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Microstructural Observation of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after Charge and Discharge by Scanning Transmission Electron Microscopy

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A lithium cell of pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder was operated in a voltage window of 4.2 – 2.5 V at C/40 rate at 20°C for ten cycles, and the microstructure for the ten-cycled sample was examined by scanning transmission electron microscopy (STEM), which was compared with those for pristine or first-cycled one. Microcracks appeared after the first cycle at grain boundaries, and widened after ten cycles, which are derived from 1 – 2% change in unit cell volume during charge and discharge. Grain boundary layers extended during the first cycle are almost invariable for subsequent cycles. This suggests that the extended grain boundary layers formed during the first cycle act as protection layers to prevent structural degradation during charge and discharge, which enable the materials to exhibit topotactic reaction in terms of a bulk crystal structure.

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Layered lithium transition metal oxides such as LiCoO_2 , LiNiO_2 , and their derivatives have two-dimensional lithium-ion conduction paths and can extract / insert lithium ions reversibly without the degradation of core structure, which is called topotactic reaction.¹ Layered materials have been developed and improved to a quite high level for the application to positive electrode materials for lithium-ion batteries. These materials have been improved in terms of the formation of solid solution between LiNiO_2 and LiCoO_2 ,^{2–4} or LiNiO_2 and LiAlO_2 ,^{5,6} which leads to $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ for the battery applications. Materials innovation has been made in terms of bulk modification by metal substitution or doping.^{7–10}

Recently, surface modification or coating of layered materials by metal oxides or inorganic compounds has been performed to improve their electrochemical behavior.^{11–15} Of these, mechanism of aluminum-based coating such as AlPO_4 or Al_2O_3 to LiCoO_2 was proposed to form $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$ solid solution at the surface,^{13–15} while bulk of materials does not change by surface modification. More recently, Sasaki et al. and Muto et al. examined degradation mechanism of lithium-ion battery of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with graphite after extended-cycling test for more than 500 cycles at elevated temperatures above 60°C, and found that inactive divalent and trivalent nickel ions were formed and NiO-like phase was detected near the grain surface and boundaries in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ by a spatial-distribution map.^{16,17} These results reported so far indicate that spectral analyzes and microscopic observations of the bulk crystal structure are not enough to understand the reaction mechanisms in batteries. In our previous paper,¹⁸ we reported that the grain boundary layers in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ changed only after the first cycle into the rock-salt like structure with an ascending sequence of partially layered structure although crystal structure in the grain interior is $\alpha\text{-NaFeO}_2$ -type layered structure. According to such microstructural observations, questions arise as to how lithium-ion extraction / insertion of electrode materials takes place through the grain boundary layers and how topotactic reaction can be retained from a viewpoint of microstructure. Understanding of the microstructure at the grain surface and boundaries is important to advance electrode materials and hence battery performance. In this paper, the microstructure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after ten cycles in lithium cells was examined by scanning transmission electron microscopy (STEM), and was compared among pristine, first-cycled, and ten-cycled samples to discuss the above issues.

Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was prepared by a coprecipitation method and the obtained powder can be identified as $\alpha\text{-NaFeO}_2$ -type layered structure in a space group of $R\bar{3}m$ with lattice parameters of $a = 2.864 \text{ \AA}$ and $c = 14.171 \text{ \AA}$ in hexagonal setting. The electrochemical behavior of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was examined by using the electrochemical cell, Type TJ-AC (Tomcell Co. Ltd., Japan). The positive electrode mix consisted of 85 weight percent (wt%) $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, 10 wt% carbonblack, and 5 wt% polyvinylidene fluoride (PVdF) binder, and the negative electrode was lithium foil supported on a stainless steel plate. Positive and negative electrodes were separated by porous polypropylene membrane, and the sandwich-type cell body was immersed in 1M LiPF_6 ethylene carbonate (EC)/diethyl carbonate (DEC) (3/7 v/v) electrolyte. To prepare a positive electrode, black viscous slurry of an electrode mix dissolved in N-methyl-2-pyrrolidone (NMP) was casted on an aluminum foil with blade. NMP was evaporated preliminary by a drier, and finally the electrodes were dried under vacuum at 120°C for 12 h. The painted sheet was pressed to increase electrode density and was punched out into a disk (16 mm of dia.). All materials except the electrolyte and lithium metal were dried under vacuum at 60°C for at least 2 h to avoid possible contamination of water, and the lithium cells were fabricated in an argon-filled glove box. The cells were operated in a galvanostatic mode at C/10-rate based on 175 mAh g⁻¹ of capacity in a voltage window of 4.2 – 2.5 V at 20°C.

