of tetrabutylammonium hydroxide for 24 h, both at room temperature.⁴ A 10-fold mol amount of ethylammonium or tetrabutylammonium hydroxide to tetratitanate was taken in these reactions. A colloidal suspension of tetratitanate nanosheets was prepared by dispersing the tetrabutylammonium-intercalated tetratitanate compound in distilled water. Though direct intercalation of tetrabutylammonium into tetratitanate also leads to obtaining a colloidal suspension of tetratitanate nanosheets, it takes no less than 10 days.^{5,7,8} Relatively large particles were centrifugally separated at 2000 rpm. The supernatant was used for the reassembly of the tetratitanate. The colloidal suspension was mixed with 0.1 M HCl for the reassembly, and the precipitates were centrifugally separated, washed with purified water, and dried at 70 $^\circ\text{C}$. The tetratitanate synthesized by the reassembly of nanosheets was heated at 200 $^\circ\text{C}$ for 2 h to convert it into octatitanate. The tetratitanate and octatitanate synthesized by the reassembly of nanosheets are denoted reassembled-tetratitanate and reassembled-octatitanate, respectively, hereafter.

The structures of the titanates were confirmed by X-ray diffraction (XRD) analysis. The morphologies of the titanates were observed by atomic force microscopy (AFM), scanning electron microscopy (SEM), and N_2 adsorption measurement.

A reassembled-octatitanate was mixed with 45 wt % carbon powder (acetylene black) and 10 wt % poly(tetrafluoroethylene) (PTFE) to fabricate cathodes for electrochemical measurements. A reassembled-octatitanate of approximately 50 mg was employed for a cathode of 2 cm^2 . Electrochemical measurements were performed using a three-electrode cell with lithium strips as the reference electrode and counter electrode, and the prepared electrode as the working electrode. The electrolyte solution was 1 M lithium perchlorate in propylene carbonate (Kishida Chemical). Galvanostatic discharge/charge tests and cyclic voltammetry tests were carried out in the voltage range of 1.2–3.6 V (vs Li^+/Li) with the HAG-5001 potentiostat/galvanostat (Hokuto Denko).

Results and Discussion

Figure 2 shows the XRD patterns of (a) the tetratitanate used as the starting material, (b) fibrous octatitanate obtained by the heat treatment of a, (c) films of the tetrabutylammonium-intercalated tetratitanate compound prepared by casting the colloidal suspension onto a glass substrate, (d) reassembled-tetratitanate, and (e) reassembled-octatitanate. The basal spacings $d(200)$ were 1.8 nm for the tetrabutylammonium-intercalated tetratitanate compound (c) and 0.90 nm for the starting tetrati-

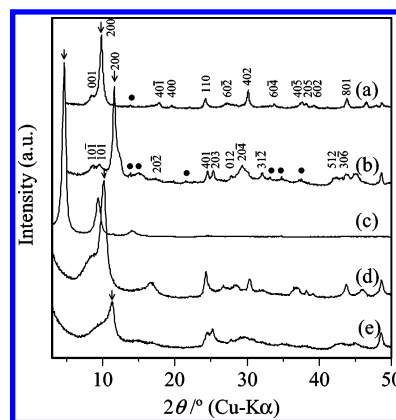


Figure 2. XRD patterns of (a) tetratitanate used as the starting material, (b) octatitanate obtained by heat treating tetratitanate at 200 $^\circ\text{C}$ for 2 h, (c) films of tetrabutylammonium-intercalated tetratitanate compound prepared by casting the colloidal suspension onto glass substrate, (d) reassembled-tetratitanate, and (e) reassembled-octatitanate. Arrows indicate 200 peaks. Solid circles indicate unknown peaks.

