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The effect of the interlayer anions on the electrochemical performance of layered double hydroxide electrode materials

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ABSTRACT

Both high energy density and high power density are vitally required for new applications such as electric vehicles. Here we present a comparison of two well-crystallised layered double hydroxides, $[Ni_4Al(OH)_{10}]OH$ and $[Ni_4Al(OH)_{10}]NO_3$, which shows that the former can maintain a better discharge capacity, 294–299 $mAh\,g^{-1}$, than the latter, 233–287 $mAh\,g^{-1}$ at a current density of 2000 $mA\,g^{-1}$ within about 300 cycles, although both electrodes deliver a similar capacity of 326 $mAh\,g^{-1}$ at 200 $mA\,g^{-1}$ initially. It is believed that both the more watery interlayer space in $[Ni_4Al(OH)_{10}]OH$ than in $[Ni_4Al(OH)_{10}]NO_3$ and the morphologic changes induced by anion exchange of NO_3^- by OH^- during electrochemical cycles play key roles in their behaviour.

1. Introduction

Secondary batteries are devices that supply wireless power; they reversibly transform electric energy into chemical energy without any pollution. Therefore, they are supposed to be green energy sources for city transportation. Recently, great efforts have been made to increase their energy density, power density, along with cycle life, which are vital to make electric facilities run longer, faster and more energetic [1]. Moreover, if the electric vehicles are used in transportation among cities, it must be emphasised that the batteries can be fully charged in short time, such as 10–15 min, in addition to that they can discharge high energy in short time (peak power output).

Of the known candidates of secondary batteries, matured lead acid batteries and Ni–Cd batteries can be fully charged in short time, but their environmental toxicity and low energy density may expel their future use. Therefore, new technology and engineering from lithium [1], magnesium [2,3], hydrogen [4–6] are being required and developed recently. As for the ultrafast chargeable batteries, NiMH battery turns out to be the most promising one since other technologies are either far from maturity (e.g. magnesium-based batteries), or unable to be fast charged for safety reasons (e.g. lithium-based batteries), or being restricted by their toxicity to the environment (e.g. nickel–cadmium batteries). Moreover, there is still a problem that charging and discharging batteries at high rates will dramatically lower dischargeable energy, and most importantly, it will significantly decrease the cycle life of the battery.

Currently, NiMH batteries employ β-$Ni(OH)_2$ as the positive electrode material, therefore it, together with its additives was studied extensively in the past years [7–14]. It is well-known that β-$Ni(OH)_2$ turns to β-NiOOH when it is charged or oxidized, and the latter turns to γ-NiOOH when it is overcharged. Because density of α-NiOOH is much less than β-NiOOH, the positive electrode expands seriously when it is overcharged. The expansion may lead to poor electric contact between the current collector and β-$Ni(OH)_2$/β-NiOOH, and subsequent decrease of discharge capacity of the battery. However, for ultrafast charging, overcharges cannot be avoided.

To avoid the limitations from high charge/discharge rate capability of β-$Ni(OH)_2$-based batteries, one has to design and synthesise new electrode materials. From the electrochemical point of view, such electrode materials must be reversible, which can undo perfectly what has been done while they were charged or discharged; secondly, the electrodes must be capable of absorbing and desorbing high rates of fast ions and electrons while they are charged or discharged rapidly; thirdly, the materials must have channels for fast movements of ions and electrons, since the speed of the electrode reactions is controlled by both their

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inherent properties and the flux of the ion and electron currents [15]. Also, important but always being neglected, the ions being exchanged between the electrodes must be an as-good-as-possible runner.

Layered double hydroxides of nickel and other metal(s), also called doped or stabilized α-$Ni(OH)_2$ in literature [16–22], can be one of such kind of electrode materials. The reasons are: (1) structurally, layered double hydroxides are composed of rigid layers and loosely attracted anions and water molecules in between the rigid layers [23,24]. Those materials can be presented by $[Ni_{1-x}M_x(OH)_2]A_y{\cdot}mH_2O$, where M could be a trivalent cation or a mix of trivalent and bivalent metal cations; A is an interlayer anion, which could also be one or a mix of anions; and x, y, m are numbers. Therefore, they may supply a channel for anions to move very fast; (2) it has been found that aluminium doped nickel hydroxides discharge more than 300 mAh g^{-1} and can be electrodes of light weight [16,18–20,25,26]. Crystallinity of the active materials has important impact on the electrochemical properties [18,19,27]; and (3) metal ions can be easily introduced to the lattice to improve its electronic conductivity, and anion like OH^- can be introduced into the interlayer space to improve the ionic conductivity. It is well known that those two kinds of conductivity limit the peak power output.

However, although there are a plenty of papers on those materials, few papers were found to study their discharge capacities at high power output and their fast chargeability except one by the authors [27]. Here we report two layered double hydroxides with an ideal composition of $[Ni_4Al(OH)_{10}]OH$ and $[Ni_4Al(OH)_{10}]NO_3$, which exhibit extraordinary, yet different electrochemical properties in high rate charge/discharge processes.

2. Experimental

2.1. Starting materials

All chemicals used in this research were analytical grade without further treatments. Distilled water used in the experiments must be first boiled for 30 min to remove any dissolved gases.

