1160 Chemistry Letters Vol.32, No.12 (2003)

# Improved Cycleability of Li-Birnessite by Coprecipitation with Nafion

Xiaojing Yang,* Weiping Tang,[†] Zong-huai Liu, Kazuya Ikeda,[†] and Kenta Ooi*
*National Institute of Advanced Industrial Science and Technology, 2217-14 Hayashi, Takamatsu 761-0395*
[†]*Research Institute for Solvothermal Technology, 2217-43 Hayashi, Takamatsu 761-0301*

(Received July 7, 2003; CL-030604)

Birnessite-type lithium manganese oxide coprecipitated with Nafion showed improved stability on cycling as a cathode material for a Li-rechargeable battery at large current density.

Layered lithium transition metal oxides Li$MO_2$ ($M$ = Co, Ni, Mn) have been the focus of extensive attention as cathode materials for lithium secondary batteries.[1,2] It is known that manganese oxides, either layered $LiMnO_2$ or spinel $LiMn_2O_4$ have electronic conductivity fundamentally lower by several orders than layered $LiCoO_2$ and $LiNiO_2$.[3] Attempts are being made to improve the electronic conductivity of manganese oxides, including coating particles with carbon[4] or oxides such as $RuO_2$,[5] or cosynthesizing the compounds with carbon[6] or polymers such as poly(3,4-ethylenedioxy)thiophene.[7] Our work on the coprecipitated composite of layered birnessite-type manganese oxide and acetylene black shows that the discharge capacity was larger than that of the physically mixed composite especially at high current density, showing a capacity of 200 mA·h·g$^{-1}$ at the rate of 1 mA/cm$^2$ (C/3) corresponding to >70% of the theoretical value.[6] However, at much higher rates, e.g. larger than 1C, this material also showed significant capacity fading.

Nafion, a perfluorinated sulfonated ionomer, is of interest in other electrochemical applications such as protonic fuel-cell electrodes or membranes for separation of hydrogen gas,[8,9] or as an electric double layer capacitor.[10] In the present work, we synthesized a composite of birnessite with Nafion by coprecipitation and used it as the active material of a cathode. The result demonstrated that stability on cycling at high charge–discharge rates can be improved.

Lithium-form birnessite manganese oxide (Li-birnessite) can be prepared by a precipitation process from $Mn(NO_3)_2$ and LiOH aqueous solutions.[11] Accordingly, the composite powder in this study was synthesized as follows. An $Mn(NO_3)_2$ solution (0.3 M 38 mL) was mixed with a 5 g Nafion polymer solution (5% Nafion 117 polymer solution, obtained from Wako Pure Chemical Industries, Ltd.) While stirring, a mixed solution of LiOH (0.5 M, 76 mL) and $H_2O_2$ (2 M, 8 mL) was poured into the mixture. After stirring for 4 h, the product was filtered using a membrane filter with a pore size of 0.45 µm (Toyo Roshi Kaisha, Ltd., Japan). The precipitate was washed with distilled water several times until pH ≈7, and then dried at 70 °C. For comparison, a Li-birnessite sample was prepared under the same synthesis conditions but without Nafion.

The XRD patterns (Figure 1), recorded on a Rigaku RINT 2100 X-ray diffractometer, did not show any marked difference between the coprecipitated sample and Li-birnessite samples; each had a basal spacing of 7.03 Å, i.e. the introduction of the Nafion polymer did not affect the formation of birnessite-type manganese oxide. Two kinds of water, physisorbed and interlayer water exist in the composite, corresponding to the two endothermic peaks below and above 130 °C, respectively, in the DTA curves (Figure 2), as measured by a MAC Science thermal analyzer TG-DTA 2000, at 10 °C/min rate in air. The exothermic peaks from 360 to about 500 °C in the DTA curve of the composite accompanied by a weight loss of 14.3% are related to the combustion of the Nafion polymer in the coprecipitated sample. Table 1 shows the metal contents analyzed by atomic absorption spectrophotometry after dissolving the samples in a mixed solution of HCl and $H_2O_2$ and the total carbon and fluorine contents analyzed in the Sumika Chemical Analysis Service, Japan. The higher Li/Mn molar ratio in the coprecipitated sample than in Li-birnessite is due to the exchange of $Li^+$ ions with $Na^+$ ions in the Nafion polymer. The Nafion content, calculated from the F content in the sample and in Nafion solution where F content was analyzed as 3.3%, is 15.0 % in weight, agreeing with the TG result. These results confirm that a composite of birnessite-

**Table 1.** Chemical analysis composition of the coprecipitated composite

| Sample | Element content/mmol/g | | | | | Li/Mn |
|---|---|---|---|---|---|---|
| | Li | Na | Mn | F[a] | C | |
| Composite | 2.60 | 0.011 | 7.75 | 5.2 | 9.33 | 0.34 |
| Li-birnessite | 2.61 | — | 9.48 | — | — | 0.28 |

[a]according to JIS K 0102 34.1.

