Application of Layered Nickel Double Hydroxide for Alkali Secondary Battery Using the Liquid Phase Deposition Method

Mizuhata, Minoru
Hosokawa, Akinobu
Béléké, Alexis Bienvenu
Deki, Shigehito

(Citation)
ECS Transactions,19(27):41-46

(Issue Date)
2009

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90005894

ECS Transactions, 19 (27) 41-46 (2009)
10.1149/1.3265867 ©The Electrochemical Society

Application of Layered Nickel Double Hydroxide for Alkali Secondary Battery Using the Liquid Phase Deposition Method

Minoru Mizuhata, Akinobu Hosokawa, Alexis Bienvenu Béléké, and Shigehito Deki

Department of Chemical Science and Engineering,
Faculty of Engineering, Kobe University,
1-1 Rokkodai-cho, Nada, Kobe, 657-8501 Japan
E-mail: mizuhata@kobe-u.ac.jp

The effects of fluoride ions scavenger in the liquid phase deposition synthesis of nickel-aluminum layered double hydroxide/carbon (Ni-Al LDH/C) composite have been investigated. $Al(NO_3)_3.9H_2O$, $AlCl_3$, Al metal plate, and a mixed solution of [$Al(NO_3)_3.9H_2O$ and H_3BO_3] were employed as F^- scavengers. In the case that Al material is solely used as F- scavenger, α-nickel hydroxide is the predominant phase, and a small amount of β-phase is detected. In contrast pure phase Ni-Al LDH/C composites, isostructural and isomorphic to α-$Ni(OH)_2$ are obtained when a mixed solution of $Al(NO_3)_3.9H_2O$ and H_3BO_3 is used at any range of Al content. High purity LDHs without cationic species exhibited good stability in 6M KOH for 7 days. Short-term charge-discharge measurements at 1C-rate for the electrodes containing 0, 13.6 and 17.8 Al mol % showed an increase of the discharge capacity with increasing Al content.

1. Introduction

Al containing nickel layered double hydroxide was prepared by the liquid phase deposition (LPD) method using aluminum metal or compound as the fluorine scavenger in the equilibrium reaction of nickel-fluorine complex ion. the obtained phases depend on the Al content when it is solely used as F- scavenger; α-nickel hydroxide is the predominant phase, and a small amount of β-phase is detected. In contrast pure Ni-Al LDH/C composites, isostructural and isomorphic to α-$Ni(OH)_2$ are obtained at any range of Al content from 0 to ca 30 mol% of [Al]/[Al+Ni]. High purity of LDH without any other cation species caused high stability of LDH structure was performed in 6M KOH aqueous solution.

Layered double hydroxide (LDH) materials are ideally described by hydrotalcite, a natural anionic clay of the composition $Mg_2Al(OH)_6(CO_3^{2-})_{0.5}.2H_2O$ with general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}.[A^{n-}_{x/n}.{}_yH_2O]^{x-}$, A^{n-} = OH^-, CO^{2-}_3, NO_3^-, etc., in which the substitution of a certain fraction *x*, of the divalent cations by trivalent cations gives rise to a net positive charge. The excess of charge is counterbalanced with anions present in the interslab [1]. The unique approach to stabilize α-$Ni(OH)_2$, which is expected as the high energy density of commercial nickel secondary batteries, in alkaline media is by partial substitution of some fractions of nickel ions with trivalent metal ions such as Al [2, 3], Mn [4, 5], in the lattice of $Ni(OH)_2$ to form layered double hydroxides (LDHs).

In our previous works, we have described the synthesis of α-$Ni(OH)_2$ thin films [6] and α-$Ni(OH)_2$/carbon composite [7] by the liquid phase deposition (LPD) method. In our prospects to make α-$Ni(OH)_2$/carbon composite a candidate for the active materials of the positive electrode in nickel-metal hydride batteries, in this study we have extended the work to its stabilization by fabricating Ni-Al LDH/C composite. The main reaction of the LPD reaction is expressed as follows [8] :