2.2. Preparations of the electrode materials

$[Ni_4Al(OH)_{10}]NO_3$: 50 ml of aqueous solution containing 6.4 g $LiOH{\cdot}H_2O$ was slowly dropped into 100 ml of aqueous solution containing 17.4 g $Ni(NO_3)_2{\cdot}6H_2O$ and 5.6 g $Al(NO_3)_3{\cdot}9H_2O$ under vigorous stirring and Ar flow at 100 °C in an hour. After the reaction mixture was aged under stirring at the same temperature for 10 h, the product suspension was transferred into Teflon-lined autoclaves, which were placed into an oven and maintained at 180 °C for 1 day. The solid product was then filtered, washed three times with distilled water, acetone and then dried in vacuum at 60 °C. Elemental analyses gave values (wt.%) of Li: not detected; Ni: 44.0; Al: 5.15; N: 2.29; H: 2.56, those calculated for $[Ni_4Al(OH)_{10}](OH)_{0.1}(NO_3)_{0.9}{\cdot}2.5H_2O$ are Ni: 43.9; Al: 5.05; N: 2.36; H: 2.85.

$[Ni_4Al(OH)_{10}]OH$ was prepared by anion exchange of as-prepared $[Ni_4Al(OH)_{10}]NO_3$. 4.6 g of the as-prepared $[Ni_4Al(OH)_{10}]NO_3$ had been stirred in a solution of 1.1 g of $LiOH{\cdot}H_2O$ in 50 ml of distilled water at 100 °C for 8 h. The product was then filtered out, washed and dried as above. Elemental analyses gave values (wt%) of Li: not detected; Ni: 42.8; Al: 5.00; N: 0.34; H: 3.40, those calculated for $[Ni_4Al(OH)_{10}](OH)_{0.8}(NO_3)_{0.2}{\cdot}5H_2O$ are Ni: 42.9; Al: 4.92; N: 0.51; H: 3.83.

3. Methods

Analyses of metals were done with a J-A1100 ICP spectrometer, that of C, H, N were performed on a CHN-O-Rapid Heraeus elemental analyzer by the analytical service at Nanjing University. Power X-ray diffractograms (XRD) were recorded on a Philips X'pert pro MPD diffractometer using Cu Kα (λ = 1.5406 Å) radiation. IR was measured on a Nicolet 5700 in KBr discs.

The electrodes used in electrochemical studies were prepared on a piece of nickel foam sized 2.5 cm × 0.8 cm. 50 mg of $[Ni_4Al(OH)_{10}]X$ (X = OH^- or $NO_3{}^-$) powder, 160 mg of Ni powder, 40 mg Co powder and a few drops of 5% aqueous suspension of polytetrafluoroethylene (PTFE) was mixed, ground to obtain a highly viscous paste. The nickel foam was sandwiched with the paste using a spatula, and then the electrode was dried at 80 °C for 24 h. Thereafter, it is pressed at 20 MPa for 1 min to assure good electrical contact between the foam and the active material. The average pellet thickness is less than 0.5 mm. The current densities, discharge capacities in the context of this paper were all calculated according to the actual mass of $[Ni_4Al(OH)_{10}]X$ used in the electrode preparations.

Electrochemical studies were performed in a three-compartment electrolysis cell at ambient temperature using a CHI 660B electrochemical workstation (Shanghai, China). The cell contains a $[Ni_4Al(OH)_{10}]X$ electrode as the working electrode, a piece of nickel foam of the same size as the counter electrode, a Hg/HgO reference electrode, and a 7-mol l^{-1} KOH aqueous solution as the electrolyte. The $[Ni_4Al(OH)_{10}]X$ electrode was immersed in 7 mol l^{-1} KOH for 24 h and then activated by repeated potential scan between −0.2 and 0.8 V vs. Hg/HgO for 10 times at a rate of 10 mV s^{-1} prior to the electrochemical characterisations. Charge/discharge measurements were then performed under constant currents or potentials. The cycle life of the electrode was tested on a LAND CT-2001A tester (Wuhan, China).

4. Results

4.1. Characterisation of the samples

Both samples have typical XRD patterns of LDHs (Fig. 1), and share great similarities. They can be indexed on a hexagonal cell, space group P6222 (a = b = 0.3058 and 0.3060 nm; c = 2.362 and 2.359 nm for $[Ni_4Al(OH)_{10}]OH$ and $[Ni_4Al(OH)_{10}]NO_3$, respectively). The samples are well-crystallised, and the peaks at angels higher than 30° are very weak compared with the first two peaks, which is probably caused by hydrothermal treatment, as other samples reported in the literatures are only aged at lower temperatures [16,18]. From the XRD patterns, d-spacing and particle size of the sample were calculated, which are 0.79 and 40 nm, respectively,

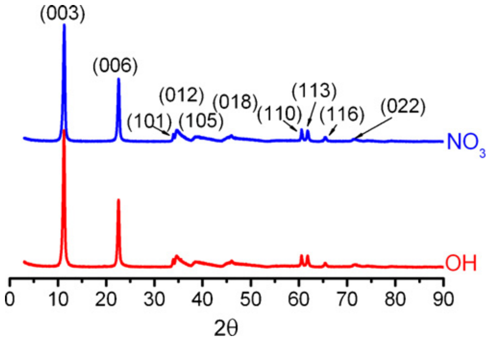

Fig. 1. XRD patterns of (a) $[Ni_4Al(OH)_{10}]OH{\cdot}5.0H_2O$ and (b) $[Ni_4Al(OH)_{10}]NO_3{\cdot}2.5H_2O$.