

# Fabrication in a Single Synthetic Step of Electrochemically Active $\text{LiMO}_2$ ( $M = \text{Ni}$ and $\text{Co}$ ) Thin-Film Electrodes Using Soft Solution Processing at 20–200 °C

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Well-crystallized and electrochemically active  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  and  $\text{LiCoO}_2$  thin-film electrodes for lithium rechargeable microbatteries can be fabricated in a single synthetic step using an economical, less energy consuming, and environmentally friendly “Soft Solution Processing” method in a concentrated  $\text{LiOH}$  solution at fixed temperatures between 20 and 200 °C without any postsynthesis annealing. While the purely hydrothermal treatment of cobalt plates directly leads to the formation of  $\text{LiCoO}_2$  films,  $\text{Ni}(\text{OH})_2$  films on nickel plates are fabricated under the same hydrothermal conditions. By using the electrochemical–hydrothermal approach under supplementary galvanostatic charge with the same hydrothermal conditions,  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films can only be effectively prepared in a single synthetic step from nickel plates. Such different activation methods required for the preparation of  $\text{LiCoO}_2$  and  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films respectively can be ascribed to the different metal cation valencies between dissolved nickel species (that contain divalent nickel) and dissolved cobalt species (that should possess trivalent cobalt).

## Introduction

Improvements in the miniaturization of electronic devices have imposed various demands on chemists, physicists, and material scientists. The most essential demand may be to develop suitable microbattery systems as power sources for the microelectronics. All-solid-state lithium and lithium ion rechargeable microbatteries represent a major breakthrough, since they have ameliorated many problems of secondary microbatteries while keeping most of their favorable features.<sup>1–6</sup> In this way, the preparation of lithiated intercalation cathode films has been intensively investigated.<sup>1–10</sup> Especially,  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$  films have captured the limelight as the most

prospective cathodes. However, the major difficulty in fabricating these microbatteries is in the preparation of the lithiated thin-film cathodes. The previous fabrication procedures involve highly sophisticated multistep processes, including preparation of a bulk cathode material or its precursors and its subsequent deposition from the gas phase using chemical vapor deposition (CVD) or sputtering. These procedures unfortunately require high energy and material consumption, complicated instrumentation, as well as postsynthesis heat treatments at high temperature, around 800 °C, to provide the proper electrochemical activity.<sup>1–8</sup> It should be noted how difficult it is to make the gas phase from solid state lithiated ternary oxide in these methods. What is worse, the structure and chemical composition of the film prepared by the deposition techniques are not identical to those of a predeposition cathode material. Such techniques might result in environmental and economic problems, so that its perspective might be questionable. While intensive attention has been paid to the fabrication of long-lasting and high-capacity microbatteries, the economic, environmental, and energy factors of the fabrication processes have not been adequately considered. Therefore, an alternative synthetic route to produce the desired lithiated cathode films on a chip in economical, less energy and material consuming, and environmentally friendly ways is highly desirable. Such a novel synthetic approach should first decrease the number of synthetic steps and second be highly compatible with electronic components. A process called “soft solution processing” seems to be able to fulfill these requirements.<sup>11–20</sup> Soft solution process-

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(1) Shokoohi, F. K.; Tarascon, J. M.; Wilkens, B. J.; Guyomard, D.; Chang, C. C. *J. Electrochem. Soc.* **1992**, *139*, 1845.

(2) Birke, P.; Chu, W. F.; Weppner, W. *Solid State Ionics* **1997**, *93*, 1.

(3) Striebel, K. A.; Deng, C. Z.; Wen, S. J.; Cairns, E. J. *J. Electrochem. Soc.* **1996**, *143*, 1821.

(4) Lee, S. J.; Lee, J. K.; Kim, D. W.; Baik, H. K.; Lee, S. M. *J. Electrochem. Soc.* **1996**, *143*, L268.

(5) Hwang, K. H.; Lee, S. H.; Joo, S. K. *J. Electrochem. Soc.* **1994**, *141*, 3296.

(6) Shokoohi, F. K.; Tarascon, J. M.; Wilkens, B. J. *Appl. Phys. Lett.* **1991**, *59*, 1260.

(7) Antaya, M.; Cearn, K.; Preston, J. S.; Reimers, J. N.; Dahn, J. R. *J. Appl. Phys.* **1994**, *76*, 2799.

(8) Antaya, M.; Dahn, J. R.; Preston, J. S.; Rossen, E.; Reimers, J. N. *J. Electrochem. Soc.* **1993**, *140*, 575.

(9) Jones, S. D.; Akridge, J. R.; Shokoohi, F. K. *Solid State Ionics* **1994**, *69*, 357.

(10) Chen, C. H.; Kelder, E. M.; Jak, M. J. G.; Schoonman, J. *Solid State Ionics* **1996**, *86–88*, 1301.