$$MF_x^{(x-2n)-} + nH_2O = MO_n + xF^- + 2nH^+ \qquad (1)$$

$$H_3BO_3 + 4HF = BF^{4-} + H_3O^+ + 2H_2O \qquad (2)$$

$$Al + 6HF = H_3AlF_6 + {}^3/_2H_2 \qquad (3)$$

offers the possibility to control the amount of Al and the composition. The conventional procedure involves the use of either H_3BO_3 (eq.2) or Al (eq.3) as F^- scavenger. In the case of $Ni(OH)_2$, (eq. 2) leads to typical turbostatic α-phase while the reaction with Al (eq. 3) results in the formation of Ni-Al LDH/C composite in which a small amount of β-phase coexists with the predominant α-phase at a certain range of the composition [6, 7]. In contrast, the use of a mixed solution of H_3BO_3 and $Al(NO_3)_3{\cdot}9H_2O$ leads to a pure Ni-Al LDH/C composite, isostructural and isomorphic to α-$Ni(OH)_2$ at any range of Al concentrations.

2. Experiment

For the fabrication of Ni-Al LDH/C composite, four types of F^- scavengers were used; $Al(NO_3)_3{\cdot}9H_2O$ (sample A), $AlCl_3$ (sample B), Al metal (sample C), a mixed solution of $Al(NO_3)_3{\cdot}9H_2O$ and H_3BO_3 (sample D). For comparison purpose, H_3BO_3 (sample E) was used to prepare α-$Ni(OH)_2$/C composite. In a typical procedure, 20 mg of oxidized carbon was loaded in a plastic bottle and the reaction solution made of 30 mmol dm^{-3} Ni solution and 0.5 mol dm^{-3} NH_4F constituting the Ni parent solution, an appropriate amount of F^- scavenger, and ion exchange water were poured on. The final concentrations of Ni parent solution and H_3BO_3 were 12.5 mmol dm^{-3} and 0.1 mol dm^{-3}, respectively, while that of $Al(NO_3)_3{\cdot}9H_2O$ varied from 0.6 to 32 mmol dm^{-3} in the reaction solution. Thereafter, the subsequent steps were conducted according to the experimental procedure described in our previous work [7]. The concentrations of Ni and Al within the parent solution were determined by inductively coupled plasma – atomic emission spectroscopy (ICP-AES, HORIBA Ltd.,ULTIMA 2000). 5 mg of the composite was ultrasonically dispersed into 50 ml of diluted HNO_3 solution (0.26 mol dm^{-3}) for 10 min, and stored in the oven at 50°C for 48h to allow dissolution of Ni and Al. The dispersion was then filtrated to remove carbon, and the filtrate was used for the measurements as sample.

3. Results and Discussion

Characterization of obtained LDH

Powder XRD patterns of the as-prepared samples using different F^- scavengers are shown in Fig.1. All the diffraction peaks of samples A, B, C and D are identical and could be indexed as the α-phase of Ni-Al LDH[3], while those for sample E are consistent with those reported for α-$Ni(OH)_2$ [9] and α-$Ni(OH)_2.0.75H_2O$ (JCPDS card No 38-715). The peak positions of (003) and (006) reflections for LDH samples shifted to lower 2θ degree values compared to those for sample E of which (006) reflection plane

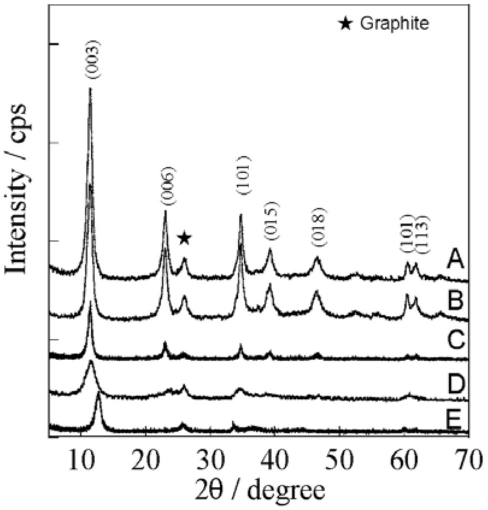

Figure 1. XRD patterns of the as-prepared samples using different fluoride scavengers: (A) 1.8 mmol dm^{-3} $Al(NO_3)_3.9H_2O$, (B) 1.2 mmol dm^{-3} $AlCl_3$, (C) 2 x 1.5 cm^2 Al metal, (D) 1.2 mmol dm^{-3} $Al(NO_3)_3.9H_2O$ and 0.1 mol dm^{-3} H_3BO_3, (E) 0.1 mol dm^{-3} H_3BO_3. Reaction time: 48 h. Temperature: 50°C

