

Nanostructured Ni-Mn double hydroxide for high capacitance supercapacitor application

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Abstract

Recently, transition-metal-based hydroxide materials have attracted significant attention in various electrochemical applications owing to their low cost, high stability, and versatility in composition and morphology. Among these applications, transition-metal-based hydroxides have exhibited significant potential in supercapacitors owing to their multiple redox states that can considerably enhance the supercapacitance performance. In this study, nanostructured Ni-Mn double hydroxide is directly grown on a conductive substrate using an electrodeposition method. Ni-Mn double hydroxide exhibits excellent electrochemical charge-storage properties in a 1 M KOH electrolyte, such as a specific capacitance of 1364 Fg⁻¹ at a current density of 1 mAcm⁻² and a capacitance retention of 94% over 3000 charge-discharge cycles at a current density of 10 mAcm⁻². The present work demonstrates a scalable, time-saving, and cost-effective approach for the preparation of Ni-Mn double hydroxide with potential application in high-charge-storage kinetics, which can also be extended for other transition-metal-based double hydroxides.

Keywords : Nickel hydroxide, Manganese hydroxide, Nanostructure, supercapacitor, Thin film

1. INTRODUCTION

Pseudocapacitors are considered as a better alternative for charge-storage devices in comparison with electrochemical double layer capacitors (EDLCs), owing to the significantly high redox activity of their electrodes [1-3]. The electrodes of pseudocapacitors are mainly prepared using metal oxides/hydroxides, such as RuO₂ [4], MnO₂ [5], NiCo₂O₄ [6], Co(OH)₂ [7], and Ni(OH)₂ [8]. However, the capacitance of pseudocapacitor electrodes with single metal-based electrodes is considerably low for practical applications. Therefore, recently, multi-transition metal-based double hydroxides have attracted considerable attention owing to their ability to increase the capacitance of pseudocapacitors. In particular, Ni-Mn layered double hydroxide (Ni-Mn LDH) electrodes have been anticipated to be a desirable material for high-performance supercapacitors [9]. Both Mn and Ni metals have excellent redox properties, which can be utilized

for electrochemical charge-storage process through preparation of Ni-Mn LDH electrodes for pseudocapacitors. For example, Sim et al. reported the synthesis of Ni-Mn LDH nanoplatelets using a reverse micelle method, and the Ni-Mn LDH electrode obtained improved capacitance (881 Fg⁻¹ at 0.5 Ag⁻¹, compared with that of Ni(OH)₂) [9]. In the present study, Ni-Mn double hydroxide is directly prepared on a conductive substrate using a solution-based scalable method within a short duration (5 min) and without the utilization of an alkaline source. The Ni-Mn double hydroxide electrode with nanostructure features exhibits excellent charge-storage properties in a 1 M KOH electrolyte.

2. EXPERIMENTAL

A.R. grade nickel chloride (NiCl₂), potassium permanganate (KMnO₄), sodium sulphate (Na₂SO₄), and methanol (CH₃OH) were purchased from Sigma Aldrich Company. All the chemicals were used as received.

2.1 Nickel hydroxide synthesis

Initially, a stainless steel (SS) substrate was polished with silicon carbide paper and washed with ethanol and deionized (DI) water. Then, a 0.05 M NiCl₂ solution was prepared in 40 mL DI water and 0.1 M Na₂SO₄ was added into the NiCl₂ solution under constant magnetic stirring for 300 s at room temperature. Then, a

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Ni precursor was deposited on the well cleaned SS substrate using a three-electrode setup in the above prepared solution as an electrolyte. The three-electrode set up consisted of SS substrate as working electrode, platinum plate as counter electrode and saturated calomel as reference electrode. To deposit the nickel hydroxide thin film, a -1.0 V/SCE potential was applied to the SS substrate for 300 s. After electrodeposition of the nickel hydroxide thin film, the substrate was rinsed in DI water and dried in natural light.