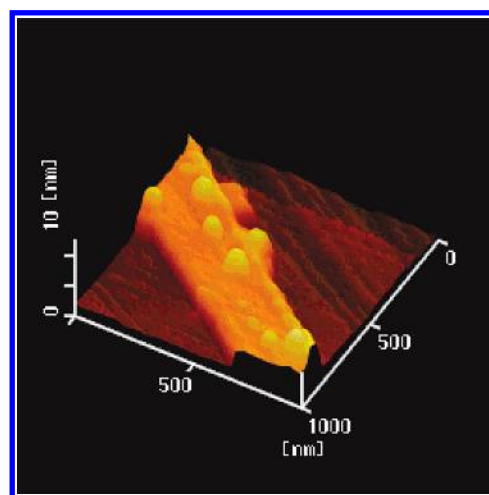


Figure 3. Atomic force micrograph of the thin film obtained by casting the colloidal suspension onto glass substrate.

tanate (a) and reassembled-tetratitanate (d). The 200 diffraction peak in c, shifted by the intercalation treatment, returned to the original position for the reassembled-tetratitanate in d. These results indicate the shrinkage of the interlayer space and the reassembly of nanosheets upon the acid treatment. The octatitanate was found to be formed by the heat treatment of the reassembled-tetratitanate though its crystallinity was relatively low. The composition of the nanosheet-octatitanate determined by thermogravimetry was $\text{H}_2\text{Ti}_8\text{O}_{17} \cdot \text{H}_2\text{O}$.

Figure 3 shows an atomic force micrograph of the thin film obtained by casting the colloidal suspension of nanosheets onto a glass substrate, that is the tetrabutylammonium-intercalated tetratitanate compound. A thin sheet of approximately 300 nm width was observed. The width of the thin sheet is approximately equal to the diameter of the fibrous tetratitanate. This indicates that the thin sheet was formed by the exfoliation of a tetratitanate. The exfoliation of a tetratitanate into nanosheets would occur on bc planes, since only $h00$ peaks were observed in the XRD pattern of this nanosheet (Figure 2b). The thickness of this sheet shown in Figure 3 was approximately 4 nm. The average thickness of the thin sheets, determined by observing several sheets using AFM, was 5 nm. This average thickness of 5 nm suggests that the sheet contained in the colloidal suspension was multilamella: containing three or four oxide

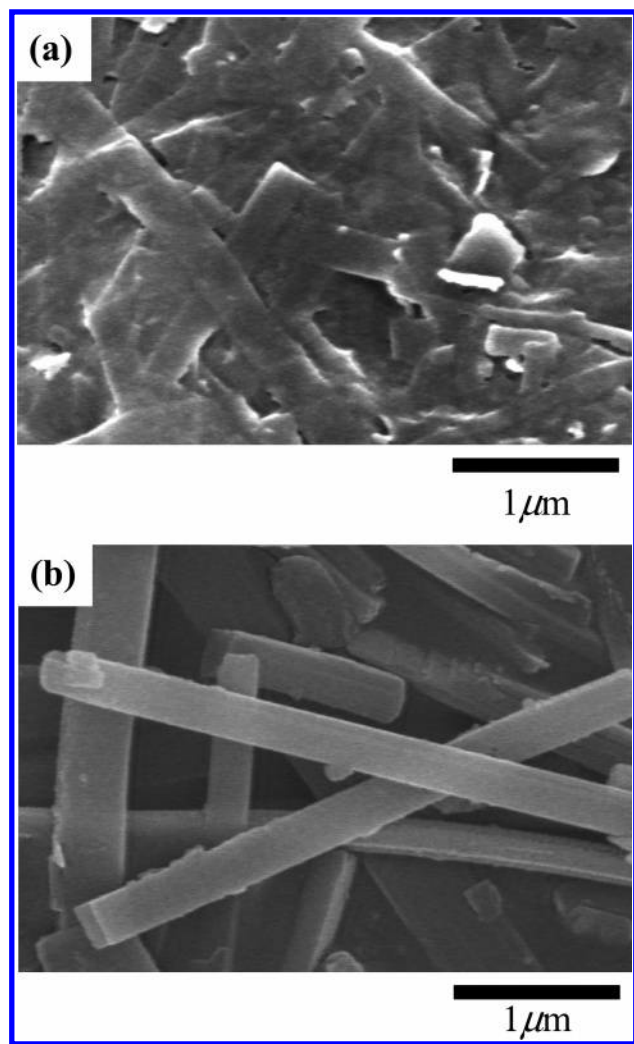


Figure 4. Scanning electron micrographs of (a) reassembled-octatitanate and (b) fibrous octatitanate.

