



ELECTROCHEMICAL STUDIES ON EFFECT OF Mg(OH)₂ DEPOSIT ON Ni ELECTRODE SURFACE

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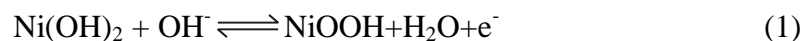
Abstract

Deposition of Mg(OH)₂ on to the bare Ni electrode surface was done by dipping bare Ni electrode in magnesium nitrate and KOH solutions. The Ni electrode was first immersed in the magnesium nitrate solutions of different concentrations and dried in the open atmosphere and then immersed in the 10% KOH solution for five minutes and dried in the open atmosphere. The effect of Mg(OH)₂ deposit on the Ni electrode surface was electrochemically studied by electrochemical impedance spectroscopy, cyclic voltammetry and chronoamperometry. A “H” type cell was used to construct the Ni-Cd cell and to study the effect of Mg(OH)₂ deposit on Ni electrode surface. The experimental results revealed that addition of the smaller quantities (~5%) of Mg(OH)₂ does not affect the electrochemical characteristics of nickel electrode and addition of the larger quantities (10 and 15%) affects the function of nickel electrodes considerably.

Key words: Battery; Electrodes; Surface Modification; Cyclic Voltammetry; EIS.

1. Introduction

Ni-Cd batteries are used for various applications under different charging rates and over wide range of temperature [1]. Ni-Cd batteries became one of the near -term power sources for electric vehicles [2]. Several mathematical models have been proposed to explain the performance of Ni electrode in the Ni-Cd cell [3-6]. The capacity of Ni-Cd and other Ni based batteries is limited by Ni electrode [7]. Hence, attention has to be given to increase the energy density of Ni electrode to increase the energy density of whole Ni-Cd cell. The electrode reaction at the Ni electrode of Ni-Cd electrode is represented as;



The above reaction is viewed as proton intercalation/deintercalation reaction in the solid phase [8-11]. When the cell is charged nickel hydroxide is oxidized into nickelic hydroxide and on discharging the reverse reaction occurs. The charged form of nickel hydroxide is considered to be an n type semiconductor [12], while the reduced form, namely $Ni(OH)_2$, is considered as p type semiconductor [10]. When the discharge of Ni-Cd cell takes place at high rate the kinetics of nickel electrode discharge are controlled by solid state proton diffusion [11,12]. The high rate discharge of Ni-Cd cell proceeds the conductivity of active material on the Ni electrode decreases gradually until both proton transfer and surface charge transfer contribute to the electrode kinetics [7]. The discharge also led to formation of a semiconductor layer at the interface of current collector and active material. This interface is due to depleted charge carriers and has relatively high resistance. To overcome this problem C, Ni, Co and CoO additives were added to the electrode. The addition of highly conductive $CoOOH$ was found to be good in the effective utilization of active material on the Ni electrode [13-16].

The present work is undertaken to study the effect of $Mg(OH)_2$ deposited on the Ni electrode surface of Ni-Cd cell. The performance of Ni-Cd cell was analysed by modifying the surface of Ni with $Mg(OH)_2$ precipitate employing electrochemical impedance spectroscopy, cyclic voltammetry and chronoamperometric techniques.

2. Experimental

For the experimental study and for evaluating charge performance of the nickel electrode, three different concentrations of Magnesium nitrate solutions were prepared, namely 5%, 10% & 15%. The electrodes were fabricated by using electrochemical impregnation process are soaked in these solutions and performances of these electrodes were evaluated.

The preparation of additives in varying concentration, processing methods, evaluation are detailed as follows.

2.1 Preparation of an active Nickelic hydroxide:

It is an electro chemical impregnation technique in which the electrode is subjected to electrical polarization in a Nickel nitrate solution. Counter electrode is inert which is used as positive electrode. When the impregnation is over the electrode is treated with hydroxide.

2.2 Preparation of Magnesium nitrate solutions:

A 5% $Mg(NO_3)_2$ solution has been prepared by dissolving in DM (Demineralised) water and made up to 1000 ml. Also 10% and 15% Magnesium nitrate solutions were prepared, by dissolving 100g and 150g Magnesium nitrate respectively in DM water and solution is made up to 1000ml.