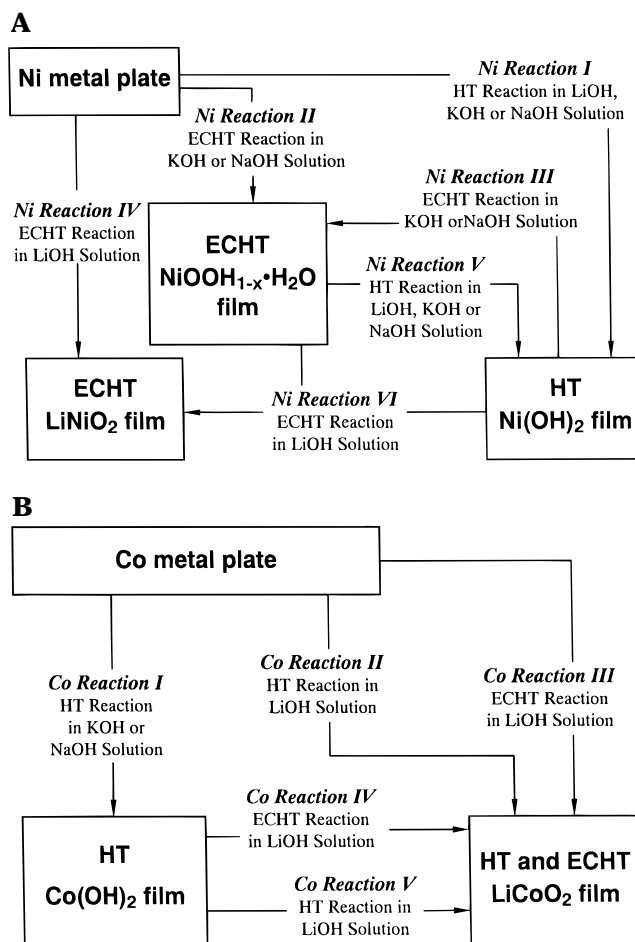
ing encompasses a wide group of synthetic processes used to prepare inorganic materials using a solution treatment at a low temperature.

In this contribution, we present the results of the direct and indirect fabrication of  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  and  $\text{LiCoO}_2$  films using environmentally friendly, less energy consuming, and economical soft solution processing. In addition, the effective design of how to combine activation methods for the successful fabrication of the desired materials will be discussed.

### Experimental Section

**Materials.** The indispensable soft solution processing on Ni (99.7%, Nilaco Co.,  $0.1 \times 1.0 \times 5.0$  cm) and Co (99.9%, Nilaco Co.,  $0.1 \times 1.0 \times 5.0$  cm) plates to fabricate thin-film  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$  electrodes, respectively, is shown schematically in Figure 1. Though the solution treatment of the starting substrate can be combined with various activation methods, such as hydrothermal reactions, electrochemical reactions, photochemical excitation, and/or application of microwaves, from the preliminary experiments, it is found that the hydrothermal treatment (HT) of Co plates and the electrochemical-hydrothermal treatment (ECHT) of Ni plates in LiOH solution are the simplest ways to fabricate  $\text{LiCoO}_2$  and  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films, respectively. The hydrothermal and electrochemical-hydrothermal treatments of both substrates were carried out in a laboratory-made stainless steel autoclave with a PTFE vessel adapted to the pressure vessel ( $\phi 10.0 \times 15.0$  cm) at fixed temperatures between 20 and 200 °C for 20 h in three different alkaline solutions: 200 mL of 4 M LiOH, KOH, and NaOH. No external pressure and gas injection were added during the hydrothermal and electrochemical-hydrothermal treatments. The pressure in the autoclave is just ascribed to water evaporation at a given temperature. The reaction temperature in the autoclave was automatically regulated using an external heating system, a Chromel-Alumel thermocouple, and an automatic controller. The heating processed to the reaction temperature with an approximate heating rate of 1.5 °C/min and the subsequent isothermal process followed by the cooling process. All electrochemical processes during the film preparation were performed in a three-electrode arrangement using Ni or Co working and auxiliary electrodes and a temperature controlled Ag/AgCl reference electrode.<sup>21</sup> The electrochemical process, the electrochemical oxidation of Ni or Co substrates, was galvanostatically realized with a fixed current density between 0.1 and 5.0 mA/cm<sup>2</sup> using the Toho-Giken potentiostat/galvanostat 2000 (Toho-Giken Co.). Prepared films were rinsed several times with doubly distilled water, to eliminate residual alkaline solutions, and then air-dried. It should be noted that the prepared films did not undergo any postsynthesis heat treatment.

**Film Characterization.** The X-ray diffraction pattern analysis of the prepared films was performed using a MAC



**Figure 1.** (A) Direct and indirect preparation scheme of  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films using soft solution processing. (B) Direct and indirect preparation scheme of  $\text{LiCoO}_2$  films using soft solution processing.