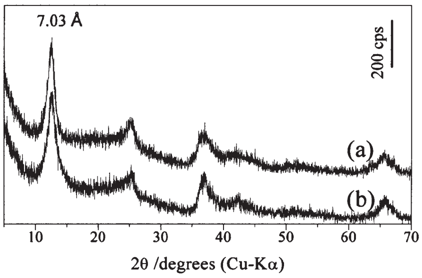

**Figure 1.** X-ray diffraction patterns for (a) coprecipitated composite and (b) Li-binessite.

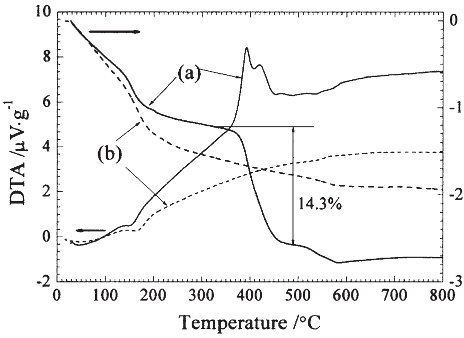

**Figure 2.** Thermogravimetric and differential thermal analysis curves (a) coprecipitated composite and (b) Li-binessite.

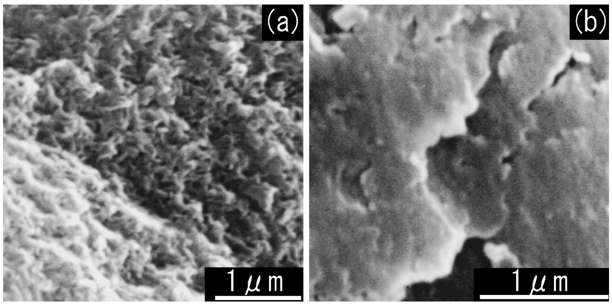

**Figure 3.** SEM images of (a) coprecipitated composite and (b) Li-binessite.

type lithium manganese oxide and Nafion polymer can be obtained by this coprecipitation method.

The composite has a different morphology from Li-birnessite which has layer-shaped slips stacked to form particles as shown in Figure 3b. The coprecipitated composite has a network-like texture formed by particles of around 0.1 μm in size (Figure 3a), suggestive of a homogeneous distribution of birnessite crystal particles on the Nafion polymers.

After heating at 100 °C for 12 h in a vacuum, the composite and Li-birnessite samples were mixed with acetylene black (conducting material) and polyvinylidene fluoride binder, coated on an aluminum foil, and finally heated at 100 °C for 24 h in a vacuum again. The water contents of the composite and birnessite electrodes were roughly evaluated as 2.5 and 8.5%, respectively, from the weight loss by heating up to 200 °C. The samples were then subjected to galvanostatic charge–discharge test using a laboratory-scale cell. Measurement conditions were set as described elsewhere.[6] Counter and reference electrodes were lithium metal; electrolyte, 1 M $LiPF_6$ in ethylene carbonate (EC)–dimethyl carbonate (DMC) (1:1 volume); voltage limits, 2.0 and 4.0 V; and temperature, 25 °C. The cells were usually recharged at a relatively high C/*n* rate, where C is the nominal capacity of the cell and *n* is the time, in hours. By assuming that the insertion of 1 equiv. of lithium per equivalent of Mn in birnessite,[12] the nominal capacities were calculated as 208 and 254 $mA·h·g^{-1}$ for the composite and Li-birnessite, respectively, according to their Mn contents (Table 1). As shown in Figure 4a, the composite showed a capacity of 110 $mA·h·g^{-1}$ corresponding to 54% of the theoretical value at 1.4C rate, but for Li-birnessite the capacity was 70 $mA·h·g^{-1}$ at 1.3C rate, and the recharge rate had to be as low as C/3 to reach 55% of the theoretical value.

