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Research Article

ELECTROCHEMICAL SUPERCAPACITOR BEHAVIOR OF NICKEL ALUMINIUM BASED LAYERED DOUBLE HYDROXIDE

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ABSTRACT

Nickel aluminium based layered double hydroxide (NiAl LDH) was prepared by coprecipitation method. NiAl LDH derives its crystal structure from brucite mineral. The sample was characterized using powder X-ray diffraction and Infrared spectroscopy. Specific capacitance of nickel aluminium based layered double hydroxide was measured using galvanostatic charge–discharge studies. A specific capacitance of ≈400 F g^{-1} was obtained in 6M KOH in the potential range of 0 to 0.525 V (vs. Hg/HgO/OH^-) for nickel aluminium based layered double hydroxide.

Keywords: *Nickel Aluminium Based Layered Double Hydroxide, Infrared Spectrum, Supercapacitor, Specific Capacitance*

INTRODUCTION

Layered double hydroxides have found applications in batteries, catalysis, fire retardants, sorbents, and optics and as precursors for the nanocatalysts etc (Li and Duan, 2005). Layered double hydroxide derive their crystal structure from Mg(OH)2 structure model. The structure of magnesium hydroxide comprises of hexagonal close packed hydroxyl ions in which the magnesium ion occupy the octahedral sites thus leading to Mg(OH)6 octahedrons sharing their edges to form two dimensionally [Mg(OH)2] sheets (Oswald and Asper, 1997). The [Mg(OH)2] sheets are stacked over each other with Vander Waals interactions (Wells, 1984). Isomorphic substitution of Mg2+ions in Mg(OH)2 by trivalent metal ions creates positive charge on the sheets with the composition to be $[Mg^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]$. Anions and water molecules will get intercalated in the interlamellar region (A_x^{n-}) thus increasing the basal spacing from 4.6 Å to 7.6 Å (Li and Duan, 2005). Nickel aluminium based layered double hydroxide electrode reversibly exhibits 1.7 e^- exchange with higher charge storage capacity in alkaline batteries and redox reaction is faradaic in nature (Kamath *et al*., 1994). But in case of a supercapacitor, we do not observe any phase changes or compositional variation. Carbon and activated carbon are used as electrode materials in electrochemical supercapacitor and (Miller *et al.*, 1997; Wu, 2002; Pandolfo and Hollenkamp, 2006) exhibit theoretical capacitance of 100-300 F g^{-1} with long-term stability on cycling in different electrolytes (Niu *et al.*, 1997). Electric vehicles demand higher power density at the time of starting (Conway, 1999). Electrochemical supercapacitors store energy due to the separation of electronic and ionic species at the interface of the working electrode and electrolyte (Simson *et al.*, 2008; Want *et al.*, 2003). Ruthenium oxide is most widely used which exhibit specific capacitance 788 F g^{-1} (Min *et al.*, 2006). Even though RuO_2 based compounds exhibit good pseudocapacitive nature but commercialization is not favored due to higher cost (Min *et al.*, 2006). Co_3O_4 and CoO_x based transition metal oxides are used as promising electrode materials for supercapacitor application and a maximum capacitance of 291 F g^{-1} is reported with good efficiency and better performance (Liu *et al.*, 1999). Supercapacitors that have been actively sought for charge storage purpose and several metal oxides/hydroxides have been widely investigated. Metal oxides and layered metal hydroxides have been investigated for their application as supercapacitors due to the high aspect ratio. Cobalt hydroxide exhibits electric double-layer capacitance and pseudo-capacitance due to faradaic redox process and interfacial phenomena with the theoretical specific capacitance of 3460 F g^{-1} (Wang *et al.*, 2008). As-prepared β-cobalt hydroxide has a specific capacitance of 651 F g^{-1}. Recently, graphene/cobalt oxide or hydroxide composite has been evaluated for the electrochemical supercapacitor behavior and the data shows that in presence of graphene. The hybrid film exhibits good cycling stability, while nickel oxide capacitance retention is 87% only (Xia *et al*., 2011). The electrochemical properties of nickel aluminium based layered double hydroxide are compared with nickel hydroxide. Co-Al LDHs have exhibited higher specific capacitance. Several methods have been reported to prepare layered double hydroxide with controlled size, shape and morphology (Ye *et al*., 2010). Recently we have reported the supercapacitor properties of nickel hydroxide and cobalt hydroxide which exhibits 150 F g^{-1} and 462 F g^{-1}. Electroactive surface functionalization can also assist to enhance the specific capacitance. However, there are no reports on the comparison of electrochemical supercapacitor behavior of nickel aluminium based layered double hydroxide with nickel hydroxide as well as other layered double hydroxides. In this article we have prepared examined nickel aluminium based layered double hydroxide and its supercapacitor behavior was examined during charge-discharge studies.