Science MXP-3VA diffractometer and Cu  $K\alpha$  radiation ( $\lambda = 1.5405$  Å) operated at 40 mA and 40 kV. The diffractograms were recorded in the  $2\theta$  range of 10–120° with 0.02° resolution. The scanning electron microscope (SEM) images of the cross section of the films were obtained using an Hitachi SEM S-4500. The X-ray photoelectron spectroscopy (XPS) spectra of the films were recorded after Ar sputtering for 30 s with a Shimadzu ESCA3200 using Mg  $K\alpha$  radiation. Binding energy values were all referenced to the carbon 1s line taken as 285.0 ± 0.5 eV. Room-temperature Raman measurements were performed using a Jobin Yvon/Atago Bussan T64000 triple spectrometer with a liquid nitrogen cooled CCD detector for 300–600 s. The laser beam ( $\lambda = 514.5$  nm) was focused to a ~3 μm diameter spot by a 90× microscope objective. The spectral resolution was 2–3 cm<sup>-1</sup>. The cyclic voltammogram of the films was recorded to test their electrochemical activity using an EG&G potentiostat/galvanostat 273A. The electrochemical characterization was carried out in 1.0 M  $\text{LiClO}_4$  propylene carbonate (potential is referred to a Li/Li<sup>+</sup> electrode) under an Ar atmosphere.

### Results and Discussion

The homogeneous color change of the substrate surfaces during the soft solution processing was visually detected, which might support the formation of a certain film without discontinuity and peeling of the films. However, the coloration is of an interferometric character and does not represent any property of the obtained films. The film formed on the surface of substrates was subsequently analyzed with respect to

(11) Gogotsi, Y. G.; Yoshimura, M. *Nature* **1994**, *367*, 628.

(12) Yoshimura, M.; Yoo, S. E.; Hayashi, M.; Ishizawa, N. *Jpn. J. Appl. Phys.* **1989**, *28*, L2007.

(13) Kajiyoshi, K.; Tomono, K.; Hamaji, Y.; Kasanami, T.; Yoshimura, M. *J. Am. Ceram. Soc.* **1996**, *79*, 613.

(14) Kajiyoshi, K.; Yoshimura, M.; Hamaji, Y.; Tomono, K.; Kasanami, T. *J. Mater. Res.* **1996**, *11*, 169.

(15) Yoshimura, M.; Urushihara, W.; Yashima, M.; Kakihana, M. *Intermetallics* **1995**, *3*, 125.

(16) Cho, W. S.; Yashima, M.; Kakihana, M.; Kudo, A.; Sakata, T.; Yoshimura, M. *Appl. Phys. Lett.* **1995**, *66*, 1027.

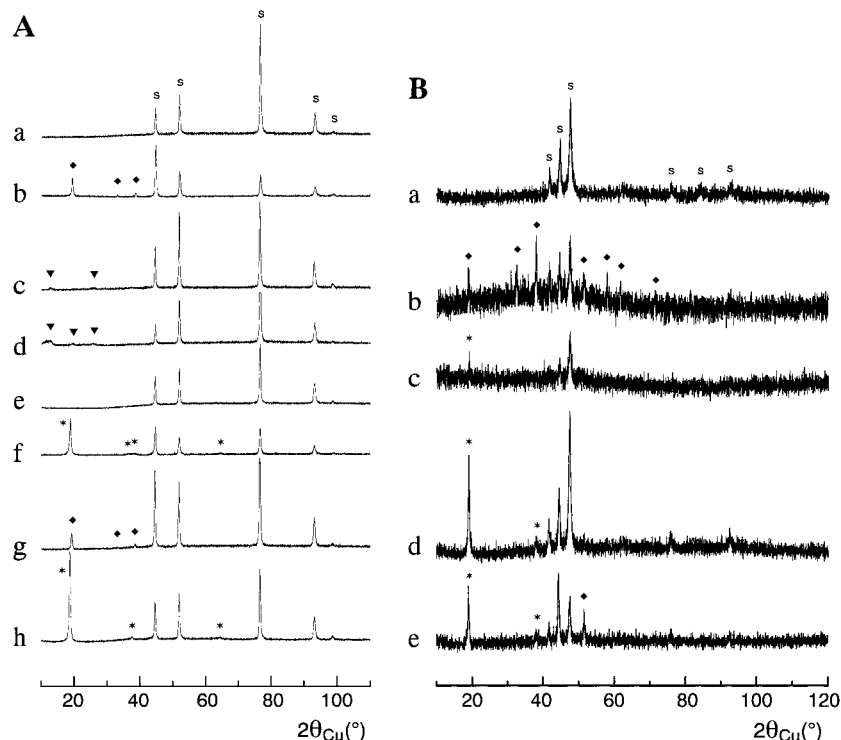
(17) Cho, W. S.; Yoshimura, M. *Jpn. J. Appl. Phys.* **1996**, *35*, L1449.