sheets since the basal spacing of the tetrabutylammonium-intercalated tetratitanate compound observed by XRD analysis was 1.8 nm.

Figure 4 shows typical scanning electron micrographs of (a) the reassembled-octatitanate and (b) fibrous octatitanate. Thin sheets of approximately 300 nm width were observed in Figure 4a, and they were similar in shape to that observed in Figure 3. Thin sheets seem to stack along the *a*-axis, maintaining their shape. The BET surface area of the reassembled-octatitanate and fibrous octatitanate determined by N₂ adsorption measurements were 100 and 16 m²/g, respectively. A specific surface area of the reassembled-octatitanate was much larger than that of fibrous octatitanate.

Pore size distribution curves for the reassembled-octatitanate and fibrous octatitanates determined by N₂ adsorption measurements are shown in Figure 5. The reassembled-octatitanate was porous with pores widely distributed ranging from 3 to 50 nm. These textural characteristics were quite similar to those of TiO₂ in thin flaky morphology prepared by exfoliation and reassembly of H_xTi_{2-x/4}□_{x/4}O₄·H₂O (□, vacancy).⁵ Openings between the randomly assembled thin sheets or flakes which are composed of several thin sheets may account for the pores.

Figure 6 shows the cyclic voltammograms for the reassembled-octatitanate in comparison with those of the fibrous octatitanate. The weight ratio of the mixture of fibrous octatitanate, carbon powder, and Teflon for fabricating the electrode was also 45:45:10. Both cyclic voltammograms were obtained

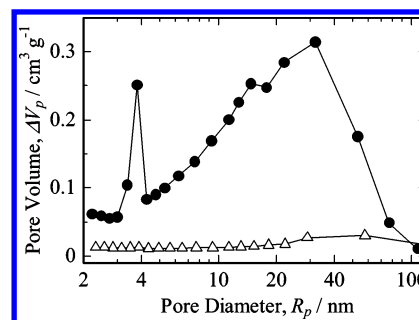


Figure 5. Pore-size distribution curves for octatitanates. The filled circles and open triangles express the pore-size distribution for reassembled-octatitanate and fibrous octatitanate, respectively.

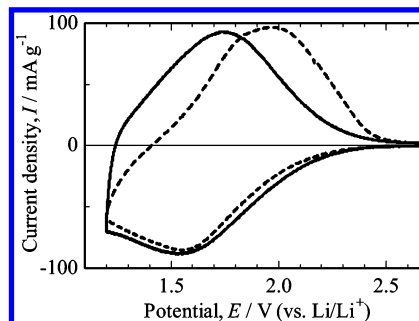


Figure 6. Cyclic voltammograms for nanosheet-octatitanate (solid line) and fibrous octatitanate (broken line). The sweep rate was 0.1 mV/s.

