



Anion-exchange properties of nickel–aluminum layered double hydroxide prepared by liquid phase deposition



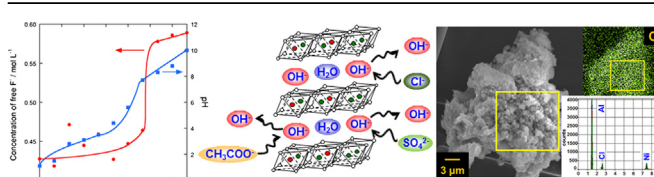
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HIGHLIGHTS

- The optimum structure of Ni–fluoro complexes for Ni–Al LDH was determined.
- The anion-exchange properties of Ni–Al LDH were quantitatively evaluate.
- $[\text{NiF}_{6-x-y}(\text{NH}_3)_x(\text{OH}^-)_y]^{n+}$ was more suitable than $[\text{NiF}_6]^{4-}$ as the precursor of Ni–Al LDH.
- The improved LPD reaction achieved high purity and high crystallinity Ni–Al LDH.
- The anion-exchange of Ni–Al LDH was accelerated by the neutralization of OH^- anions.

GRAPHICAL ABSTRACT



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ABSTRACT

The optimum coordination structure of Ni–fluoro complexes for the preparation of Ni–Al LDH by LPD process and the diverse anion-exchange properties of as-deposited Ni–Al on α -alumina powder were quantitatively evaluated for the industrial application of new positive material for alkali secondary batteries. The $[\text{NiF}_{6-x-y}(\text{NH}_3)_x(\text{OH}^-)_y]^{n+}$ was more suitable than $[\text{NiF}_6]^{4-}$ as the precursor of the deposition of Ni–Al LDH in the LPD reaction, and the improved LPD reaction achieved the synthesis of high purity and high crystallinity Ni–Al LDH. All anion-exchanged Ni–Al LDHs for OH^- , Cl^- , SO_4^{2-} , and CH_3COO^- -forms kept the high crystallinity and showed the enlargement of interlayer distances. The tilting angle of the intercalated CH_3COO^- anions was about 15° . Anion-exchange capacity remained constant at a minimum of 0.8 meq g^{-1} in $\text{pH} > 10$, increased as pH decreased, and reached a maximum of 8 meq g^{-1} at pH 2. Anion-exchange of OH^- -form of Ni–Al LDH was accelerated by the neutralization of hydroxide ions in interlayers, in addition, the anion-exchange capacity and the crystallinity of Ni–Al LDH could be controlled by the amount of doped aluminum ions.

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1. Introduction

Layered double hydroxides (LDHs) are widely known as hydroxalite-like compounds, two-dimensional anionic clays, and

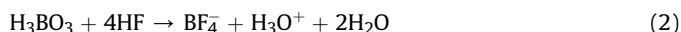
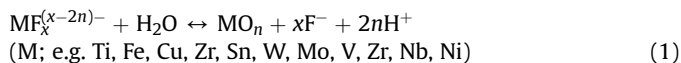
anion-exchange materials. The typical chemical composition of an LDH can be represented by $[\text{M}_1^{2+}_x\text{M}_2^{3+}_y(\text{OH})_z]^{x+y}[\text{A}^{n-}]_{(x+y)/n} \cdot y\text{H}_2\text{O}]^{x+y-n}$, where M^{2+} and M^{3+} represent metallic cations such as Ni^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Al^{3+} , Cr^{3+} , Fe^{3+} , and Co^{3+} , and A^{n-} represents an anion such as OH^- , Cl^- , NO_3^- , CO_3^{2-} , and SO_4^{2-} [1–3]. The crystal structure of LDHs consists of positively charged octahedral hydroxide layers that are electrically neutralized by exchangeable interlayer anions and water molecules occupying the interlayer spaces [4–6].

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Recently, LDH derivatives have received considerable attention because of their anion-exchange property and capacity to intercalate anions [7], allowing them to act as catalysts [8], anion-exchangers [9–12], oxides [13,14], magnetics [15,16], and electrodes for alkaline secondary batteries [17,18]. Ni–Al LDH is expected to be a useful Ni–MH battery material owing to its high discharge capacity [19,20]. In the previous studies by other workers, the LDHs have been prepared by the coprecipitation and sol–gel method; however, these LDHs had low crystallinities because alkali metal cations were intercalated into their interlayers [4,21–23].

In the case of β -Ni(OH)₂ a high crystallinity results in a lower charge–discharge capacity, on the other hand, in the case of α -Ni(OH)₂ a high crystallinity results in a better performance as an active material. The β -phase has only one channel for H⁺ to diffuse, thus, H⁺ exchange between OH, in contrast, the α -phase has two channels for H⁺ diffusion, namely, OH and interlayer water molecules. Hence, it is not necessary to expand the diffusion channel further, instead, the improvement of low crystallinity and low purity of Ni–Al LDHs which have α -phase is very useful for improvement of the electrochemical performance of Ni–MH battery materials [18,19,24]. Therefore, Mizuhata et al. suggested the liquid phase deposition (LPD) process as a novel synthesis method for a higher crystallinity Ni–Al LDH [19,25,26]. In the LPD process, metal oxide and/or hydroxide thin films can be directly coated on solid substrates by simply immersing the substrates in LPD aqueous solutions. The LPD reaction spontaneously proceeds at ambient condition in a balance of two equilibrium reactions, which are principally described as follows: a hydrolysis equilibrium (ligand-exchange) reaction of metal fluoride complex species (Eq. (1)) and F[−] consumption reaction with boric acid or aluminum ion as an F[−] scavenger (Eq. (2) or (3)) [27–32].