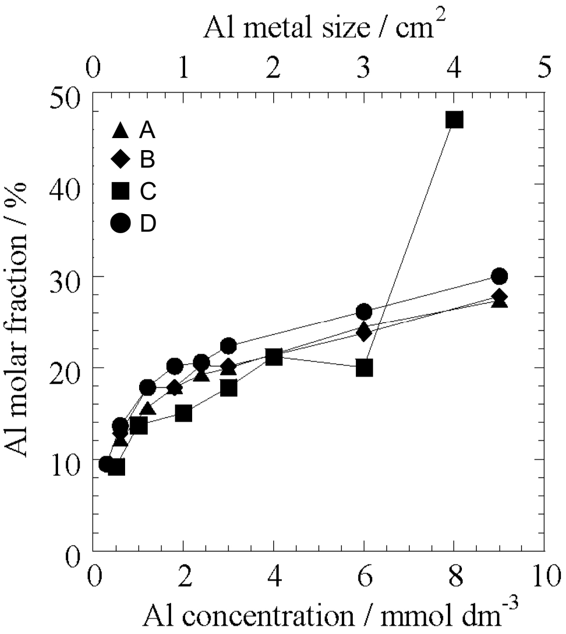

Figure 2. Dependence of Al content on initial concentration. Reaction time: 48 h. Temperature: 50°C.

coincides with that of graphite. The corresponding interlayer distances show that d_{003} and d_{006} increased from 6.96 Å and 3.48 Å for sample E to 7.76 Å and 3.86 Å for LDH/C samples.

At the same time, d_{003} differs according to the type of fluoride scavenger; it varies in the order B > D > A > C > E. These variations are caused by the substitution of Ni^{2+} by Al^{3+} in the lattice of $Ni(OH)_2$, and they are attributable to the extend of the intercalated anionic species in the α-$Ni(OH)_2$ lattice. The high intensity of the (003) plane indicates that the obtained phases have good crystallinity.

In order to control the amount of Al in the lattice of α-$Ni(OH)_2$, the effects of the concentration of each fluoride scavenger have been investigated. The variation of Al content as a function of the concentrations of F^- scavengers is shown in Fig. 2. The general trend is that the Al content increases with increasing composition for all the types of scavengers. This is especially true with Al solutions where the Al content significantly varies in the range 0.6 - 3 mmol dm^{-3} followed by a linear increase up to 9 mmol dm^{-3}. Such a behavior offers a better control of the Al content at any range of concentration. However, increasing the metal size (for even 1 cm^2) leads to a drastic increase of the Al content. Such an abrupt increase is assumed to be caused by the precipitation of Al oxides rather than the LPD process, and renders difficult the control of Al content.

Stability of the LDH samples

The stability of LDH/C composites (sample D) containing various Al contents was checked by immersing into 6 mol dm-3 KOH solution for 7 days. The X-ray diffraction patterns of samples after aging are shown in Fig. 3. For the sample E (α-$Ni(OH)_2$), the crystal phase changed from α-phase to β-phase. On the other hand, All the peaks of the as prepared samples A-C belong to Ni-Al LDH, and no peak related to β-phase was detected. After aging, the interlayer distances are constant with an average of ca. 7.6 Å even for sample A-C. This suggests that the intercalated anions have been exchanged with hydroxide ions and water molecules while the structure is maintained stable by the presence of Al ions. The high stability of LDH structure will bring the high performance for active materials of nickel-metal hydride batteries.

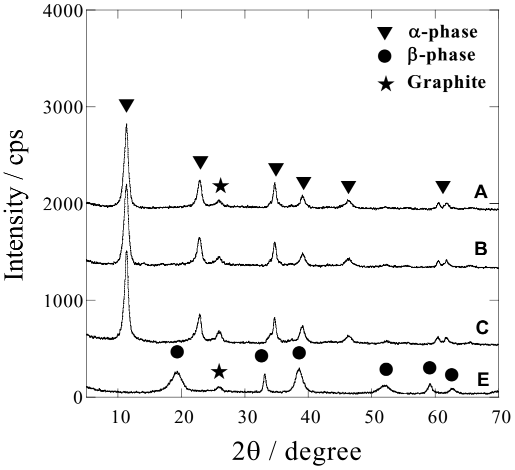

Figure 3. XRD patterns of samples after aging test in KOH aqueous solution for 7 days. Using fluoride scavengers are the same ones in Figure 1.