at the 10th cycle. The peak potential of the reduction current was approximately 1.55 V for the reassembled-octatitanate, which was almost the same as that for the fibrous octatitanate. The peak potential of the oxidation current for the reassembled-octatitanate was approximately 1.75 V, which was lower than that for the fibrous octatitanate by 200 mV. This result suggests the reduction of overvoltage and the lowering of the reaction potential for the reaction of the reassembled-octatitanate. Recently, Graetzel and co-workers have reported that nanostructured TiO₂ containing an amorphous phase showed pseudocapacitance at lower potential than that of ordinary lithium insertion into TiO₂.⁹ Although the reassembled-octatitanate exhibited an anodic peak at a lower potential than that for fibrous octatitanate, it can be said that the reactions that occurred are lithium insertion/extraction since the capacity of reassembled-octatitanate was in the same level but a little larger than that of fibrous octatitanate, as shown later. The Li⁺ diffusion pass, supposed to be the one-dimensional tunnel normal to the *ac* plane, is kept since the exfoliation occurs on *bc* planes. The decrease in overvoltage would be caused by a decrease in interfacial kinetic resistance with increasing surface area. The result that the reduction potential of the reassembled-octatitanate stayed at 1.55 V may be caused by the increase of the reduction potential due to the drop in the overvoltage and the lowering of the reaction potential. The lowering of the reaction potential would be caused by the relaxation of strain on TiO₆ octahedra derived from the exchange of counteranions on exfoliation¹⁰ and random layer stacking.

Figure 7 shows the discharge and charge curves for the reassembled-octatitanate measured at the 10th cycle, in comparison with those of the fibrous octatitanate. The charging reversibility (ratio of the charge capacity, 170 (mA h)/g, to the discharge capacity, 175 (mA h)/g), was 97%. The discharge capacity of the reassembled-octatitanate was approximately 175 (mA h)/g, which was larger than that of the fibrous octatitanate by 15 (mA h)/g. The capacity of 175 (mA h)/g corresponds to the reversible insertion/extraction of 4.3 Li in one H₂Ti₈O₁₇ unit.

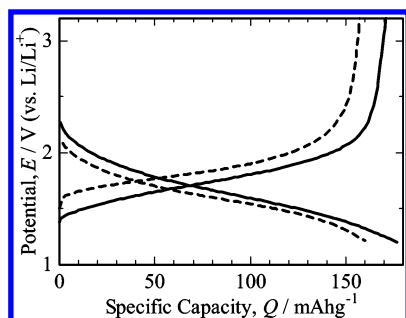


Figure 7. Discharge and charge curves for the reassembled-octatitanate (solid line) and fibrous octatitanate (broken line). The current density was 100 mA/g.

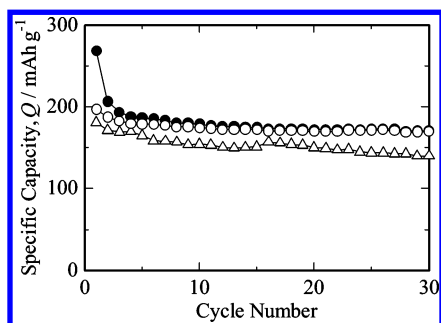


Figure 8. Cycling performance of reassembled-octatitanate. The filled and open circles represent the discharge capacity and reversible capacity of reassembled-octatitanate, respectively. The open triangles represent the reversible capacity of fibrous octatitanate. The current density was 100 mA/g.

The energy efficiency (ratio of the dischargeable power, 291 (mW h)/g, to the power needed for charging, 318 (mW h)/g), was 91%, which was higher than the 84% of the fibrous octatitanate. These results suggest that the overvoltage in the reaction of the reassembled-octatitanate was reduced.

Figure 8 shows the cycleability of the reassembled-octatitanate in comparison with that of the fibrous octatitanate. A large irreversible capacity of 71 (mA h)/g was observed only at the first cycle. We have reported for a fibrous octatitanate ($\text{H}_2\text{-Ti}_8\text{O}_{17}\cdot 0.4\text{H}_2\text{O}$) an irreversible capacity of 43 (mA h)/g at the first cycle and a contraction of a basal spacing $d(200)$ after discharge/charge cycling.¹ A dehydration of an octatitanate brings about a contraction of a basal spacing. These results suggest that an electrochemical reduction of crystal water causes a large irreversible capacity. A larger irreversible capacity for the reassembled-octatitanate than that for a fibrous octatitanate would be due to the relatively large amount of crystal water. The reversible capacity of the reassembled-octatitanate decreased gradually with the increasing number of cycles, probably due to crystal water in an octatitanate, but the capacity became stable after 10 cycles. The reversible capacity at the 30th cycle was as large as 97% of that at the 10th cycle for the reassembled-octatitanate, while that was 91% for the fibrous octatitanate. This excellent cycleability is assumed to be due to the small particle size of the active materials and the porous microstructure

