Ni–Al Layered Double Hydroxide Prepared by Liquid Phase Deposition

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Al-containing nickel layered double hydroxide was prepared by liquid phase deposition (LPD) using aluminum metal or compounds 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 stability of LDH in 6 M aqueous KOH solution was performed because of low impurity of cation species.

Layered double hydroxide (LDH) materials are ideally described by hydrotalcite, a natural anionic clay of the composition $Mg_2Al(OH)_6(CO_3{}^{2-})_{0.5}\cdot 2H_2O$ with general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}\cdot[A^{n-}{}_{x/n}\cdot yH_2O]^{x-}$, $A^{n-} = OH^-$, $CO_2{}^{3-}$, and $NO_3{}^-$, 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 charge is counterbalanced by anions present in the interslab.[1] A unique approach to stabilize α-$Ni(OH)_2$, which is expected to be useful in high density commercial secondary batteries, in alkaline media is partial substitution of nickel ions with trivalent metals such as Al[2,3] or Mn,[4,5] in the lattice to form layered double hydroxides (LDHs).

In previous work, 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). With the intent of making α-$Ni(OH)_2$/carbon composite a candidate for an active material for the positive electrode in nickel–metal hydride batteries, we have extended this work to stabilization by fabricating Ni–Al LDH/C composite. The main reaction of LPD is expressed as follows:[8]

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

$$H_3BO_3 + 4HF \rightleftarrows BF^{4-} + H_3O^+ + 2H_2O \tag{2}$$

$$Al + 6HF \rightleftarrows H_3AlF_6 + \frac{3}{2}H_2 \tag{3}$$

This 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[6,7] 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 composition. 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.

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, H_3BO_3 (sample E) was used to prepare α-$Ni(OH)_2$/C composite.

In a typical procedure, 20 mg of carbon, Valcan XC-72R, oxidized by aqueous solution of $KMnO_4$ and HNO_3 as described in ref 7 was loaded in a plastic bottle and the reaction solution made of 30 mmol dm^{-3} aqueous $Ni(NO_3)_2$ solution and 0.5 mol dm^{-3} NH_4F constituting the parent Ni solution, an appropriate amount of the F^- scavenger, and deionized water. The final concentrations of parent Ni 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. For Sample C, Al metal was cut to proper surface area from 0.2 to 4 cm^2. 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 an oven at 50 °C for 48 h to allow dissolution of Ni and Al. The residual carbon dispersion was then filtrated and the filtrate was used for the ICP measurements as sample.

Powder XRD patterns of the samples using different F^- scavengers are shown in Figure 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-$Ni(OH)_2\cdot 0.75H_2O$ (JCPDS card No 38-715). The peak positions of (003) and (006) reflections for LDH samples shifted to lower 2θ values compared to those for sample E of which the (006) reflection plane coincides with that of graphite. The corresponding interlayer distances show that d_{003} and d_{006} increased from 6.96 and 3.48 Å for sample E to 7.76 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, 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 Figure 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 solu-

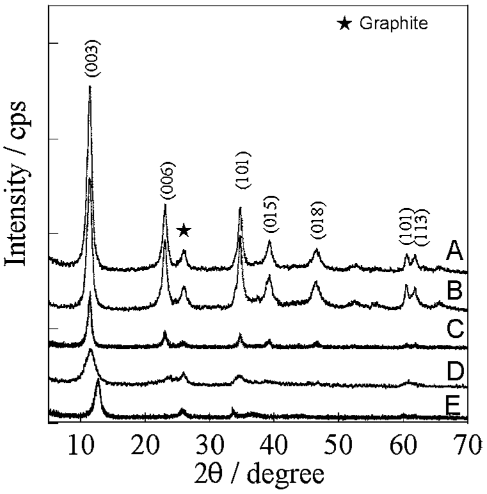

Figure 1. XRD patterns of the as-prepared samples using different fluoride scavengers: (A) 1.8 mmol dm^{-3} $Al(NO_3)_3 \cdot 9H_2O$, (B) 1.2 mmol dm^{-3} $AlCl_3$, (C) 2 × 1.5 cm^2 Al metal, (D) 1.2 mmol dm^{-3} $Al(NO_3)_3 \cdot 9H_2O$ and 0.1 mol dm^{-3} H_3BO_3, (E) 0.1 mol dm^{-3} H_3BO_3. Reaction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

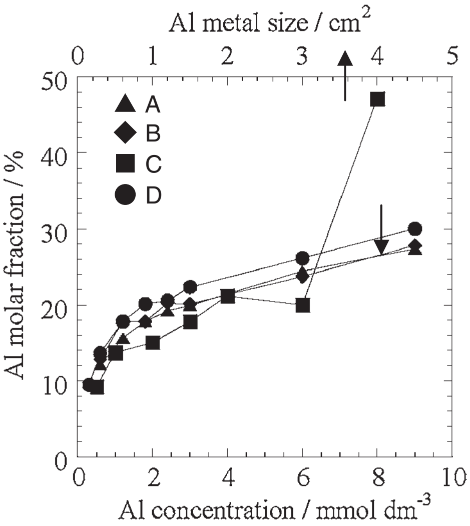

Figure 2. Dependence of Al content on initial concentration. Reaction time: 48 h. Temperature: 50 °C.

tions 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 behavior offers 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 hydroxides as contamination on and into prepared LDH samples rather than the LPD process and renders difficult the control of Al content.

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 Figure 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 samples A–C belong to Ni–Al LDH and no peak related to β-phase was detected.

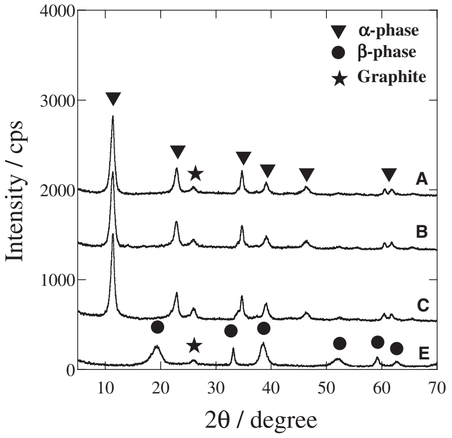

Figure 3. XRD patterns of samples after aging test in KOH aqueous solution for 7 days. Using fluoride scavengers are the same ones in Figure 1.

After aging, the interlayer distances are constant with an average of ca. 7.6 Å even for samples A–C. This suggests that the intercalated anions have been exchanged with hydroxide ions and water molecules while structural stability is maintained stable by the presence of Al ions.

The high stability of LDH will improve the high performance of active materials for nickel–metal hydride batteries.

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