For the microstructural observations, the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ powder was pressed into pellet without the addition of any carbon or binder and used as a positive electrode in a lithium cell. The lithium cell was operated for 10 cycles in a voltage window of 4.2 – 2.5 V at 0.2 mA cm⁻² corresponding to a C/40-rate based on 175 mAh g⁻¹ of capacity at 20°C. Thus-obtained $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pellet was taken out of the cell in an Ar-filled glove box, and was immersed in a DEC solution to remove the LiPF_6 salt. The pellet was crushed into powder used for STEM characterization. STEM specimens were prepared by epoxy embedding, followed by mechanical grinding and ion milling (Gatan 691, operated at 3-1kV and cooled with nitrogen liquid). STEM observation was performed on a Cs-corrected JEM-2100F transmission electron microscope (JEOL Co., 200kV).

Results and Discussion

Sample preparation for microstructural observation.— Voltage profile of a lithium cell of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ was examined and displayed in Fig. 1a to characterize the sample electrochemically. In a voltage window of 4.2 – 2.5 V at C/10 rate, the cell exhibits an ascending curve from 3.6 to 4.2 V on charge, and the discharge curve traces the charge curve in the reverse direction until the voltage drops down to 2.5 V at about 25 mAh g⁻¹ of charge capacity, which is so-called

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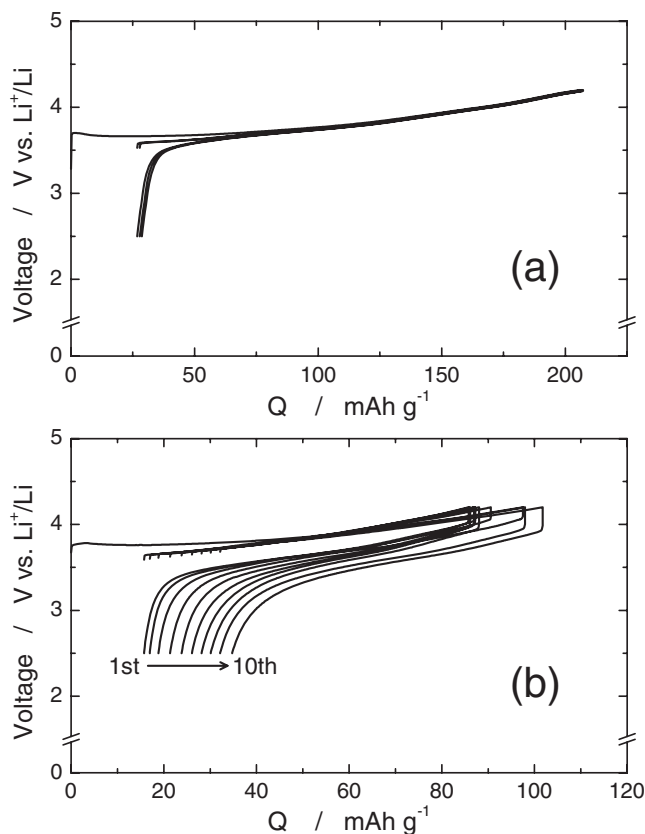


Figure 1. Voltage profiles of lithium cells of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ for 10 cycles. The positive electrode consisted of (a) 85 wt% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, 10 wt% carbonblack and 5 wt% PVdF binder, or (b) a $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pellet without carbon or binder. The cells were operated at (a) C/10-rate or (b) C/40-rate in a voltage window of 4.2 – 2.5 V at 20°C.

irreversible capacity. The charge-discharge efficiency for subsequent cycles was more than 99%. The electrochemical data shown in Fig. 1a indicates that the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ sample is battery-active having $\alpha\text{-NaFeO}_2$ -type layered structure without rock-salt structured domains in a bulk structure, which is comparable to the results reported previously¹⁸ and can be used to discuss microstructural change with respect to charge and discharge cycling.

