Preparation and Electrochemical Performance of Ni–Al LDH Doped with Co and La

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Ni–Al LDH doped with Co and La was prepared by coprecipitation. The sample obtained consisted of loose pellets which were further reunited with masses of smaller particles. Its BET surface area reached 132.5 m^2/g and was much larger than that of a sample doped only with Co. The electrode fabricated from it exhibited better electrochemical reversibility, and the proton diffusion coefficient is also much higher.

Ni–Al layered double hydroxide (LDH) is a promising active material for the positive electrode in Ni/MH, Ni/Cd, and Ni/Zn secondary batteries.[1–3] During charge–discharge it follows α/γ phase transformation[4] involving more than one electron exchanging per nickel atom and does not lead to mechanical deformation. Therefore, electrodes fabricated from it have higher capacity and longer cycle life than that of β-$Ni(OH)_2$. However, oxygen evolution becomes easier and the difference between oxygen evolution potential and oxidation potential becomes smaller after the addition of Al^{3+}. This is unfavorable to the charge efficiency of batteries. The addition of Co is an effective method for improving the conductivity of the active material and decreasing the oxidation potential. Rare earth elements such as Y,[5] Lu,[6] and La[7] are also beneficial to the improvement of charge acceptability and electrochemical performance of the electrode, particularly at high temperature. They are added to the electrode mainly in the form of oxide powders or coating layer of hydroxides on the surface of active material, because they have much larger ionic radii than Ni^{2+} and doping them into the crystal lattice of $Ni(OH)_2$ usually leads to an extremely marked distortion in the structure.

In the present study, we prepared Ni–Al LDH doped with both Co and La by coprecipitation similar to the procedure reported by Kosova et al.[8] with minor modification. The dopant Co should be easily incorporated in the lattice of LDH and substitute the position for nickel, while La may be mainly precipitated as a gel on the external surface of the crystallites under certain conditions. The final product should have relatively regular morphology, narrow particle size distribution, and preferable electrochemical performance.

The preparation was performed in the following way: a mixed metal ($Ni^{2+} + Al^{3+} + Co^{2+} + La^{3+}$, molar ratio was 80:15:2.5:2.5) nitrate solution (200 mL) with total metal ion concentration of 1.25 mol/L was prepared and assigned as A. Then, a solution (200 mL) containing 0.15 M Na_2CO_3 and 2.75 M KOH was prepared and assigned as B. With vigorous stirring, solutions A and B were simultaneously added dropwise into a reaction vessel with 100 mL of deionized water. The addition took about 3 h, during which the temperature of reaction solution was maintained at 45 ± 1 °C and pH value at 11.0 ± 0.5. The resulting suspension was further stirred for 2 h and then maintained for 24 h at the same temperature. After filtering and rinsing several times with deionized water, the precipitate was dried to constant weight at 80 °C. Electrochemical performance of the product was evaluated by cyclic voltammetry (CV) measurement at room temperature. The working electrode was a powder microelectrode with diameter 100 µm. A platinum sheet was used as counter electrode and a Hg/HgO electrode as reference electrode. The electrolyte was 7 M KOH + 15 g/L LiOH. The working electrode was scanned at 0.5, 1, 2, 5, 10, and 20 mV/s for 20 cycles, respectively.

Figure 1 shows the XRD pattern of the prepared sample. It is similar to those reported for Al-substituted nickel hydroxides[9] and consistent with the standard pattern of α-$Ni(OH)_2 \cdot 0.75H_2O$ (JCPDS38-0715). Because no peak from β-$Ni(OH)_2$ is observed, the sample is pure α-phase, at least at the XRD detection level. This indicates Ni–Al LDH has been successfully synthesized. Calculation according to the Scherrer equation ($D = k\lambda/\beta\cos\theta$) shows the crystallite size (D_c, in the direction of c axis) is about 11.2 nm.