(18) Yoshimura, M.; Suda, H.; Okamoto, K.; Ioku, K. *J. Mater. Sci.* **1994**, *29*, 3399.

(19) Yoshimura, M.; Suchanek, W. *Solid State Ionics* **1997**, *98*, 197.

(20) Yoshimura, M.; Han, K. S.; Tsurimoto, S. *Solid State Ionics* **1998**, *106*, 39.

(21) Macdonald, D. D.; Owen, D. *J. Electrochem. Soc.* **1973**, *120*, 317.



**Figure 2.** (A) X-ray diffraction patterns for (a) Ni metal substrate, (b) the HT  $\text{Ni(OH)}_2$  film by Ni reaction I at  $150^\circ\text{C}$ , (c) the ECHT  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  film by Ni reaction II at  $150^\circ\text{C}$  with the current density of  $1.0\text{ mA/cm}^2$ , (d) the ECHT  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  film by Ni reaction III at  $150^\circ\text{C}$  with the current density of  $1.0\text{ mA/cm}^2$ , (e) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at  $60^\circ\text{C}$  with the current density of  $1.0\text{ mA/cm}^2$ , (f) the ECHT  $\text{LiNiO}_2$  film by Ni reaction V at  $150^\circ\text{C}$  with the current density of  $1.0\text{ mA/cm}^2$ , (g) the HT  $\text{Ni(OH)}_2$  film by Ni reaction V at  $150^\circ\text{C}$ , and (h) the ECHT  $\text{LiNiO}_2$  film by Ni reaction VI at  $150^\circ\text{C}$  with the current density of  $1.0\text{ mA/cm}^2$ . (S, Ni substrate; ♦,  $\text{Ni(OH)}_2$ ; ▼,  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$ ; \*,  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ ). (B) X-ray diffraction patterns for (a) Co metal substrate, (b) the HT  $\text{Co(OH)}_2$  film by Co reaction I at  $150^\circ\text{C}$ , (c) the HT  $\text{LiCoO}_2$  film by Co reaction II at  $20^\circ\text{C}$ , (d) the HT  $\text{LiCoO}_2$  film by Co reaction II at  $150^\circ\text{C}$ , and (e) the HT  $\text{LiCoO}_2$  film by Co reaction V at  $150^\circ\text{C}$ . (S, Co substrate; ♦,  $\text{Co(OH)}_2$ ; \*,  $\text{LiCoO}_2$ )

its structure, composition, and electrochemical properties. The formation of different films depending on the synthetic conditions was confirmed by X-ray diffraction pattern analysis despite the superposition of important reflections of the films with those of the Ni or Co substrate (Figure 2). As shown in Figure 2A, we can distinguish the diffraction patterns characteristic for the space group  $P\bar{3}m1$  as  $\text{Ni(OH)}_2$  for the HT  $\text{Ni(OH)}_2$  film,<sup>22</sup> the space group  $R\bar{3}m$  as  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  for the ECHT  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  film,<sup>23–25</sup> and the space group  $R\bar{3}m$  or  $Fd\bar{3}m$  as  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  for the ECHT  $\text{LiNiO}_2$  film.<sup>26–29</sup> As is well-known, it is hard to prepare an exact  $\text{LiNiO}_2$  phase even by high-temperature solid-state chemistry reactions.<sup>27–29</sup> Despite the incomplete chemical characterization, the obtained lithium nickel oxide film would be conventionally denoted as the ECHT  $\text{LiNiO}_2$  film. Though the X-ray diffractograms with Cu  $K\alpha$

radiation were affected by fluorescence in the case of the Co system, it might be found that the Co reaction I and Co reactions II–V led to the formation of the  $\text{Co(OH)}_2$  and  $\text{LiCoO}_2$  films, respectively (Figure 2B).<sup>30–32</sup> The scanning electron microscope (SEM) cross section views in Figure 3 directly demonstrates the film formation despite the low fabrication temperature.

In addition to the X-ray diffraction patterns, strong evidence for the formation of the  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  film as the final product has been obtained from X-ray photoelectron spectroscopy (XPS) data. As shown in Figure 4A, the Li (1s) XPS band in the ECHT  $\text{LiNiO}_2$  film appears at  $54.5\text{ eV}$ , in contrast with the HT  $\text{Ni(OH)}_2$  film. The Ni ( $2p_{3/2}$ ) XPS bands in the HT  $\text{Ni(OH)}_2$  film and the ECHT  $\text{LiNiO}_2$  film are observed at  $853.4\text{ eV}$  and near  $855\text{ eV}$ , respectively (Figure 4B), which shows that the nickel valency in the ECHT  $\text{LiNiO}_2$  film is higher than that in the HT  $\text{Ni(OH)}_2$  film. The two XPS bands around  $860$  and  $880\text{ eV}$  in Figure 4B can be assigned to the multielectron excitations (electron shake-up).<sup>33,34</sup> Since hydrated phases can be destroyed by XPS measuring conditions such as long-term pumping in a

(22) . Powder Diffraction File, Card No. 14-117, JCPDS—International Center for Diffraction Data, Swarthmore, PA, 1991.