2.3 Preparation of 10% KOH solution

100 g of KOH pellet was dissolved in DM water (Demineralised) and made up to 1000ml. This solution is stored in a one litre beaker.

2.4 Soaking the electrodes in 5% $Mg(NO_3)_2$ solution :

13 cm X 7 cm of six Ni electrodes were taken. One litre of Magnesium nitrate solution was taken in a glass beaker. Electrodes were then soaked in the Magnesium nitrate solution, and they were kept for 10 minutes in the solution. The electrodes that were soaked, were taken and dried at ambient temperature. The dried electrodes were then soaked in 10% KOH solution again for 5 minutes.

The same evaluation method for determining Magnesium nitrate solution retention in electrodes was followed for the solutions prepared with 10% and 15% concentration levels. The same technique was followed and the $Mg(NO_3)_2$ retention in the electrodes was evaluated.

2.5 Conversion of Magnesium nitrate to Magnesium hydroxide at the electrode's surface:

The electrodes were soaked in the 10% KOH solutions for 10 minutes, dried at ambient condition. Then the dried electrodes were again soaked in 10% KOH solution for 5 minutes. The soaked electrodes were then dried. The same procedure is followed for the electrodes in 10 % and 15 % $Mg(NO_3)_2$ solutions respectively.

2.6 The electrode washing

The soaked electrodes were washed for 5 minutes in running DM water. Now, the washed electrode was taken and washed again in a beaker till the pH of washed water is neutral. If hydroxide ions are not properly washed carbonate formation will take place and removing this carbonate would be a difficult task. After washing, the electrodes were dried at $60^{\circ}C$ for 1 hour.

2.7 Electrochemical Impedance Spectroscopy

The Ni-Cd cell was formed using H type glass cell containing 6M KOH solution. The Ni electrode served as working electrode, while Cd electrode served as counter electrode. Hg/HgO electrode was used as reference electrode. The electrochemical impedance spectra were recorded by superimposing a sinusoidal voltage of 10 mV amplitude at open circuit potential and also at different applied DC potentials after recording cyclic voltammograms.

2.8 Cyclic Voltammetry

The cyclic voltammograms were also recorded for bare and Mg(OH)₂ deposited nickel electrodes at the scan rates 20,50, and 100 mV/S using the same cell set up employed for recording electrochemical impedance spectroscopy.

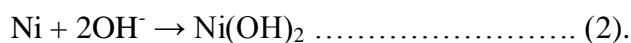
2.9 Chronoamperometry

Chronoamperometric studies have been carried out at different anodic potential using the same H type cell for evaluating the nature of Mg(OH)₂ coatings over nickel electrode.

3.RESULTS AND DISCUSSION

3.1 Cyclic voltametric analysis of Ni electrode surface

The cyclic voltammograms were first recorded for nickel electrodes- plain as well as Mg(OH)₂ deposited using Zahner Zennium XC electrochemical workstation at various scan rates ranging from 10mV/s to 100mV/s. Cyclic voltammograms of plain Ni electrode are presented in the Figure.1a to 1d. The peak observed nearly at -1.25 V corresponds to adsorption of hydroxide ion onto the Ni electrode surface. The current observed for this peak is maximum for bare Ni electrode and with increase in amount of Mg(OH)₂ deposit on the Ni electrode surface the current for adsorption of hydroxide ion decreased. This indicated the increase in surface coverage by Mg(OH)₂ on Ni surface when the concentration of nickel nitrate solution is increased from 5% to 15% for surface modification. The second anodic peak observed nearly at -0.93 V indicated the oxidation of Ni to Ni⁺² and the formation of Ni(OH)₂, indicated by the chemical reaction,



The third anodic peak observed nearly at 0.13 V indicates the formation of NiO(OH) from Ni(OH)₂ as follows,



Beyond this potential the oxygen evolution reaction, given in equation 2, takes and is indicated a sharp increase in the current. The cathodic peak observed at the potential 0.1 V is the reversible peak of reaction 2, the reversible reaction is represented by equation 4. The another cathodic peak observed nearly at -1.2 V implied the reduction of O₂, which is reversible reaction of reaction 2 as given in reaction 4. The potential of oxygen reduction or hydroxide formation is shifted in the negative direction with increase in surface coverage by Mg(OH)₂.