Electrochemical properties

For the assessment of the LPD-based positive electrode active materials, preliminary electrochemical tests were conducted. Fig. 4 shows the charge-discharge curves at 1C-rate of the test cells using pure 0 Al mol % (α-$Ni(OH)_2$/C), 13.6 Al mol % and 17.8 Al mol % of Ni-Al LDH/C composites. The charging potentials on the charging process decreased with increasing the amount of Al whereas the potential for the oxygen evolution at the end of the charging are almost unchanged. The discharge plateaux increase with increasing Al content. This could be attributed to the larger quantity of the water molecules within the interlayer space of α-$Ni(OH)_2$, which might be favorable to the proton diffusion during charge-discharge processes [10, 11]. Discharge capacities of 350, 336 and 360 mAh g^{-1} could be achieved for the electrodes containing 0, 13.6 and 17.8 Al mol %, respectively. The number of exchanged electron (NEE) calculated

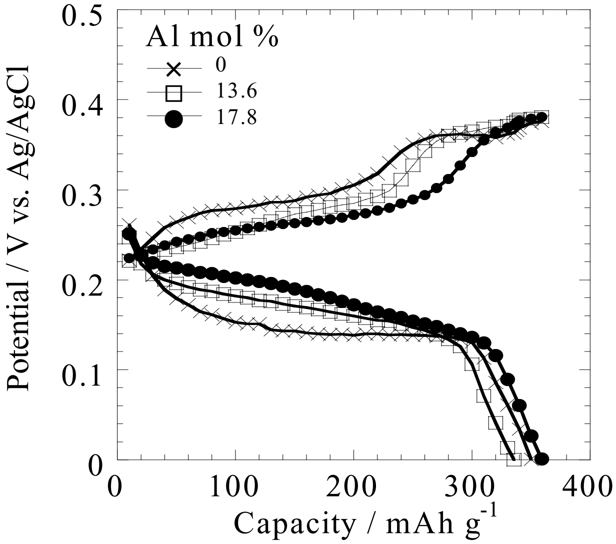

Figure 4. Charge and discharge capacities at 1C-rate for LPD-based electrodes containing 0, 13.6 and 17.8 Al mol %.

from the discharge capacity obtained at 5C-rate according to the formula below [12]:

$$NEE = \frac{3600C_{\exp}}{nF} \qquad (3)$$

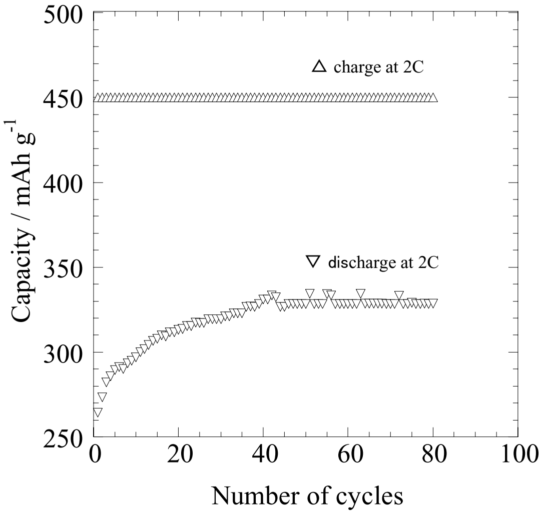

Figure 5. Life performance at 2C-rate of sample D with 17.8 Al mol % for 80 cycles