(23) Glemser, O.; Einerhand, J. Z. *Anorg. Allg. Chem.* **1950**, *261*, 46.

(24) Delmas, C.; Braconnier, J. J.; Borthomieu, Y.; Figlarz, M. *Solid State Ionics* **1988**, *28–30*, 1132.

(25) Oliva, P.; Leonardi, J.; Laurent, J. F.; Delmas, C.; Braconnier, J. J.; Figlarz, M.; Fievet, F.; DeGuibert, A. *J. Power Sources* **1982**, *8*, 229.

(26) Dyer, L. D.; Borie Jr., B. S.; Smith, G. P. *J. Am. Chem. Soc.* **1954**, *76*, 1499.

(27) Dutta, G.; Manthiram, A.; Goodenough, J. B.; Grenier, J. C. *J. Solid State Chem.* **1992**, *96*, 123.

(28) Li, W.; Reimers, J. N.; Dahn, J. R. *Solid State Ionics* **1993**, *67*, 123.

(29) Kanno, R.; Kubo, H.; Kawamoto, Y.; Kamiyama, T.; Izumi, F.; Takeda, Y.; Takano, M. *J. Solid State Chem.* **1994**, *110*, 216.

(30) Powder Diffraction File, Card No. 30-443, JCPDS—International Center for Diffraction Data, Swarthmore, PA, 1991.

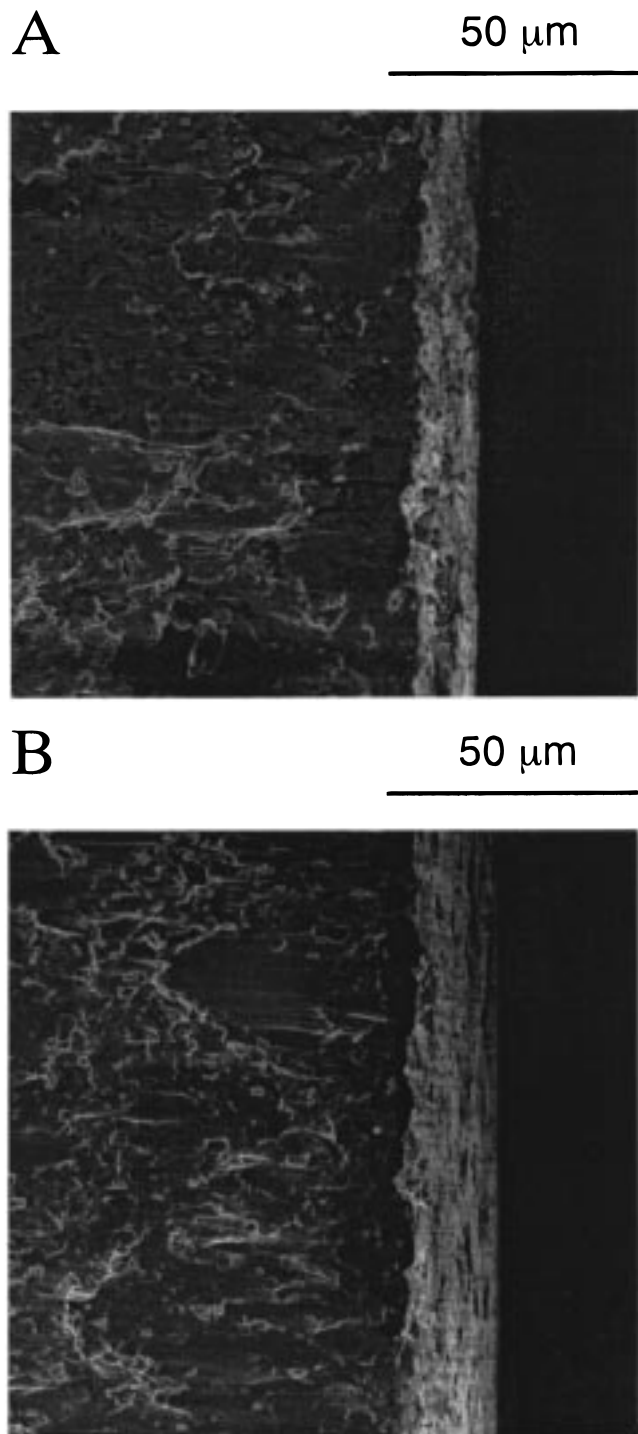
(31) Johnston, W. D.; Heikes, R. R.; Sestrich, D. *J. Phys. Chem. Solids* **1958**, *7*, 1.

(32) Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. *Mater. Res. Bull.* **1980**, *15*, 783.

(33) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Minnesota, 1978.

(34) Kim, K. S. *Phys. Rev. B.* **1975**, *11*, 2177.