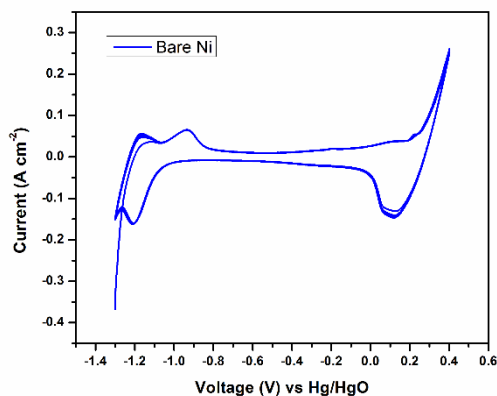
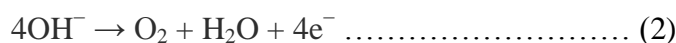


Figure.1a

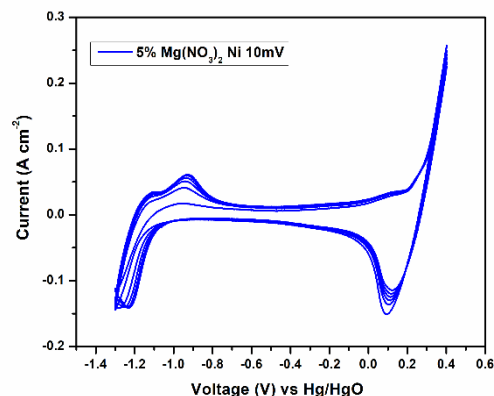


Figure.1b

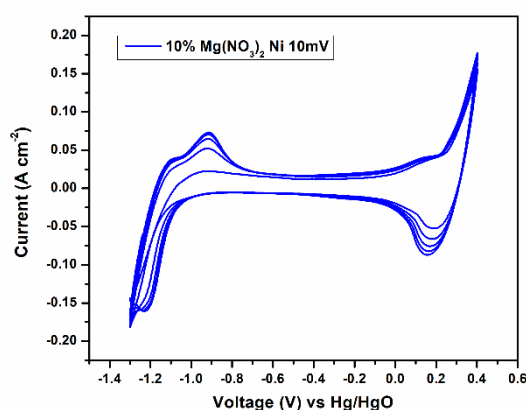


Figure.1c

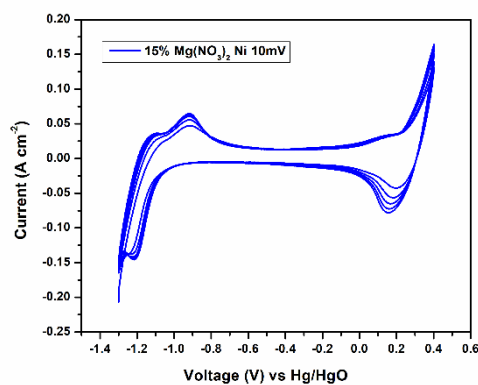


Figure.1d

Figure.1 Cyclic voltammograms of bare (1a) and Mg(OH)₂ coated Ni electrode surface using 5% (1b), 10% (1c) and 15% (1d) Mg(NO₃)₂ solutions.

The anodic and cathodic peaks observed at different potentials for the bare and Mg(OH)₂ coated Ni surface are presented in Figure.2. From these cyclic voltammograms, it can be seen that Ni surface coated with the Mg(OH)₂ using 5% magnesium nitrate solution doesn't show an appreciable deviation from bare Ni surface and at high concentrations of Mg(OH)₂ the electrochemical activity of Ni surface is appreciably affected.