Figure 2a shows the SEM image of the sample at low magnification (500×). It can be seen that the sample consists of loose pellets. The image at high magnification (5000×, Figure 2b) shows that the pellets are further reunited with masses of smaller

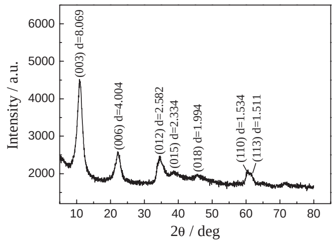

Figure 1. XRD pattern of Ni–Al LDH doped with Co and La.

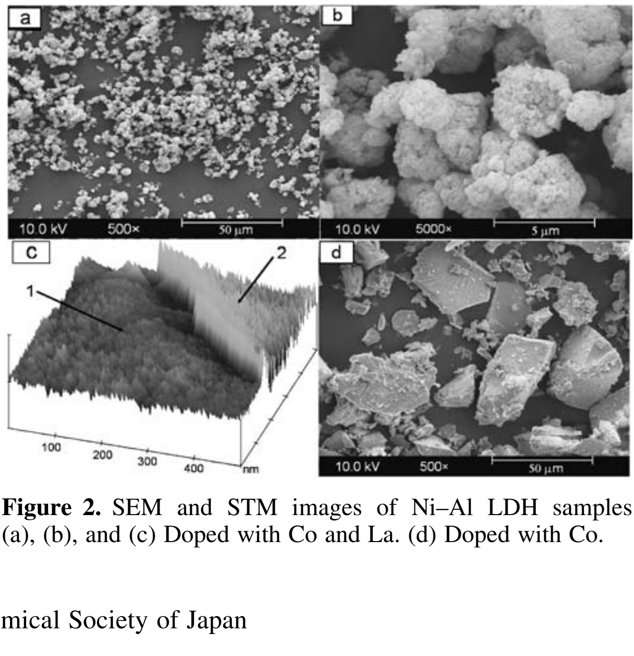

Figure 2. SEM and STM images of Ni–Al LDH samples. (a), (b), and (c) Doped with Co and La. (d) Doped with Co.

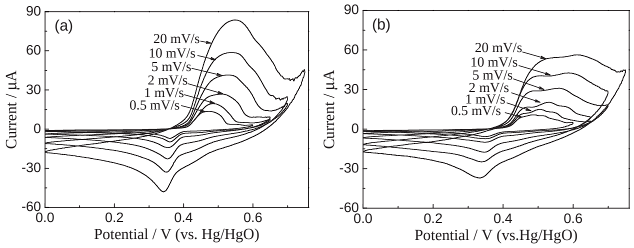

Figure 3. Cyclic voltammograms of electrodes with Ni–Al LDH samples. (a) Doped with Co and La. (b) Doped with Co.

Table 1. CV data with the electrodes scanned at 1, 5, and 20 mV/s

Electrode[a]	Scanning rate /mV s^{-1}	E_a/mV	E_c/mV	$\Delta E_{a,c}$/mV
A	1	486	360	126
B	1	505	348	157
A	5	527	353	174
B	5	556	346	210
A	20	549	341	208
B	20	611	333	278

[a] A. sample doped with Co and La, B. sample doped with Co

particles. The average diameter of the pellets is smaller than 5 μm, and the surface is very rough and porous. Figure 2c shows a 3D STM image of the sample. It is clear that the particles are the aggregate of thin crystal sheets and that the surface is still very rough at nanometer scale. XRF test result shows the molar ratio of Ni:Al:Co:La in the sample is 81.2:14.5:2.2:2.1, while XPS analysis shows the molar ratio of La^{3+}:Ni^{2+} on the sample surface reaches about 1:9.2, and neither Al nor Co is detected. Therefore, La^{3+} might be mainly coprecipitated with $Ni(OH)_2$ as a gel initially on the surface of LDH crystallites (zone 1) and then transformed into a crystal coating layer (zone 2) during the aging process. SEM image of Ni–Al LDH doped only with Co (molar ratio of Ni:Al:Co is 80:15:5) is also shown in Figure 2d for comparison. The coarse irregular particles with compact surface are obviously different from those of the former sample. Further test results show its BET surface area is only 5.4 m^2/g, while that of the former sample reaches 132.5 m^2/g.