**Figure 3.** Scanning electron microscope images of the cross section of (A) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at 60 °C with the current density of 1.0  $\text{mA}/\text{cm}^2$  for 20 h and (B) the HT  $\text{LiCoO}_2$  film by Co reaction II at 20 °C for 20 h.

separate vacuum, no XPS analysis of the ECHT  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  film has been performed. In the case of the Co system, while the presence of lithium in the HT and ECHT  $\text{LiCoO}_2$  films is confirmed (Figure 5A), the Co ( $2p^{3/2}$ ) band positions of the HT  $\text{Co}(\text{OH})_2$  film and the HT and ECHT  $\text{LiCoO}_2$  films are quite similar.<sup>33</sup> Thus, the cobalt valency in the HT and ECHT  $\text{LiCoO}_2$  films is comparable with that of Co metal (Figure 5B). Here, it should be noted that at least three different lithiated cobalt oxide phases with different lithium contents and cobalt valencies were reported such as

layered (space group  $R\bar{3}m$ ), spinel (space group  $Fd\bar{3}m$ ), and rock-salt (space group  $Fd\bar{3}m$ ) lithium cobalt oxides.<sup>7,31,32,35–40</sup> In addition, their X-ray diffraction patterns are unfortunately quite similar. Among them, layered  $\text{LiCoO}_2$  exhibits the most prospective electrochemical activity for a lithium rechargeable battery.<sup>36–38</sup> Considering the above presented data and information, the exact chemical compositions of the obtained HT and ECHT  $\text{LiCoO}_2$  films are still not determined. Nevertheless, it is evident that different crystal structures can give rise to different vibration modes. According to the factor group analysis, the total vibration modes of  $\text{LiCoO}_2$  in space groups  $R\bar{3}m$  and  $Fd\bar{3}m$  are differently obtained such as  $A_{1g} + E_g + 2A_{2u} + 2E_u$  and  $A_{1g} + E_g + 2F_{2g} + 5F_{1u}$ , respectively.<sup>41</sup> While two  $A_{1g}$  and  $E_g$  modes are Raman active in the vibration modes of the layered  $\text{LiCoO}_2$  (space group  $R\bar{3}m$ ), four  $A_{1g}$ ,  $E_g$ , and  $2F_{2g}$  modes are Raman active in those of the spinel  $\text{LiCoO}_2$  (space group  $Fd\bar{3}m$ ) and rock-salt  $\text{LiCoO}_2$  (space group  $Fd\bar{3}m$ ). In addition, it has been reported that two strong Raman bands are observed at 487 and 596  $\text{cm}^{-1}$  for the layered  $\text{LiCoO}_2$  (space group  $R\bar{3}m$ ).<sup>42</sup> On the basis of this information, the Raman spectra for the HT and ECHT  $\text{LiCoO}_2$  films were recorded and are shown in Figure 6. Two main Raman bands at 487 and 597  $\text{cm}^{-1}$  for the HT and ECHT  $\text{LiCoO}_2$  films exactly agree with those of the layered  $\text{LiCoO}_2$  phase, which confirm the formation of the electrochemically active  $\text{LiCoO}_2$  film. The minor Raman bands at 523 and 692  $\text{cm}^{-1}$  might represent the presence of a small amount of spinel and/or rock-salt  $\text{LiCoO}_2$  phases in the HT and ECHT  $\text{LiCoO}_2$  films.

It is quite surprising that electrochemically active lithiated ternary oxide thin films are directly fabricated in LiOH solution at 20–200 °C without any postsynthesis annealing since even the preparation of a bulk cathode material as a precursor for film deposition is performed at high temperature around 800 °C. As far as we are aware, there is no other reference in the literature to the synthesis of any material films applicable to lithium rechargeable microbattery systems at such a low temperature.

While the HT of cobalt substrates in LiOH solution directly leads to the formation of  $\text{LiCoO}_2$  films,  $\text{Ni}(\text{OH})_2$  films are fabricated out of nickel substrates with the same HT conditions. Why can  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films only be effectively prepared in a single synthetic step out of nickel substrates using the ECHT approach under supplementary galvanostatic charge with the same HT conditions, when  $\text{LiCoO}_2$  films can be directly fabricated by only HT of cobalt substrates? Such a difference in the products of the HT of nickel and cobalt substrates

(35) Gummow, R. J.; Liles, D. C.; Thackeray, M. M. *Mater. Res. Bull.* **1993**, *28*, 235.

(36) Gummow, R. J.; Liles, D. C.; Thackeray, M. M.; David, W. I. F. *Mater. Res. Bull.* **1993**, *28*, 1177.

(37) Rossen, E.; Reimers, J. N.; Dahn, J. R. *Solid State Ionics* **1993**, *62*, 53.