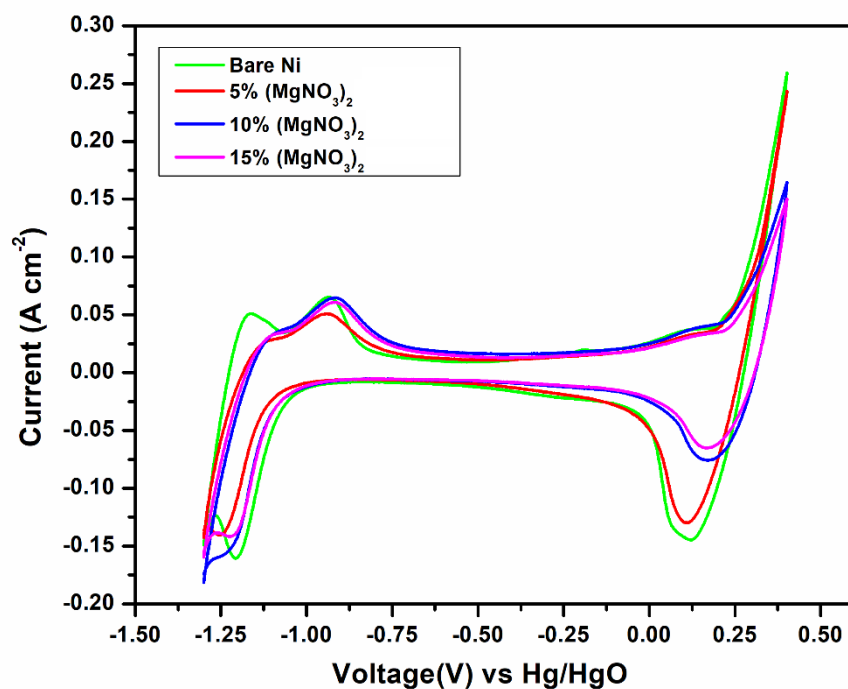


Figure.2 Effect of Mg(OH)₂ coating on the cathodic and anodic peaks.