MATERIALS AND METHODS

Nickel nitrate [Ni(NO3)2 .6H2O], aluminium nitrate [Al(NO3)3 .9H2O], sodium hydroxide (NaOH) and sodium carbonate (Na2CO3) were procured from Merck India and used without purification.

Nickel aluminium based layered double hydroxide was prepared by following the procedure described elsewhere (Roy *et al*., 2001). Mixed metal nitrate solutions were taken in stoichiometric ratios (Ni:Al-0.75:0.25) and sodium hydroxide (0.1M) was simultaneously added to sodium carbonate (0.05M) solution at 65-70 °C and the slurry was aged for 18h at 80°C. Green colored precipitate formed was filtered washed with distilled water and dried at 65°C till constant weight is obtained.

Characterization

Sample was characterized by using a Bruker D8 Advanced powder X-ray diffractometer (Cu Kα source, λ = 1·5418 Å). Data was collected at a scan rate of 4° min-1 with 2θ steps of 0.02°. Infrared spectrum was recorded using Bruker Alpha spectrometer (resolution 4 cm-1) in the range of 4000 to 400 cm-1with 24 scans using attenuated total reflectance mode.

Charge–discharge Studies

Electrodes were prepared as follows: nickel aluminium based layered double hydroxide, graphite and PTFE were taken in 0.6:0.3:0.1 weight ratios and were thoroughly mixed using isopropanol solvent. Slurry formed was placed on nickel foam and pressed at 80-100 kg cm^{-2}. Then foam was dried at 65 °C till constant weight is recorded. The electrodes were soaked in 6M KOH and galvanostatically (current, 5·5 mA; 21 h) charged with nickel plates as counter electrodes in the voltage range of 0.0 to 0.525 V for three-electrode measurement using Hg/HgO/OH- as the reference electrode (Technoscience Instruments, India) at 28–30°C. The total specific capacitance (C_g, F g^{-1}) was calculated using the discharged profile using the following formula:

$C_g = I\Delta t/\Delta V$

where

I = discharge current (A) per unit mass of electroactive material (A g^{-1}),

Δt = total discharge time (s),

ΔV = the potential window (V) during discharge.

RESULTS AND DISCUSSION

The pXRD pattern of Ni-Al LDH is shown in Figure 1.

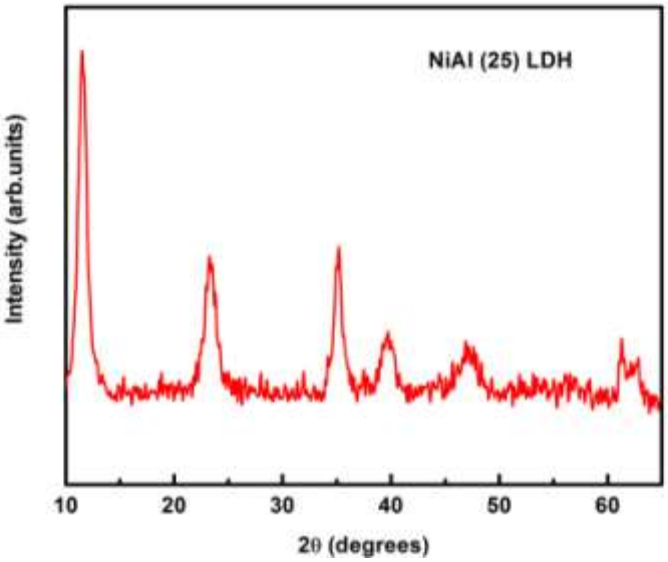

Figure 1: Powder X-ray diffraction pattern of NiAl (25%) layered double hydroxide

The basal reflections are observed at low 2θ values and weaker non-basal reflections at higher 2θ. The reflections in the Ni-Al based layered double hydroxide is indexed to rhombohedral symmetry (space group R-3m). We observe two successive reflections at 7.58 Å and 3.8 Å respectively, which could be indexed to (003) and (006) planes. The lattice parameters (*a* = 3.06 Å, *c* = 7.58 Å) could be indexed to (00*l*) and (*hk*0) reflections. The reflection in the mid-2θ region of the pXRD pattern can be indexed to *h*0*l*/0*kl* reflections and are used to determine the specific stacking sequence of layers with respect to each other. The crystal structure of layered double hydroxide is shown in Figure 2.