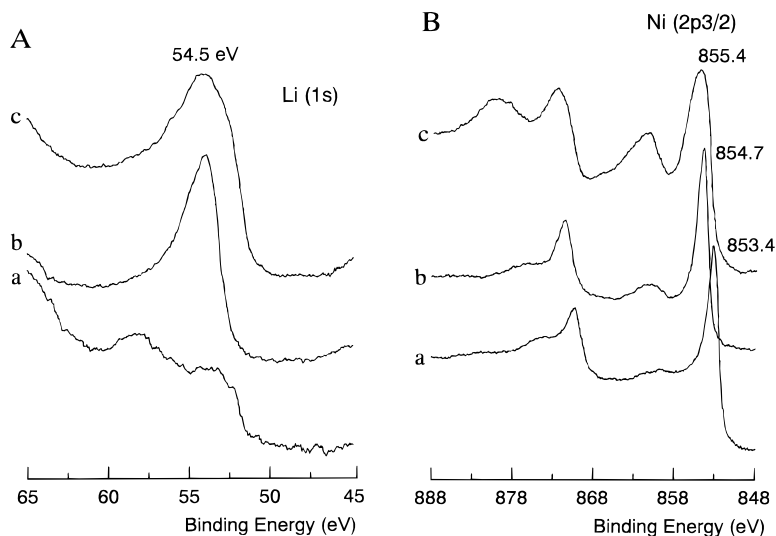
(38) García, B.; Farcy, J.; Pereira-Ramos, J. P.; Perichon, J.; Baffier, N. *J. Power Sources* **1995**, *54*, 373.

(39) Gummow, R. J.; Thackeray, M. M. *Solid State Ionics* **1992**, *53–56*, 681.

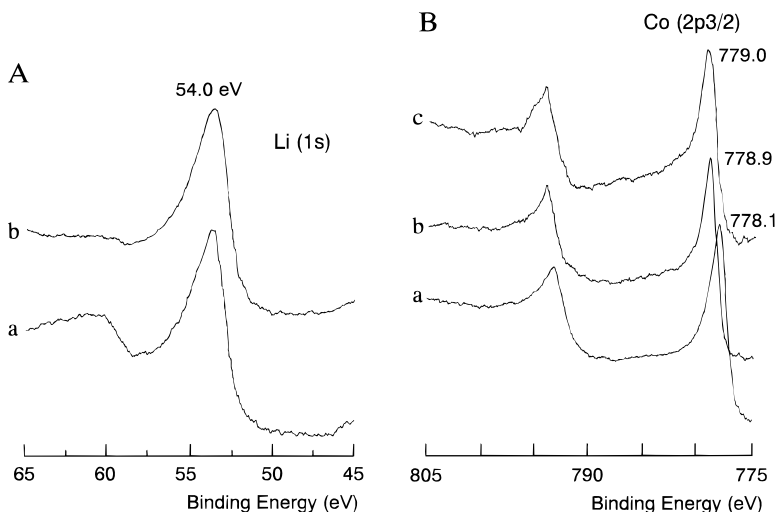
(40) Zhecheva, E.; Stoyanova, R.; Gorova, M.; Alcantara, R.; Morales, J.; Tirado, J. L. *Chem. Mater.* **1996**, *8*, 1429.

(41) Fatel, W. G. *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations*; Wiley-Interscience: New York, 1972.

(42) Kang, S. G.; Kang, S. Y.; Jang, K. H.; Chang, S. H. *Extended Abstracts of Solid State Ionics*, Honolulu, Hawaii, **1997**, 3.



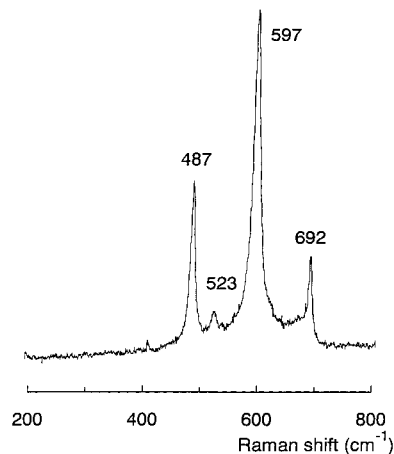
**Figure 4.** (A) Li 1s X-ray photoelectron spectroscopy (XPS) data for (a) the HT  $\text{Ni}(\text{OH})_2$  film by Ni reaction I at 150 °C, (b) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at 60 °C with the current density of 1.0  $\text{mA}/\text{cm}^2$ , and (c) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at 150 °C with the current density of 1.0  $\text{mA}/\text{cm}^2$ . (B) Ni  $2p_{3/2}$  X-ray photoelectron spectroscopy (XPS) data for (a) the HT  $\text{Ni}(\text{OH})_2$  film by Ni reaction I at 150 °C, (b) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at 60 °C with the current density of 1.0  $\text{mA}/\text{cm}^2$ , and (c) the ECHT  $\text{LiNiO}_2$  film by Ni reaction IV at 150 °C with the current density of 1.0  $\text{mA}/\text{cm}^2$ .