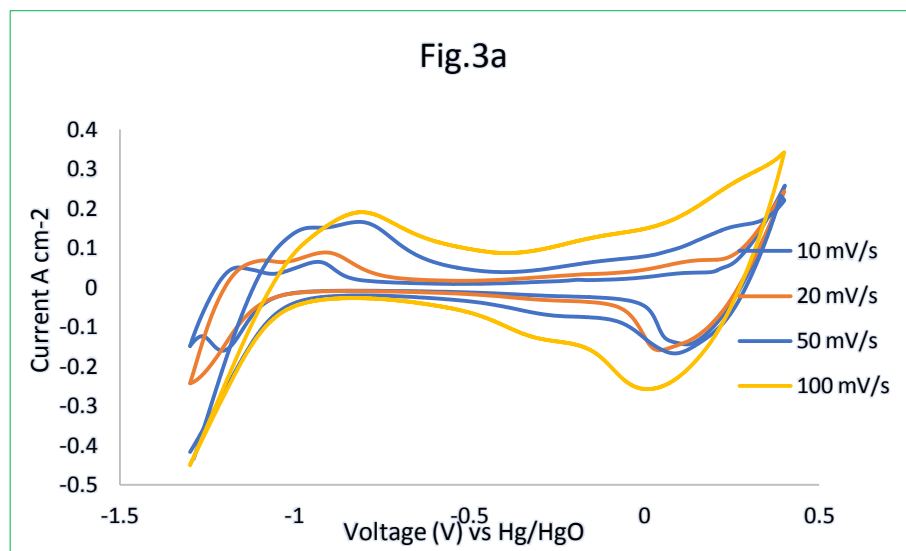


Fig.3a

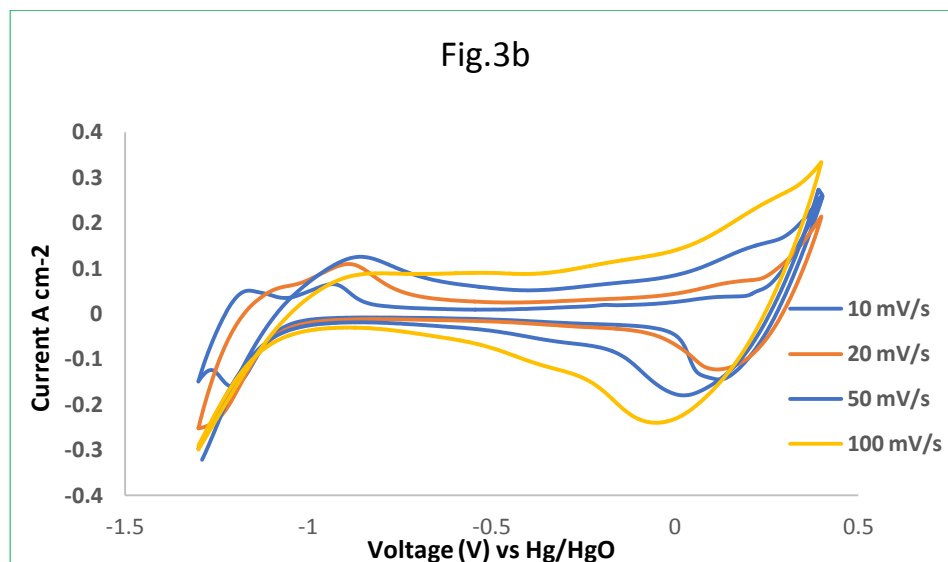


Figure.3 Effect of scan rate on the oxidation/reduction behavior of bare (3a) and $Mg(OH)_2$ coated Ni

Cyclic voltammograms were also recorded to study the effect of scan rate on the oxidation/reduction behavior of bare and $Mg(OH)_2$ coated Ni electrodes at different scan rates which are shown in Fig.3a and 3b. The experimental curves indicated that the peak current increased with sweep rate. Moreover, the peak potentials for oxidation and reduction are shifted to active and noble potentials respectively. The shift in peak potentials increased slightly when the Ni surface is coated with $Mg(OH)_2$.

3.2 Electrochemical Impedance Spectroscopy of Bare and $Mg(OH)_2$ coated Ni electrode

The Nyquist plots recorded for the bare and $Mg(OH)_2$ coated Ni electrode are presented in Fig.4. From these plots it can be seen that the charge transfer resistance values

decreased when the amount of $Mg(OH)_2$ on Ni surface increases. This indicated the enhanced conductance at electrode solution interface with the amount of $Mg(OH)_2$ precipitate on the Ni electrode surface. The experimental plots obtained fit well with the equivalent circuit shown in Fig.5. The R_u represents uncompensated solution resistance, R_p is charge transfer resistance, W_d is Warburg impedance which represents mass transport or diffusion at the electrode solution interface. Y_0 alpha represents a component of constant phase element which arises due to adsorption of anions like hydroxide ions onto the Ni electrode surface. The Nyquist plots conformed the filmed porous behavior of Ni electrode over wide frequency domain under charge transfer and diffusion control.

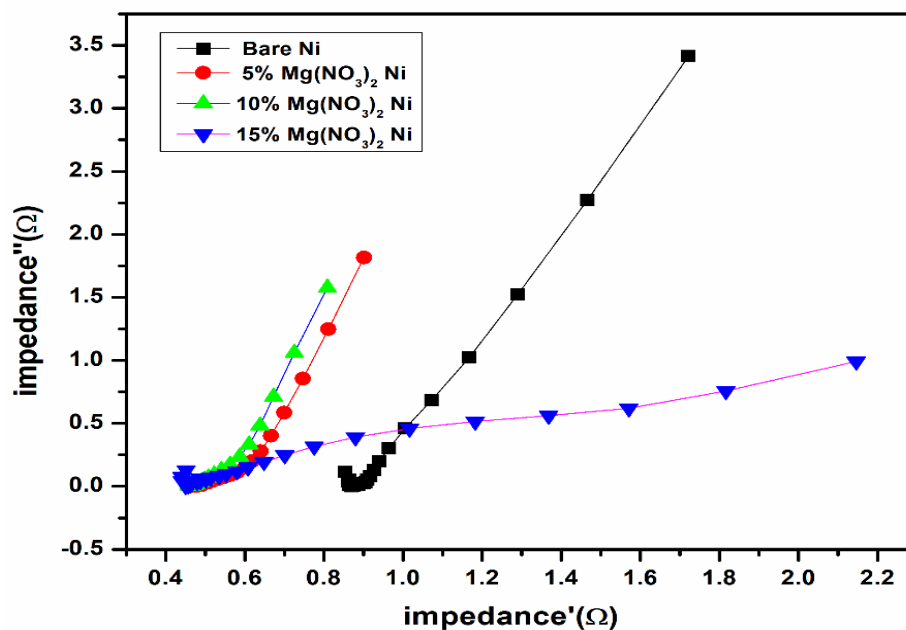


Figure.4 Nyquist plots for Bare and $Mg(OH)_2$ coated Cd electrodes in 6.0 M KOH solution