Figure 1b shows the voltage profile of the lithium cell of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pellet without carbon or binder. The cell can be reversibly operated for 10 cycles since we applied a small current density corresponding to a C/40-rate. Reversible capacities of the voltage profile shown in Fig. 1b are limited with some scatter of charge and discharge curves in comparison to those in Fig. 1a, and charge-discharge efficiency was about 96% after the second cycle, since the pellet does not have carbon or binder. Although there is a difficulty to operate the cells without carbon or binder in a positive electrode, microstructural observations of the electrode mix with carbon and binder cannot be made because of the indistinct STEM image caused by electrode contaminations. The pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ sample obtained after 10 cycles in a lithium cell was used for the purpose since the lithium cell can be reversibly operated for 10 cycles.

Change in morphology after ten cycles.— Low magnification STEM image for ten-cycled sample is shown in Fig. 2b in comparison to that for the first-cycled one in Fig. 2a, which corresponds to the sample reported in our previous paper.¹⁸ Many grains gathered to be large agglomerate. As displayed in Fig. 2a and 2b, microcracks ran at grain boundaries after the first cycle, especially at the regions near the surface of agglomerate, and the microcracks widened

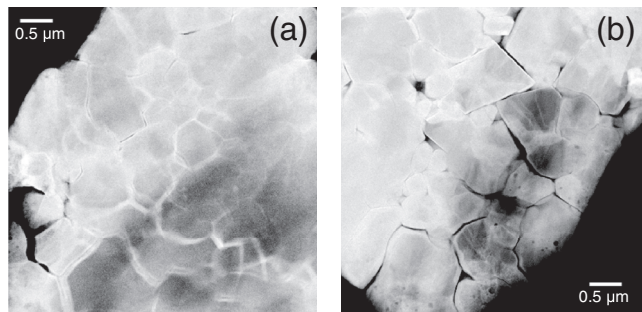


Figure 2. STEM images of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after (a) the first cycle or (b) ten-cycles. The lithium cells of pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder were operated in a voltage window of 4.2 – 2.5 V at 20°C.

so much after ten cycles. Nickel-based layered materials including $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ shrink 1 – 2% in volume on charge and expand back on discharge during the battery operation.^{19,20} Microcracks, which were opened and widened upon cell-cycling at grain boundaries, are caused by the change in unit cell volume during charge and discharge.²¹ This STEM image shown in Fig. 2b suggests that some grains in the agglomerates are electrically isolated, which is a reason why charge-discharge efficiency displayed in Fig. 1b was as small as 96% after the second cycle, while electric connection can be retained among the grains and agglomerates in the electrode mix with carbon and binder as shown in Fig. 1a.

Grain boundary variations after cell-cycling.— STEM images displayed in Fig. 2 show bright contrast especially at grain boundaries. Grains have thin layer adjacent to the grain boundaries, which can be defined as grain boundary layers. Figure 3a and 3b displays magnified STEM images of the sample after ten cycles to show a variety of grains and grain boundaries. Grain boundary layers shown in Fig. 3a seem to be thicker than those in Fig. 3b. According to the observation of grains as many as possible, various thicknesses of grain boundary layers were found in the ten-cycled sample. The thicknesses of grain boundary layers are within the range of 45 ± 15 nm among the grains after ten cycles. This difference is considered to depend on the grain boundary character, e.g., grain boundary orientation and grain boundary plane.²² Figure 4 displays a high-resolution STEM image at a grain boundary of the ten-cycled $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. A high-resolution image in the grain interior is also shown in the inset for comparison. In the grain interior, bright spots are arranged to draw straight lines, which are transition metal layers of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Lithium layers are invisible because of the low atomic-number of lithium whereas transition metal layers are clearly seen as bright spots. Lithium and transition metal layers stack alternately to form $\alpha\text{-NaFeO}_2$ -type layered structure in the grain interior. At the grain boundary layer of the ten-cycled sample, bright spots exist even in the lithium layers and increase from the grain interior to the boundary, indicating that cation mixing between lithium and transition metal layers occurs and increases gradually in a layered structure at the region adjacent to the boundary. At the lower part of the image shown in Fig. 4, the contrast of the lithium layers marked with double-headed arrows are relatively low as compared with that of the transition metal layers and therefore the layered structure is still visible. However, at the grain boundary layer adjacent to the microcrack, lithium and transition metal layers have the same contrast as marked with single-headed arrows, which corresponds to the formation of rock-salt like structure owing to random distribution of lithium and transition metal ions. A grain boundary layer of a selected grain for ten-cycled sample can be displayed and compared with those for pristine and first-cycled one as the profiles of image-intensity ratio of lithium layers to neighboring transition metal layers. Figure 5 displays the thickness of a grain boundary layer of ten-cycled sample, as well as pristine and first-cycled one. As discussed in our previous paper,¹⁸ the thickness of grain boundary layers is about