2.2 Manganese hydroxide synthesis

A 0.01 M potassium permanganate solution was prepared in 40 mL DI water and 0.2 mL methanol was added into the potassium permanganate solution under constant magnetic stirring for 300 s at room temperature. Then, manganese precursor was coated on the well cleaned SS substrate using the three-electrode setup using the prepared solution as an electrolyte. A -1.0 V/SCE potential was applied on the SS substrate for 300 s to deposit the manganese hydroxide thin film. Finally, the thin film of manganese precursor was rinsed in DI water and dried in natural light.

2.3 Nickel-manganese double hydroxide (Ni-Mn DH) synthesis

0.01 M nickel chloride, 0.01 M potassium permanganate, and 0.1 M Na_2SO_4 solutions were added into 40 mL DI water under constant magnetic stirring and 0.2 mL methanol was added into it to form the final electrolyte solution. Then, the Ni-Mn DH thin film was prepared on the SS substrate in a final electrolyte solution by applying a -1.0 V/SCE potential for 300 s using a three-electrode setup. After the electrodeposition process, the Ni-Mn DH thin film was rinsed with DI water and designated as Ni-Mn-DH-1.

2.4 Materials Characterization

Surface morphology observation and elemental mapping of material were performed using field-emission scanning electron microscopy (FE-SEM) technique with the help of FE-SEM; SU-70, Hitachi High Technologies. The composition and elemental valence states of Ni-Mn DH thin film were analysed using X-ray photo emission spectroscopy (XPS) technique with the help of XPS; ESCALab Mark II, VG Scientific Ltd. model. The electrochemical charge-storage analyses of thin film electrodes were performed using cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) techniques in aqueous 1 M KOH

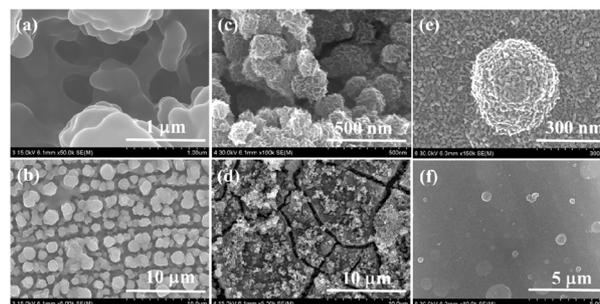


Fig. 1. FE-SEM images of (a), (b) manganese hydroxide (c), (d) nickel hydroxide and (e), (f) nickel-manganese layered double hydroxide thin films.

electrolyte. Impedance study of thin film electrodes was performed within a frequency range of 0.1 to 100 kHz at 10 mV ac amplitude.

3. RESULTS AND DISCUSSIONS

3.1 Physico-chemical study

Electrodeposited thin films of manganese precursor, nickel precursor, and manganese nickel double hydroxide are scanned using FE-SEM technique to find surface micro/nanostructure analysis. Fig. 1(a)-(b) shows a surface microstructure similar to that of micro-bushes for the manganese precursor with macropores that are formed at the bottom of micro-bushes structure. Fig. 1(c)-(d) presents nano-spheres surface morphology of nickel precursor, with nano-spheres of nickel precursor that are composed of very fine nano-flakes. While, Fig. 1(e)-(f) depicts very fine nanoparticles of nickel manganese double hydroxide with dimensions less than 30 nm. Thus, the manganese-nickel double hydroxide demonstrates an ultra-fine nanostructure compared with that of individual manganese and nickel precursors. Such an ultra-fine nanostructure surface nanomaterial can be highly useful electrode for increasing the electrochemical charge-storage properties of pseudocapacitor.