of the electrode. The decrease in capacity during cycling is caused mainly by microstructural changes, such as connection of active material particles and active material particles/carbon particles, due to the expansion and contraction accompanied by lithium insertion and extraction.¹¹ Such a change for one particle is expected to be smaller in fine particles of the reassembled-octatitanate than in those of the fibrous octatitanate, resulting in small microstructural changes and a stable capacity during cycling.

It was demonstrated that the nanosheet process, that is, exfoliation and reassembly, is effective in improving the energy density and cycleability of lithium intercalation host materials. The electrode used in the present study was prepared by mixing powders of reassembled-octatitanate and carbon. However, composite electrodes could also be prepared by mixing carbon powders with a colloidal suspension of nanosheets before a reassembly process. This method will yield a more homogeneous mixture with a small electrical contact resistance between nanosheets and carbon powders, and further improvement in the cycleability and also a high rate capability can be expected.

Conclusions

An octatitanate synthesized through exfoliation and reassembly, denoted reassembled-octatitanate, was prepared by the exfoliation and reassembly of a tetrabutylammonium-intercalated tetratitanate compound followed by heat treatment. The reassembled-octatitanate showed a reversible capacity of 175 (mA h)/g. In the reassembled-octatitanate, a smaller overvoltage (by 200 mV), a higher energy efficiency, and a better cycleability than those of octatitanate without the nanosheet process were confirmed. The nanosheet process was found to be a promising method of producing a lithium intercalation host material with excellent electrode properties.

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References and Notes

- (1) Suzuki, S.; Miyayama, M. *Key Eng. Mater.* **2003**, *248*, 151–154.
- (2) Izawa, H.; Kikkawa, S.; Koizumi, M. *J. Phys. Chem.* **1982**, *86*, 5023–5026.
- (3) Sasaki, T.; Watanabe, M.; Komatsu, Y.; Fujiki, Y. *Inorg. Chem.* **1985**, *24*, 2265–2271.
- (4) Sugimoto, W.; Terabayashi, O.; Murakami, Y.; Takasu, Y. *J. Mater. Chem.* **2002**, *12*, 3814–3818.
- (5) Sasaki, T.; Nakano, S.; Yamauchi, S.; Watanabe, M. *Chem. Mater.* **1997**, *9*, 602–608.
- (6) Fuller, T. F.; Doyle, M.; Newman, J. *J. Electrochem. Soc.* **1994**, *141*, 1–10.
- (7) Omomo, Y.; Sasaki, T.; Wang, L.; Watanabe, M. *J. Am. Chem. Soc.* **2003**, *125*, 3568–3575.
- (8) Wang, L.; Takada, K.; Kajiyama, A.; Onoda, M.; Michiue, Y.; Zhang, L.; Watanabe, M.; Sasaki, T. *Chem. Mater.* **2003**, *15*, 4508–4514.
- (9) Kavan, L.; Kalbáček, M.; Zúkalová, M.; Exnar, I.; Lorenzen, V.; Nesper, R.; Graetzel, M. *Chem. Mater.* **2004**, *16*, 477–485.
- (10) Fukuda, K.; Nakai, I.; Oishi, C.; Nomura, M.; Harada, M.; Ebina, Y.; Sasaki, T. *J. Phys. Chem. B* **2004**, *108*, 13088–13092.
- (11) Wen, S. J.; Richardson, T. J.; Ma, L.; Striabel, K. A.; Ross, P. N., Jr.; Cairns, E. J. *J. Electrochem. Soc.* **1996**, *143*, L136–L138.