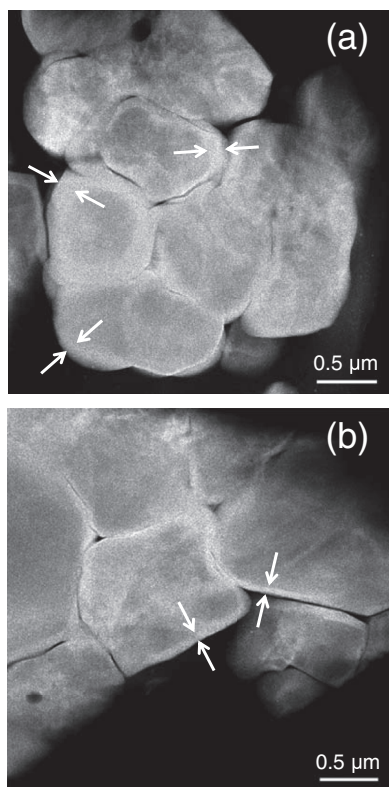


Figure 3. STEM images of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after ten cycles to show a variety of grains. Grain boundary layers in (a) are thicker than those in (b) as marked with arrows. The lithium cells of pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder were operated in a voltage window of 4.2 – 2.5 V at 20°C for ten cycles.

5 nm for pristine sample, in which a small amount of transition metal ions exists in lithium layers, i.e., a partially layered structure. After the first cycle, grain boundary layer extended from 5 nm for pristine sample to about 25 nm for the first-cycled one in which the region with a partially layered structure expands to about 20 nm and a rock-salt like structure of about 5 nm forms at the boundary. As shown in Fig. 5, ten-cycled sample shows about 32 nm thick grain boundary layer containing about 7 nm of rock-salt like structure and about 25 nm of

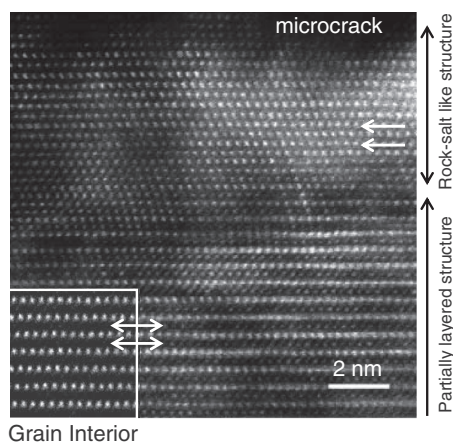


Figure 4. High-resolution STEM image of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at a grain boundary layer after ten cycles. Double-headed and single-headed arrows are given to indicate lithium layers in the regions of partially layered structure and rock-salt like structure, respectively, in comparison to those in the grain interior shown in the inset.

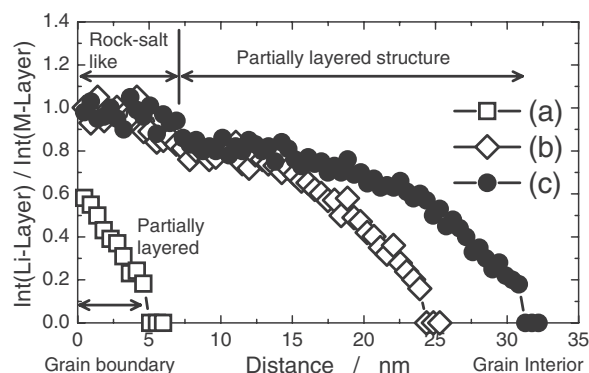


Figure 5. Concentration of transition metal ions at the lithium layers in the grain boundary, which was estimated as image-intensity ratios of lithium layers to neighboring transition metal layers in STEM images for (a) pristine, (b) first-cycled, and (c) ten-cycled $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$.