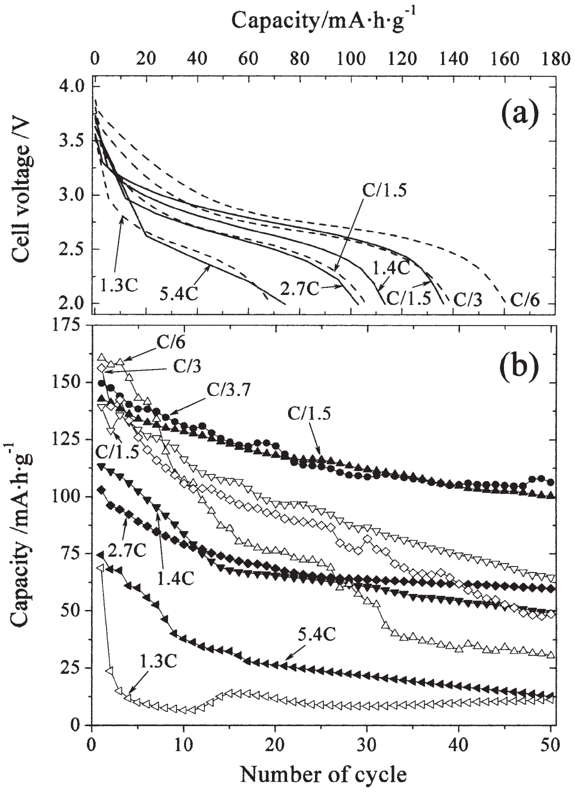

**Figure 4.** Galvanostatic discharge of coprecipitated composite (solid lines and markers) comparing with Li-binessite (dashed lines and open markers) at different C/*n* rates. Panel (a) shows the voltage vs capacity behavior. Panel (b) illustrates the cycle performance upon galvanostatic lithium insertion cycles.

Li-birnessite loses a large fraction of its initial capacity in the first few cycles (Figure 4b), matching the results of the only reference in the literature to direct synthesis for Li-birnessite.[13] The coprecipitated material showed fairly improved cycle performance. At C/1.5 (0.5 $mA/cm^2$) rate, the average capacity fading was less than 0.85% (per cycle) and the composite cathode was able to deliver over 100 $mA·h·g^{-1}$. At higher current rates, the fading was larger in the first 10 cycles than after that. e.g. for 2.7C rate (2 $mA/cm^2$), over the first 10 cycles it was about 5% per cycle over the first 10 cycles, but decreased to less than 0.45% between the 11th and 50th cycles.

The improvement of cycling stability of Li-birnessite with the introduction of Nafion can be attributed mainly to the increase of ionic transport through active materials. Our preliminary examination of conductivity found that the conductivity is noticeably higher in the composite than in the Li-birnessite sample. In addition, the small and homogeneous distribution of birnessite particles precipitated on the Nafion polymers may advantageously improve cycle efficiency. Nafion may be useful as binder, and then contact between active materials and conduction materials is enhanced resulting in decrease of capacity fading.

## References

1 T. Ohzuku and Y. Makimura, *Chem. Lett.*, **2001**, 744.
2 M. E. Arroyo y de Dompablo, C. Marianetti, A. Van der Ven, and G. Ceder, *Phys. Rev. B*, **63**, 144107 (2001).
3 M. Yoshio, in “Lithium Ion Rechargeable Batteries,” 2nd ed., ed. by M. Yoshio and A. Ozawa, Nikkan Kogyo Shimbun, Tokyo (2000), p 5.
4 H. Kawaoka, M. Hibino, T. Watanabe, H. Zhou, and I. Honma, Proceedings of the 43rd Battery Symposium in Japan, The Electrochemical Society of Japan, Fukuoka, 2002, Abstr., No. 2002, p 406; W. Tang, X. Yang, and K. Ooi, Proceedings of the 43rd Battery Symposium in Japan, The Electrochemical Society of Japan, Fukuoka, 2002, Abstr., No. 1A12, p 136.
5 M. Carewska, G. B. Appetecchi, F. Cardellini, and S. Passerini, *Solid State Ionics*, **139**, 211 (2001).
6 X. Yang, W. Tang, Z.-h. Liu, Y. Makita, S. Kasaishi, and K. Ooi, *Electrochem. Solid-State Lett.*, **5**, A191 (2002).
7 C. Arbizzani, M. Mastragostino, and M. Rossi, *Electrochem. Commun.*, **4**, 545 (2002).
8 S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, *J. Electrochem. Soc.*, **149**, A1556 (2002).
9 J. H. Fang, X. X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, and K. Okamoto, *Macromolecules*, **35**, 9022 (2002).
10 P. Staiti, M. Minutoli, and F. Lufrano, *Electrochim. Acta*, **47**, 2795 (2002).
11 Q. Feng, K. Yanagisawa, and N. Yamasaki, *J. Ceram. Soc. Jpn.*, **104**, 897 (1996).
12 B. J. Aronson, A. K. Kinser, S. Passerini, W. H. Wmyrl, and A. Stein, *Chem. Mater.*, **11**, 949 (1999).
13 L. Li and G. Pistoia, *Solid State Ionics*, **47**, 231 (1991).

Published on the web (Advance View) November 17, 2003; DOI 10.1246/cl.2003.1160