The chemical composition or elemental mapping of thin films is performed using energy dispersive X-ray spectroscopy (EDS) technique. Fig. 2(a)-(c) show manganese and oxygen elements present in the manganese hydroxide thin film. Nickel hydroxide thin film [Fig. 2(d)-(f)] shows homogeneous distribution of nickel and oxygen elements, and manganese-nickel double hydroxide thin film shows [Fig. 2(g)-(i)] presence of manganese, nickel and oxygen elements. Fig. 3(a) shows comparative FT-IR curves of different thin films recorded for different wave numbers within the

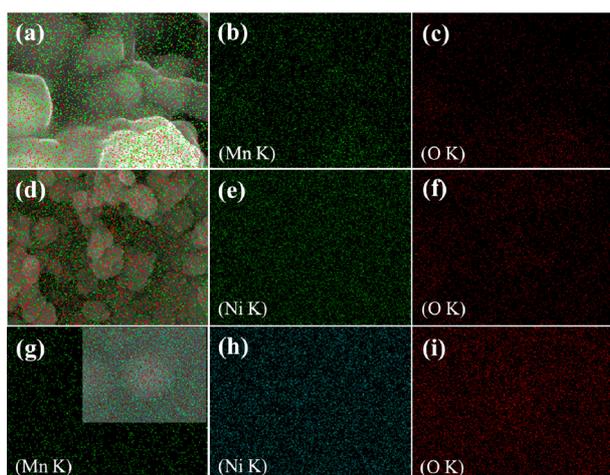


Fig. 2. EDAX elemental mapping of (a)-(c) manganese precursor, (d)-(f) nickel precursor and (g)-(i) nickel-manganese layered double hydroxide thin films.

range of in 648 to 4000 cm^{-1} . A broad FT-IR peak in the range of 3680 to 2780 cm^{-1} is attributed to stretching vibrations of molecular water and hydrogen bond ($-\text{OH}$) groups [10]. Similarly, the weak bond at 1627 cm^{-1} corresponds to bending mode of water molecules [11]. The presence of CO_3^{2-} in the thin film samples is evidenced by its vibration bands from middle to lower wave numbers. The bands observed at 1052 , 827 , 697 cm^{-1} wave numbers are attributed to $-\text{CO}$, $-(\text{CO}_3)^{2-}$ and O-C-O bonds, which are introduced in the material owing to the exposure of thin films to atmospheric carbon and oxygen species. Finally, the band at 961 cm^{-1} present in all thin films, which is attributed to metal hydroxide (M-OH) bending modes [12]. Thus, manganese hydroxide, nickel hydroxide, and manganese nickel hydroxide materials are confirmed from FT-IR study of all metal hydroxide thin films.

XPS technique was used to find oxidation state of the elements in the nickel-manganese double hydroxide thin film. Fig. 3(b) shows Mn 2p XPS profile of manganese with the doublet of Mn $2p_{3/2}$ and Mn $2p_{1/2}$ at 642.7 and 653.8 eV binding energies, respectively. The energy difference between Mn 2p doublets of 11.1 eV indicates that manganese is present with Mn^{+3} state in the nickel-manganese double hydroxide thin film [13]. Ni 2p XPS profile [Fig. 3(c)] in Ni-Mn double hydroxide shows spin-orbit doublets of Ni $2p_{3/2}$ and Ni $2p_{1/2}$ at the binding energies of 855.9 and 873.8 eV , respectively with a 17.9 eV energy difference and two satellite shake up peaks at the higher energy side [14]. It is attributed to Ni^{+2} oxidation state of nickel in Ni-Mn double hydroxide thin film [14]. O 1s profile [Fig. 3(d)] shows that metal hydroxide bond is present in the material.