The LPD process also has major advantages of a successful synthesis of multilayer oxides from multicomponent solutions that consist of several metal fluoride complexes [33,34]. In addition, a high purity Ni–Al LDH can be synthesized because no alkali cations are present in the LPD aqueous solutions. However, in the previous study, the yield of Ni–Al LDH synthesis by the LPD process was too low for industrial application to Ni–MH battery materials because of low solubility of β -Ni(OH)₂ in neutral NH₄F aqueous solution, which served as a nickel source for Ni–Al LDH [19]. Thus in this study, the β -Ni(OH)₂ was first dissolved into acidic HF aqueous solution, and NH₃ aqueous solution was added subsequently in order to control the pH of the LPD aqueous solution and the coordination structure of Ni–fluoro complexes. A remarkable improvement in the yield of Ni–Al LDH synthesis by the LPD method can be expected by this improvement; therefore, the equilibrium considerations for the LPD reaction solution are indispensable in order to estimate the optimal synthesis conditions (e.g., amount of added ammonia and pH of LPD reaction solution). However, the coordination structures of Ni–fluoro complexes that are appropriate for the LPD process have not been clarified, nor have the anion-exchange characteristics of Ni–Al LDH prepared by the LPD process been clarified. This information will greatly contribute to the industrial development of Ni–MH batteries.

In this study, the influences of the coordination structures of Ni–fluoro complexes on the amounts of Ni²⁺ ion deposited and the crystallinities of Ni–Al LDH on glass substrates have been

investigated, and the optimum coordination structure of Ni–fluoro complex for the LPD reaction has been determined. The crystallinities and chemical compositions of Ni–Al LDH on α -alumina powder and its various anion-exchanged Ni–Al LDHs have been examined. Furthermore, the pH dependences of various anion-exchange capacities of Ni–Al LDH and the interlayer distances of anion-exchanged Ni–Al LDHs have also been investigated.

2. Experimental section

2.1. Chemicals

All chemicals used in this work were of analytical grade. A stock solution of nickel nitrate for a potentiometric analysis was prepared by dissolving analytical grade nickel nitrate hexahydrate, Ni(NO₃)₂•6H₂O purchased from Wako Pure Chemical Industries, Ltd., and was standardized by a volumetric titration with EDTA using Murexide as an indicator. The properties of α -alumina powder (Sumitomo Chemical Co., Ltd., AA-03) are following: particle diameter is 0.3 μm , mean particle size is 0.2–0.3 μm , and BET surface area is 6.5 m² g^{−1}. Hydrogen fluoride (HF) was purchased from Stella–Chemifa Inc., and all other reagents were purchased from Nacalai Tesque Inc.

2.2. Determination of the coordination structures of Ni–fluoro complexes

2.2.1. Preparation of Ni–fluoro complexes solutions

0.045 g of Ni(NO₃)₂•6H₂O were dissolved into ca. 20 mL of ion-exchanged water and 9.75 g of 10 vol.% of aqueous HF were added. Then 15% of NH₃ aqueous solution was added to the solutions, and the total volume of these solutions was adjusted to 50 mL with ion-exchanged water. The ratios of total concentration, $R = ([\text{NH}_3] + [\text{NH}_4^+])/[\text{Ni}^{2+}]$, of a series of the solutions were from 0 to 33.3. All of mixture solutions were left to stand for 48 h at room temperature, in order to achieve to stable equilibrium because of slow ligand-exchange of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

2.2.2. UV–vis and HPLC measurements of Ni–fluoro complexes solutions

UV–vis absorption spectra were performed using a UV–vis spectrophotometer (JASCO V7200), and all measurements were conducted within the range from 350 to 800 nm. An HPLC system (JASCO Gulliver 1500) was employed for the determination of the concentration of free F[−] ion in Ni–fluoro complex solution. Chromatographic separations were conducted on an ion-exchange column (IC I-524A, Showa Denko K.K.) in an intelligent column oven (JASCO CO-2065) at 40 °C. The mobile phase consisted of 2.3 $\times 10^{-3}$ mol L^{−1} tris(hydroxymethyl) aminomethane aqueous solution and 2.5 $\times 10^{-3}$ mol L^{−1} phthalic acid aqueous solution, and the flow rate was set at 1.0 mL min^{−1}.

2.3. Syntheses of various Ni–Al LDH derivatives

2.3.1. Preparation of Ni–Al LDH on glass substrate

Ni parent solution was prepared as follows (see also Scheme 1): 100 g of Ni(NO₃)₂•6H₂O was dissolved into ca. 800 mL of ion-exchanged water, and ca. 100 mL of 15% NH₃ aqueous solution was added dropwisely until pH 7.5 under stirring at 90 rpm for 3 h. The precipitate of β -Ni(OH)₂ was washed with ion-exchanged water, dried at room temperature, loaded into a plastic Erlenmeyer flask, and 0.5 mol L^{−1} HF was added until the precipitate dissolved. Then, 15% NH₃ aqueous solution was added dropwisely until pH 7.5, and an insoluble substance was removed by suction filtration. The total volume of the filtrate was adjusted to 1 L with

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