an ascending sequence of a partially layered structure. Although the thickness of grain boundary layers has some error-range among the grains after 10 cycles as described above, a significant growth of the grain boundary layer during the first cycle is the most remarkable. The grain boundary layers do not extend much for subsequent cycles in comparison to those of the first-cycled sample.

Extended grain boundary layers formed during the first cycle.

The thickness of grain boundary layers increases during the first cycle and many grains of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ are covered by the extended grain boundary layers. LiNiO_2 -based materials having a large amount of cation mixing in the bulk crystal structure exhibit an increased polarization and limited capacity during charge and discharge in a usual voltage range.^{19,23} In spite of poor electrochemical behavior owing to the cation mixing, such materials still have the ability of lithium-ion transportation in the entire solid matrix,²⁴ and furthermore the extended grain boundary layers consist of nanometer-scaled thin layer of rock-salt like structure and partially layered structure in terms of the sequence of cation mixing in a layered structure. Nanometer-scaled thin films of oxides or inorganic compounds have been reported to exhibit reversible electrochemical reactions in lithium cells while these materials are inactive as a macroscopic scale.^{25,26} The grain boundary layers are thin enough to transport lithium ions well during charge and discharge. This suggests that the extended grain boundary layers formed during the first cycle is a lithium-ion conductor which can act as a protection layer to prevent structural degradation during charge and discharge. The extended grain boundary layers can avoid the direct contact between material grains and electrolyte in lithium cells. This may be one of the reasons why the materials can extract and insert lithium ions reversibly without the degradation of core structure, i.e., topotactic reaction in terms of the bulk crystal structure.

The cycling-test for lithium-ion batteries of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ with graphite at elevated temperature above 60°C for more than 500 cycles was, however, reported to cause materials degradation localized near the grain surface and boundaries, leading to capacity fading of the lithium-ion batteries.^{16,17} The extended grain boundary layers are not tough enough to protect the layered structure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ in a severe condition. Although the change in grain boundary for other layered materials such as LiCoO_2 after a few cycles has not been reported as far as we know, Gabrisch et al.²⁷ reported the TEM investigations of LiCoO_2 after extended-cycling at room temperature in comparison to the sample after thermal treatment in a charged state. They found that the spinel-related phase of $\text{Li}_{1-y}\text{Co}_2\text{O}_4$ was distributed homogeneously throughout some grains after extended-cycling, which formed first at the grain surface and then grew into the grain interior. Such a difference in materials degradation after extended-cycling between LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ may be derived from

their different structures and thicknesses for grain boundary layers formed during the first cycle. From such a viewpoint, surface-selective modification of electrode materials can prevent materials degradation if the modification can be properly made, as has been reported by several research groups.^{11–15}

Conclusion

Microstructure of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ after ten cycles was examined and compared with those of pristine and first-cycled samples. Microcracks are clearly seen for the sample after ten cycles in comparison to the first-cycled one, which were widened during ten cycles because of 1 – 2% volume change during charge and discharge. These microcracks reduce charge-discharge efficiency to about 96% after the second cycle of pelletized $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ without carbon or binder, since some grains may be electrically isolated by the microcracks. However, the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ electrode mix with carbon and binder works very well because of the enough electric-connection among $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ grains and agglomerates. The extended grain boundary layers formed during the first cycle act as lithium-ion conductor. These layers can prevent degradation of layered structure during reversible lithium extraction / insertion reactions, which make it possible to exhibit topotactic reaction with respect to the bulk crystal structure. The extended grain boundary layers seem to have some relationship to so-called irreversible capacity appeared only in the first cycle of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Understanding of the relation between the extended grain boundary layers and so-called irreversible capacity is now in progress in our research group.