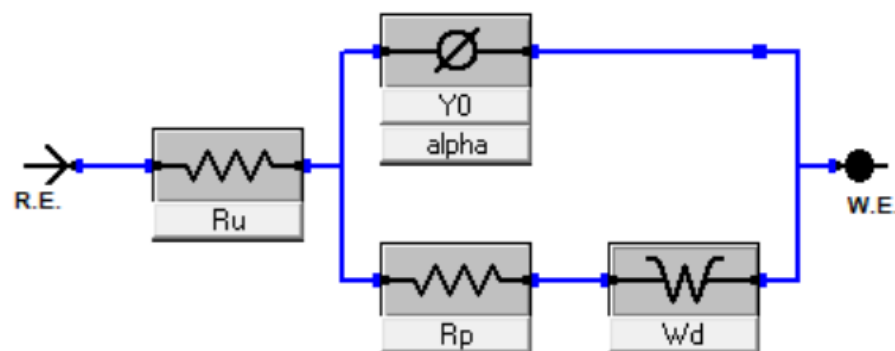


Figure.5 Equivalent Circuit fitting with the experimental Nyquist plots

3.3 Chronoamperometry

A series of experiments were carried out to study the anodic oxidation of Ni electrode in the alkaline solution in the absence and presence of Mg(OH)₂ precipitate. The current vs time curves so obtained are presented in Fig.6. Before recording chronoamperograms, firstly, the electrode was allowed to equilibrate in alkaline solution for 25 minutes until a steady open circuit potential is reached. An anodic voltage of -950 mV against Hg/HgO and stepped anodically towards -800 mV. The rapidly rising current response can be seen in the Fig.6 for stepping the potential of Ni electrode from -950 mV against Hg/HgO to -800 mV. This lies active dissolution region of Ni.

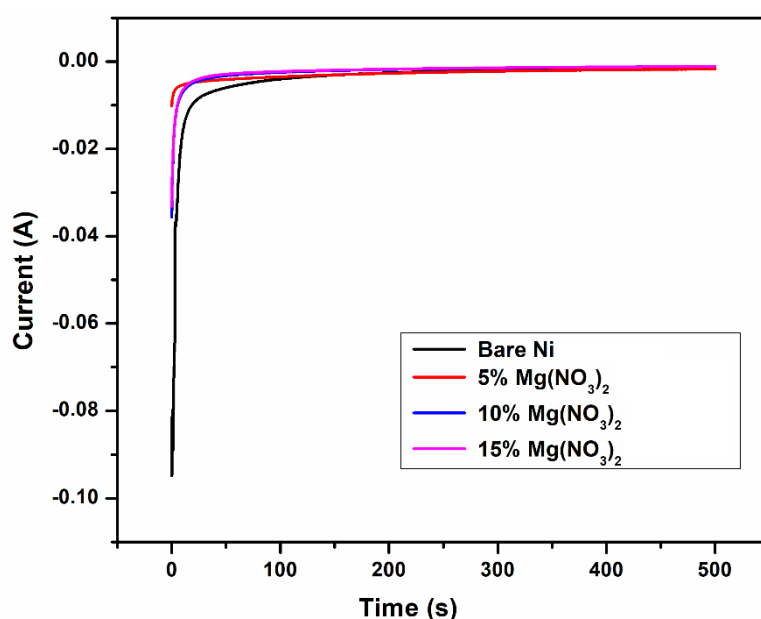


Figure.6 Current- time transients for Ni electrode in alkaline medium.

4. Conclusion

The following conclusions arrived in the present study.

Mg(OH)₂ can be deposited on the surface of Ni coated with electrochemically active Ni(OH)₂ and its electrochemical response can be studied by cyclic voltammetry, electrochemical impedance spectroscopy and chronoamperometry. The experimental results indicated that addition of the smaller quantities (~5%) of Mg(OH)₂ does not affect the

electrochemical characteristics of nickel electrode and addition of the larger quantities (10 and 15%) affects the function of nickel electrodes considerably.

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