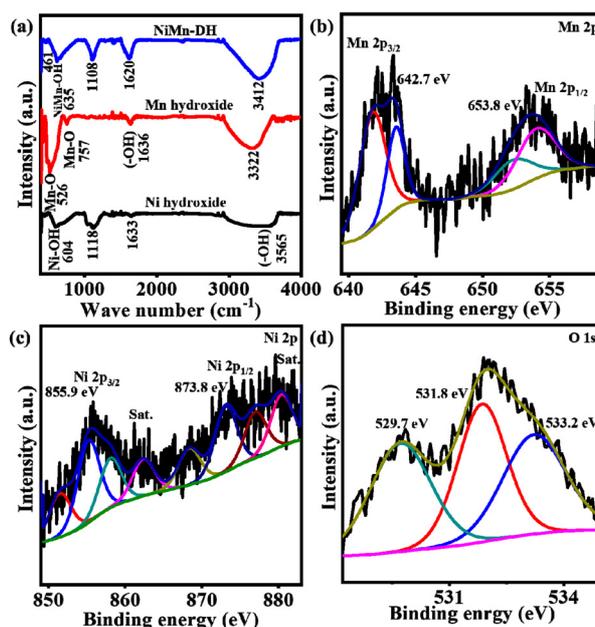
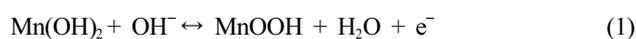


Fig. 3. Comparison (a) FTIR spectra of different thin films. Narrow scan XPS profiles of (b) Mn 2p, (c) Ni 2p and (d) O 1s energy states of different elements present in the nickel-manganese double hydroxide thin film.

3.2 Electrochemical study

Freshly prepared nickel hydroxide, manganese hydroxide, and nickel manganese double hydroxide thin films were evaluated for electrochemical charge-storage in aqueous 1 M KOH within a potential window of 0 to $+0.5\text{ V/AgCl}$. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) techniques were used in this regard. The CV curves from 5 to 100 mVs^{-1} scan rates of manganese hydroxide in Fig. 4(a) show semi-rectangular shapes without obvious redox peaks, which are related to reversible redox reactions between manganese and hydroxyl (OH^-) ion shown by the following equation.



However, strong reduction and oxidation peaks are seen in the CV curves of nickel hydroxide [Fig. 4(b)] or Ni-Mn double hydroxide [Fig. 4(c)], which is related to reversible electron exchange between nickel and hydroxyl ion (OH^-), is represented by the following reaction [8].



The current density peak and integrated area under the CV

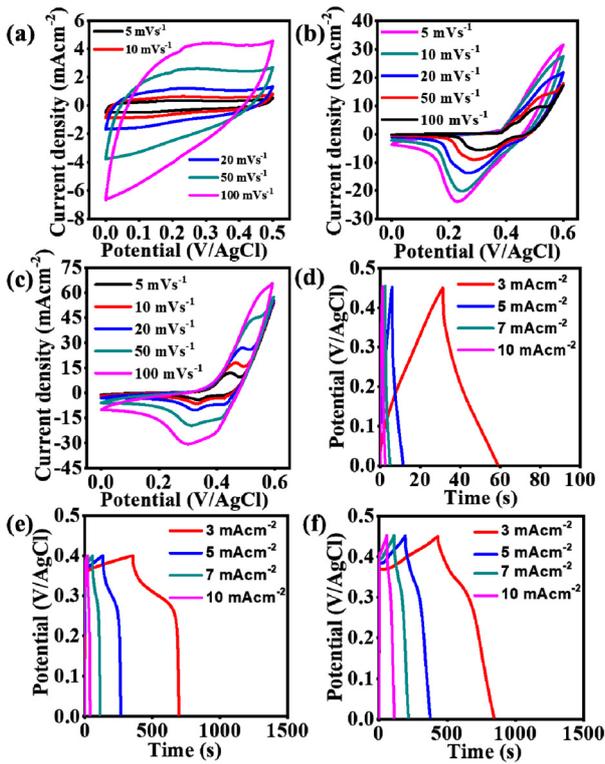


Fig. 4. Cyclic voltammetry and galvanostatic charge-discharge curves of (a), (d) manganese hydroxide, (b), (e) nickel hydroxide and (c), (f) nickel-manganese double hydroxide thin films measured in 1 M KOH.