Figure 3a shows the cyclic voltammogram of an electrode comprising of Ni–Al LDH doped with Co and La. That of the Ni–Al LDH electrode doped only with Co is also shown in Figure 3b. The anode oxidation ($Ni(OH)_2 \rightarrow NiOOH$) peaks and cathodic reduction ($NiOOH \rightarrow Ni(OH)_2$) peaks of the former electrode are narrower than those of the latter, suggesting the electrochemical reaction processes are easier. This can be confirmed by the CV data summarized in Table 1. The anode peak potentials E_a of the former electrode are less positive than those of the latter at the same scanning rates, while the cathodic peak potentials E_c are more positive. So the former electrode is more easily oxidized or reduced. $\Delta E_{a,c}$, the difference between E_a and E_c is taken as an estimate of the reversibility of the redox reaction. The former electrode has smaller $\Delta E_{a,c}$ than the latter, indicating it has better electrochemical reversibility.[10]

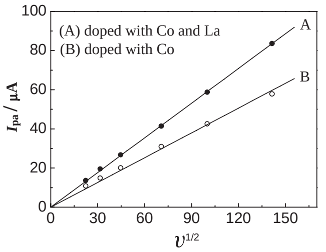

Figure 4. The relationship of I_{pa} with $v^{1/2}$.

Figure 4 shows the relationship of anodic peak currents I_{pa} with $v^{1/2}$, where v is the potential scanning rate in CV measurement. It can be seen that I_{pa} against $v^{1/2}$ gives a reasonably linear relationship for each electrode according to the classical Randles–Sevick equation. That is,

$$I_p = 2.69 \times 10^5 n^{3/2} A D_0{}^{1/2} v^{1/2} C_0$$

From this equation and the slopes of the I_{pa} against $v^{1/2}$ plots, we calculate that the proton diffusion coefficients (D_0) in the above electrodes are 5.7×10^{-9} and 4.5×10^{-10} cm^2/s, respectively. This implies the electrode composed of the sample doped with Co and La exhibits smaller polarization in electrode processes and thus exhibits better electrochemical performance. The main reason may be that the sample has smaller particle size, rougher surface, and much larger specific surface area.

In summary, Ni–Al LDH doped with Co and La has been prepared by coprecipitation. The loose pellets obtained are reunited with masses of smaller particles and further composed of thin crystal sheets. The BET surface area reaches 132.5 m^2/g and is much larger than that of the sample doped only with Co. The electrode composed of it exhibits better electrochemical reversibility, and the proton diffusion coefficient is also much higher.

References

1 P. V. Kamath, M. Dixit, L. Indira, A. K. Shukla, V. G. Kumar, N. Munichandraiah, *J. Electrochem. Soc.* **1994**, *141*, 2956.
2 Y. Li, W. Li, S. Chou, J. Chen, *J. Alloys Compd.* **2008**, *456*, 339.
3 H. Chen, J. M. Wang, T. Pan, Y. L. Zhao, J. Q. Zhang, C. N. Cao, *J. Power Sources* **2005**, *143*, 243.
4 H. Bode, K. Dehmelt, J. Witte, *Electrochim. Acta* **1966**, *11*, 1079.
5 K. Shinyama, H. Nakamura, T. Nohma, I. Yonezu, *J. Alloys Compd.* **2006**, *408–412*, 288.
6 J. X. Ren, J. Yan, Z. Zhou, X. J. Wang, X. P. Gao, *Int. J. Hydrogen Energy* **2006**, *31*, 71.
7 Y. P. Yang, P. M. Zhang, Y. B. Zhang, Y. G. Tang, K. Y. Liu, S. B. Sang, *J. Cent. S. Univ. (Sci. Technol.)* **2005**, *36*, 988.
8 N. V. Kosova, E. T. Devyatkina, V. V. Kaichev, *J. Power Sources* **2007**, *174*, 735.
9 C. Y. Wang, S. Zhong, K. Konstantinov, G. Walter, H. K. Liu, *Solid State Ionics* **2002**, *148*, 503.
10 Q. S. Song, C. H. Chiu, S. L. I. Chan, *J. Appl. Electrochem.* **2006**, *36*, 97.

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