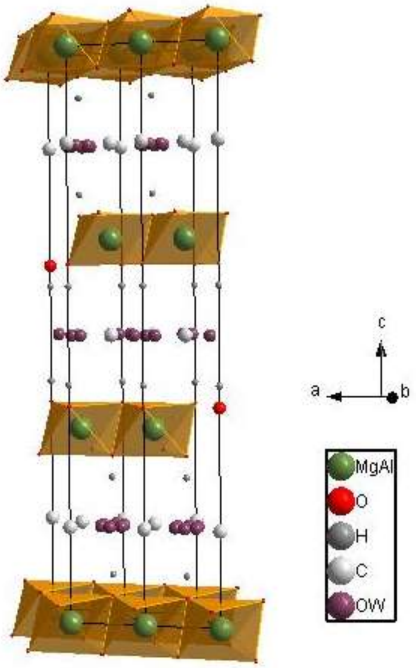

Figure 2: Crystal structure of nickel aluminium based layered double hydroxide

Infrared spectra of Ni-Al LDH samples are shown in Figure 3.

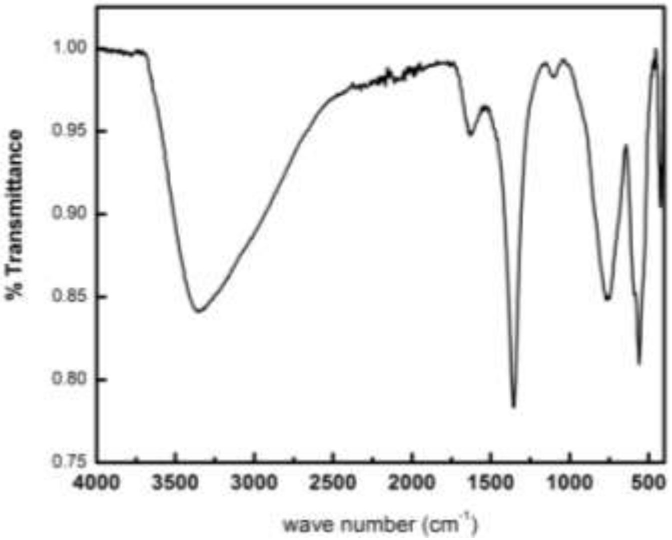

Figure 3: Infrared spectrum of NiAl (25%) layered double hydroxide

The broad bands in the range of 3000-3600 cm^{-1} are assigned to the stretching modes while 1630 cm^{-1} to the bending modes of adsorbed and intercalated water molecules in between the lamellar sheets of nickel aluminium based layered double hydroxide. The ν3(CO_3^{2-}) peak around 1340-1358 cm^{-1} splits into 1357 cm^{-1} and 1665 cm^{-1}, and an additional peak was observed at 1100 cm^{-1}, which can be attributed to the ν1(CO_3^{2-}) vibration mode. The ν2(CO_3^{2-}) peak is observed around 840-855 cm^{-1} (Nakamoto, 2008). The maximum super capacitance of 400 F g^{-1} is obtained during the charge-discharge studies for nickel aluminium based layered double hydroxide (see Figure 4).

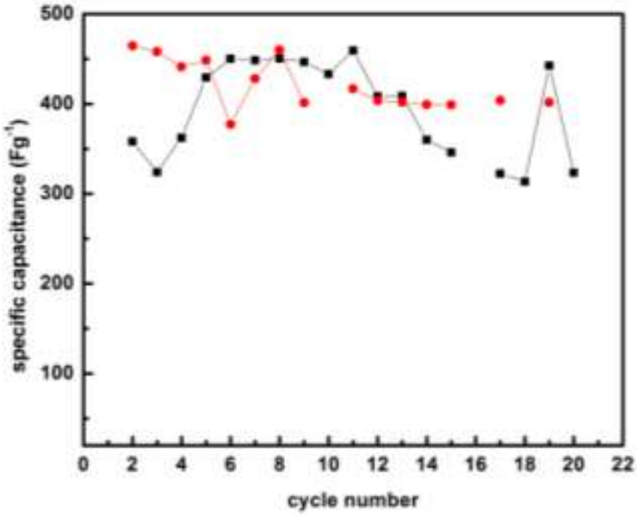

Figure 4: Cycle life data of NiAl (25%) layered double hydroxide

The electrochemical performance could be well explained based on the storage mechanism. The electrochemical redox reaction involves a reversible electron transfer processes between the anode and the cathode. Reversibility of electroactive nickel aluminum based layered double hydroxide determines the overall performance of an electrochemical capacitor.

Conclusion

This study reports on the electrochemical performance of NiAl based layered double hydroxide and the specific capacitance of 400 F g^{-1} has been reported. This promotes us to explore other isostrucutural layered materials for supercapacitor properties.

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Declaration

The author declares no conflict of interest.

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