curve of Ni-Mn double hydroxide thin film is significantly higher compared with that of the current density of corresponding CV curve of manganese hydroxide and nickel hydroxide thin films. This signifies that the charge-storage capacity of Ni-Mn double hydroxide thin film is higher. Furthermore, shapes of CV curves of each electrodes are consistent without considerable change in their pattern, which indicate suitable capacitive characteristics of thin films. GCD study was performed for evaluating the specific capacitance of each thin film in 1 M KOH. GCD profiles of manganese hydroxide [see Fig. 4(d)] and nickel hydroxide [Fig. 4(e)] at different current densities show less charging-discharging times than that of corresponding GCD profiles of the Ni-Mn double hydroxide thin film [Fig. 4(f)], which is consistent with the CV study. The GCD profiles show non-linear behaviour, which is related with reversible redox reaction processes of thin film during charging/discharging cycle as shown by equation (1) and (2). Furthermore, the initial potential drop of the discharge profile of manganese hydroxide is slightly higher than that of nickel hydroxide and the Ni-Mn double hydroxide. It is proportional to the intrinsic resistance of the electrode, which adversely affects the charge-storage kinetics of the material during the charging and

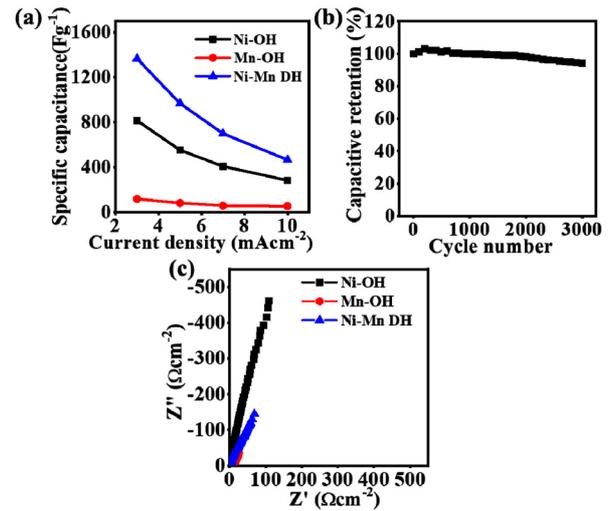


Fig. 5. (a) Comparative specific capacitances of different thin films. (b) Cyclic stability and (c) comparative impedance spectra of nickel hydroxide, manganese hydroxide and nickel manganese double hydroxide.

discharging process.

The specific capacitance versus current density plot [Fig. 5(a)] of the Ni-Mn double hydroxide thin film shows (obtained from discharging profiles of GCD curves) a maximum value of 1364 Fg^{-1} at 3 mAcm^{-2} compared with that of 815 and 120 Fg^{-1} for nickel hydroxide and manganese hydroxide, respectively. The increased specific capacitance of the Ni-Mn double hydroxide is associated with the increase in redox reactions owing to the incorporation of two transition metals compared with that of single metals in nickel hydroxide and manganese hydroxide. The capacitance of Ni-Mn double hydroxide is higher than that reported by Chen *et al.* [15] (736.3 Fg^{-1}) for $\alpha\text{-MnO}_2$, and Vidhya *et al.* [8] for Ni(OH)_2 (1038 Fg^{-1}). Cyclic lifetime of Ni-Mn double hydroxide thin film in 1 M KOH was evaluated for successive 3000 cycles at 10 mAcm^{-2} current density [See Fig. 5(b)]. It shows 94% capacitance retention after successive cycling of the thin film. The electrochemical impedance spectroscopy plots in Fig. 5(c) show higher capacitive features for the nickel hydroxide and manganese hydroxide electrodes, because their imaginary impedance is higher compared with that of manganese hydroxide.

4. CONCLUSIONS

Ni-Mn double hydroxide nanostructure has been successfully prepared on stainless steel substrate by electrodeposition technique

at room temperature of 303 K. It showed promising properties for the application of electrochemical charge storage in 1 M KOH such as an operation potential window of 0 to +0.6 V/AgCl, the highest specific capacitance of 1364 Fg⁻¹ at 10 mAcm⁻² current density, and 94% capacitance retention after 3000 successive charge/discharge cycles.

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