**Figure 5.** (A) Li 1s X-ray photoelectron spectroscopy (XPS) data for (a) the HT  $\text{LiCoO}_2$  film by Co reaction II at 20 °C and (b) the HT  $\text{LiCoO}_2$  film by Co reaction II at 150 °C. (B) Co  $2p_{3/2}$  X-ray photoelectron spectroscopy (XPS) data for (a) Co metal substrate, (b) the HT  $\text{LiCoO}_2$  film by Co reaction II at 20 °C, and (c) the HT  $\text{LiCoO}_2$  film by the Co reaction II at 150 °C.

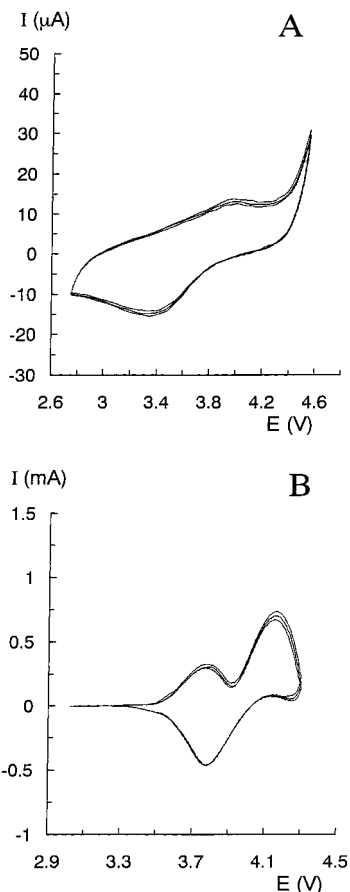
can be ascribed to the different oxidation states of the metal cations between dissolved nickel species (that contain divalent nicks) and dissolved cobalt species (that should possess trivalent cobalts). Thus, the electrochemical anodic process at the Ni working electrode during the ECHT in LiOH solution, the oxidation of precipitated  $\text{Ni}(\text{OH})_2$  film on a nickel plate, is necessary to fabricate the desired  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  films in a single synthetic step. In addition, the indirect fabrication of the  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  film through the ECHT  $\text{NiOOH}_{1-x}\cdot\text{H}_2\text{O}$  film shows that an exchange reaction between  $\text{Li}^+$  and  $\text{H}^+$  occurs in the presence of a large amount of  $\text{Li}^+$ . The apparent difference in the cobalt valency of the products upon the HT in 4 M KOH solution (divalent cobalt) and 4 M LiOH solution (trivalent cobalt) can be attributed to the difference in the association degree of  $\text{OH}^-$  in 4 M KOH solution and 4 M LiOH solution.

According to the cyclic voltammograms (Figure 7), the  $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$  and  $\text{LiCoO}_2$  films prepared at 150 °C can be reversibly oxidized and reduced in lithium perchlo-



**Figure 6.** Raman spectrum of the HT  $\text{LiCoO}_2$  film by Co reaction II at 150 °C.

rate ( $\text{LiClO}_4$ ) propylene carbonate solution, which suggests their prospective electrochemical activity for lithium



**Figure 7.** Cyclic voltammograms taken in 1.0 M LiClO<sub>4</sub> propylene carbonate electrolyte (potential is referred to Li/Li<sup>+</sup> electrode) with the scan rate of 5 mV/s of (A) the ECHT LiNiO<sub>2</sub> film by Ni reaction IV at 150 °C with the current density of 1.0 mA/cm<sup>2</sup> and (B) the HT LiCoO<sub>2</sub> film by Co reaction II at 150 °C.

rechargeable microbatteries. Their peak potentials characterizing both the oxidation and reduction pro-

cesses are similar to those for the LiNiO<sub>2</sub> and LiCoO<sub>2</sub> powder electrodes.<sup>38,39,43</sup> Though a detailed characterization of the obtained films such as battery performance is necessary, it is quite difficult when the obtained Li<sub>1-x</sub>Ni<sub>1+x</sub>O<sub>2</sub> and LiCoO<sub>2</sub> films are on the Ni and Co metal substrates.

### Conclusion

Soft solution processing can be used to prepare lithiated ternary oxide films as a cathode for lithium rechargeable microbatteries in a single synthetic step. The effectively designed combination of solution treatment on metal substrates with a hydrothermal and/or electrochemical reaction improved the desired material preparation such as a dramatic decrease in the fabrication temperature and no postsynthesis heat treatment. In addition, the estimated film properties show the obtained films to be prospective as a desired cathode film for lithium rechargeable microbatteries. Therefore, the soft solution processing should be expected to serve as one of the ideal routes for the fabrication of lithiated ternary oxide films.

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(43) Broussely, M.; Perton, F.; Labat, J.; Staniewicz, R. J.; Romero, A. *J. Power Sources* **1993**, *43-44*, 209.