where C_{exp} is the experimental discharge capacity in A h g^{-1} of composite in the electrode, n is the number of moles of nickel per gram of sample, and F is Faraday's constant (96485 C mol s^{-1}) corresponds to 1.07, 1.56 and 1.74 electrons exchanged for the electrodes containing 0, 13.6 and 17.8 Al mol %, respectively. LDH composites have higher NEE than pure α-$Ni(OH)_2$/C composite. This is because LDHs stabilize the α-$Ni(OH)_2$ phase so that cycling between α-$Ni(OH)_2$ and γ-NiOOH can occur and more electron can be exchanged owing the high oxidation state of Ni in γ-NiOOH [13]. The life performance of the cell containing 17.8 Al mol % conducted by running the charge and discharge at 2C-rate for 80 cycles is shown in Fig, 10. The discharge capacity increases from 260 mAh g^{-1} at the start up to 330 mAh g^{-1} to 40 cycles, which corresponds to the activation time, then it was constant during the remaining cycling period. The charge capacity was maintained at 450 mAh g^{-1}during the whole period of measurements. 80 cycles may not be sufficient to evaluate the maximum life performance of the cells. However, the current trend indicates that the fabricated electrodes possess a good stability and reversibility which may be ascribed to good proton diffusion within the interlayer assumed to contain only water molecules and hydroxide anions.

The overall electrochemical characteristics of the cathode materials presented in this work are encouraging even if they are somewhat lower than the targeted or the theoretical values expected for Ni-Al LDHs for which significant progress have been achieved. Several factors such as ohmic drop, the energetics of the ion insertion-expulsion reaction [14, 15] which includes the proton concentration and electrolytic concentration, or the correlation between the capacity of the electrode to intercalate or deintercalate the number of proton with the volume of the active materials are yet to be understood [16]. Further investigations are on process in order to optimize the synthetic procedure for the improvement of the electrochemical performance.

This study was carried out as the Energy and Environment Technologies Development Projects; "Development of an Electric Energy Storage System for Grid-connection with New Energy Resources" supported by Kawasaki Heavy Industries (KHI) Ltd. and New Energy and Industrial Technology Organization (NEDO). We are thankful to Professor

Hiroshi Inoue and Dr. Eiji Higuchi of Osaka Prefecture University for helpful discussions and experimental evaluation of the electrodes.

References

1. R. Allman, *Chimia,* **24**, 99 (1970).
2. F. Portemer, A. Delahaye-Vidal, M. Figlarz, *J. Electrochem. Soc.*, **139**, 671 (1992).
3. P. V. Kamath, M. Dixit, L. Indira, A. K. Shukla, V. G. Kumar, N. Munichandraiah, *J. Electrochem. Soc*., **141**, 2956 (1994).
4. L. Demourgues-Guerlou, C. Delmas, *J. Electrochem. Soc.*, **143**, 561 (1996).
5. M. Morishita, S. Ochiai, T. Kakeya, T. Ozaki, Y. Kawabe, M. Watada, T. Sakai, *J. Electrochem. Soc.*, **156**, A366 (2009).
6. S. Deki, A. Hosokawa, A. B. Béléké, M. Mizuhata, *Thin Films Solids*, **517**, 1546 (2009).
7. A. B. Béléké, A. Hosokawa, M. Mizuhata, S. Deki, *J. Ceram. Soc. Japan*, **117**, 392 (2009).
8. M. Mizuhata, Y. Saito, M. Takee, S. Deki, *J. Ceram. Soc. Japan*, **117**, 1363 (2009).
9. T. A. Han, J. P. Tu, J. B. Wu, Y. Li, Y. F. Yuan, *J. Electrochem. Soc*., **153**, A738 (2006).
10. W. K. Hu, D. Noréus, *Chem. Mater.* **15**, 974 (2003).
11. L. J. Yang, X. P. Gao, Q. D. Wu, H. Y. Zhu, G. L. Pan, *J. Phys. Chem. C,* **111**, 4614 (2007).
12. G. A.Caravaggio, C. Detellier, Z.Wronski, *J. Mater. Chem.*, **11**, 912 (2001).
13. W. E. O'Grady, K. I. Pandya, K. E. Swider, D. A. Corrigan, *J. Electrochem. Soc.*, **143**, 1613 (1996).
14. A. M. Bond, S. Fletcher, P. G. Symons, *Analyst*, **123**, 1891 (1998).
15. A. M. Bond, S. Fletcher, M. Marken, S. J. Shaw, P. G. Symons, *J. Chem. Soc. Faraday Trans*., **92**, 3925 (1996).
16. K. P. Ta, J. Newman, *J. Electrochem. Soc*., **146**, 2769 (1999).