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References

1. T. Ohzuku and A. Ueda, *Solid State Ionics*, **69**, 201 (1994).
2. T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, and H. Komori, *Electrochim. Acta*, **38**, 1159 (1993).
3. A. Rougier, I. Saadoune, P. Gravereau, P. Willmann, and C. Delmas, *Solid State Ionics*, **90**, 83 (1996).
4. T. Ohzuku and Y. Makimura, *Res. Chem. Intermed.*, **32**, 507 (2006).
5. T. Ohzuku, A. Ueda, and M. Kouguchi, *J. Electrochem. Soc.*, **142**, 4033 (1995).
6. M. Guilmard, C. Pouillier, L. Croguennec, and C. Delmas, *Solid State Ionics*, **160**, 39 (2003).
7. C. Delmas, M. Ménétrier, L. Croguennec, I. Saadoune, A. Rougier, C. Pouillier, G. Prado, M. Grüne, and L. Fournès, *Electrochim. Acta*, **45**, 243 (1999).
8. C. Delmas and L. Croguennec, *Mater. Res. Bull.*, **27**, 608 (2002).
9. M. S. Whittingham, *Chem. Rev.*, **104**, 4271 (2004).
10. B. L. Ellis, K. T. Lee, and L. F. Nazar, *Chem. Mater.*, **22**, 691 (2010).
11. J. Cho, Y.-J. Kim, and B. Park, *Chem. Mater.*, **12**, 3788 (2000).
12. J. Cho, C.-S. Kim, and S.-I. Yoo, *Electrochem. Solid-State Lett.*, **3**, 362 (2000).
13. A. T. Appapillai, A. N. Mansour, J. Cho, and Y. Shao-Horn, *Chem. Mater.*, **19**, 5748 (2007).
14. S. Verdier, L. E. Ouatani, R. Dedryvère, F. Bonhomme, P. Biensan, and D. Gonbeau, *J. Electrochem. Soc.*, **154**, A1088 (2007).
15. L. Dahéron, R. Dedryvère, H. Martinez, D. Flahaut, M. Ménétrier, C. Delmas, and D. Gonbeau, *Chem. Mater.*, **21**, 5607 (2009).
16. T. Sasaki, T. Nonaka, H. Oka, C. Okuda, Y. Itou, Y. Kondo, Y. Takeuchi, Y. Ukyo, K. Tatsumi, and S. Muto, *J. Electrochem. Soc.*, **156**, A289 (2009).
17. S. Muto, Y. Sasano, K. Tatsumi, T. Sasaki, K. Horibuchi, Y. Takeuchi, and Y. Ukyo, *J. Electrochem. Soc.*, **156**, A371 (2009).
18. S. Zheng, R. Huang, Y. Makimura, Y. Ukyo, C. A. J. Fisher, T. Hirayama, and Y. Ikuhara, *J. Electrochem. Soc.*, **158**, A357 (2011).
19. T. Ohzuku, A. Ueda, and M. Nagayama, *J. Electrochem. Soc.*, **140**, 1862 (1993).
20. T. Ohzuku, K. Nakura, and T. Aoki, *Electrochim. Acta*, **45**, 151 (1999).
21. K. Dokko, M. Nishizawa, S. Horikoshi, T. Itoh, M. Mohamedi, and I. Uchida, *Electrochem. Solid-State Lett.*, **3**, 125 (2000).
22. Y. Ikuhara, *J. Ceram. Soc. Jpn.*, **109**, S110 (2001).
23. A. Rougier, P. Gravereau, and C. Delmas, *J. Electrochem. Soc.*, **143**, 1168 (1996).
24. C. Delmas, J. P. Pérès, A. Rougier, A. Demourgues, F. Weill, A. Chadwick, M. Broussely, F. Pertion, Ph. Biensan, and P. Willmann, *J. Power Sources*, **68**, 120 (1997).
25. V. Pralong, J.-B. Leriche, B. Beaudoin, E. Naudin, M. Morcrette, and J.-M. Tarascon, *Solid State Ionics*, **166**, 295 (2004).
26. Y. Makimura, A. Rougier, and J.-M. Tarascon, *Appl. Surf. Sci.*, **252**, 4587 (2006).
27. H. Gabrisch, R. Yazami, and B. Fultz, *J. Electrochem. Soc.*, **151**, A891 (2004).