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CHARACTERIZATION OF ELECTROLESS NICKEL DOPED ELECTROLYTIC MANGANESE DIOXIDE

Madzlan Aziz, Jamil Yusuf, Raizul Azita Abd Rashid and Suhaila Mohd Sanip

Chemistry Department, Faculty of Science,
Universiti Teknologi Malaysia,
81310 UTM Skudai, Johor, Malaysia.

ABSTRACT

Electrolytic manganese dioxide (EMD) is a major component of the composite cathode for the rechargeable alkaline manganese (RAM ™) cells. Attempts have been made by many researchers to further improve the rechargeability of the EMD for this application.
In this work, EMD was doped with nickel via electroless plating technique. This technique requires EMD to be immersed in a plating solution of sodium hypophosphite and sodium pyrophosphate as the reducing agent, nickel sulphate as the nickel source and tin chloride as a sensitizing agent. The reaction was catalysed by palladium chloride in an ultrasonic bath. From the Energy Dispersive X-Ray analysis, it was found that 10-30 % of nickel was successfully coated. However the percentage of nickel coated depends greatly upon the concentration of chemicals in the plating solution. The electrical conductivity was studied using the van der Pauw method. It was found that the conductivity was influenced by the presence of phosphorus in the nickel-doped EMD samples.

INTRODUCTION

Electrolytic manganese dioxide (EMD) is used as a major component of composite cathode in rechargeable alkaline manganese dioxide cells. The rechargeability of these batteries depends on the partial discharge of the manganese dioxide cathode. Evidently, there is a correlation between structural parameters of the MnO_2 and its rechargeability. To improve rechargeability, physically and chemically modified manganese dioxide materials have been prepared. Most of the work reported in the literature has been concentrated on electrode materials doped with Bi or Pb ions [1]. Ti(IV) is another potential candidate for stabilizing the structure of EMD [2]. A defined quantity of graphite is added to increase the low electronic conductivity of EMD. The main electronic transport from the current collector through the MnO_2 grain is carried out via carbon phases, the electrons have to pass through the MnO_2 grain between the carbon-MnO_2 interface and the electrochemically active center.

In this paper we report on the introduction of Ni into EMD through electroless deposition. Electroless nickel plating is a chemical process whereby nickel ions are being reduced to nickel metal in a solution by the process of chemical reduction. This technique is chosen due to its uniform deposition on an irregular and non conducting surface [3]. It is suggested that the Ni doped EMD would help to increase the electronic conductivity of the bulk cathode composite apart from other properties that nickel possess. Klien [4] has shown that depositing nickel on nickel hydroxide electrodes results in a higher capacity nickel-metal hydride battery system.

This work will elucidate the parameters to be looked into to produce the type of nickel that will enhance the conductivity of EMD. The plating product is subjected to elemental analysis, structural studies and will in turn relate to the electronic conductivity.

EXPERIMENTAL

The plating process involves several steps and begins with sensitization of the EMD surface using a tin salt followed by activation of nucleation sites with palladium salt before employing nickel through its salt. Nickel ions is reduced to nickel metal by adding sodium hypophosphite as a reducing agent.

The surface of the EMD powder was activated by soaking it in an aqueous $SnCl_2$/HCl solution which act as a sensitizer. The powder was then soaked in a nucleating of $PdCl_2$/HCl solution. The plating process was done in an ultrasonic bath at a temperature range of 60 – 70 ^{o}C and at pH 10. The chemical compositions of the nickel baths are listed in Table 1.

Table 1: Chemical compositions of plating baths

Sampel	Composition ratio $SnCl_2:PdCl_2:NiSO_4$	Sampel identification
EMD-Ni	1:1:1	EMD-Ni 1
i) EMD-Ni ($SnCl_2$)	4.0:1:1	EMD-Ni 2
	2.0:1:1	EMD-Ni 3
	1.6:1:1	EMD-Ni 4
	1.4:1:1	EMD-Ni 5
ii) EMD-Ni ($PdCl_2$)	1:1.40:1	EMD-Ni 7
	1:0.84:1	EMD-Ni 8
	1:0.68:1	EMD-Ni 9
	1:0.54:1	EMD-Ni 10
iii) EMD-Ni ($NiSO_4$)	1:1:2.38	EMD-Ni 12
	1:1:1.90	EMD-Ni 13
	1:1:0.86	EMD-Ni 14

After plating, the powder was thoroughly washed with deionized water and filtered. The powder was dried and the percentage nickel evaluated using the energy dispersive X-ray analysis (EDAX). The crystallinity is determined from X-ray diffraction studies and the specific resistivity from the van der Pauw method. The conductivity is calculated from the resistivity values.

RESULTS AND DISCUSSION

From the EDAX analysis, it was observed that nickel was coated on EMD in all the bath compositions prepared but with varying amount in the range 3 to 30 %. Table 2 gave the results of the electroless plating and conductivity measurements of the nickel coated EMD.

Table 2: Results of nickel plated EMD in various bath compositions

Samples	% Ni	% P	Conductivity (x10^{-5} Ω^{-1} cm^{-1})
EMD-Ni 1	18.53	8.48	5.495
($SnCl_2$)			
EMD-Ni 2	15.28	2.92	1.004
EMD-Ni 3	12.26	5.59	6.634
EMD-Ni 4	19.54	12.79	0.246
EMD-Ni 5	23.46	16.83	0.568
($PdCl_2$)			
EMD-Ni 7	3.74	1.52	3.343
EMD-Ni 8	11.11	7.91	3.843
EMD-Ni 9	29.53	14.03	6.748
EMD-Ni 10	18.26	9.71	3.254
($NiSO_4$)			
EMD-Ni 12	13.25	7.89	0.601
EMD-Ni 13	16.56	8.15	2.149
EMD-Ni 14	21.46	8.29	1.677

The highest amount of nickel arrives from a plating bath containing 68% $PdCl_2$ and the least nickel came from the bath containing the most $PdCl_2$ in the study, i.e. 140% $PdCl_2$. This suggests that the nucleation stage is the determining factor in the deposition process. As for the sensitizing stage, it is not as crucial as reflected in the amount of nickel deposited and the lowest amount in the composition used in the study gives the highest amount of nickel in the group at 23%. The amount of phosphorus is also noted since studies have shown that an increase in the phosphorus content, attributed to the reducing agent, sodium hypophosphite, has resulted in an increase of resistivity and therefore a decrease of the conductivity of electroless nickel due to the disruption of the regular lattice structure of high purity nickel by the codeposition of phosphorus [5]. There is no direct correlation between the amount of phosphorus alone and conductivity but there seems to be a correlation between Ni/P ratio and conductivity. A Ni/P ratio of 2.1 in the deposit gave high conductivity value in this study. It shows that having higher amount of nickel doesn't mean having a higher conducting deposit.

This study illustrates that two forms of nickel can be deposited through the electroless technique, namely amorphous and crystalline. X-ray diffractograms of the deposited samples with the various compositions of the plating bath are shown in Figure 1 and 2.

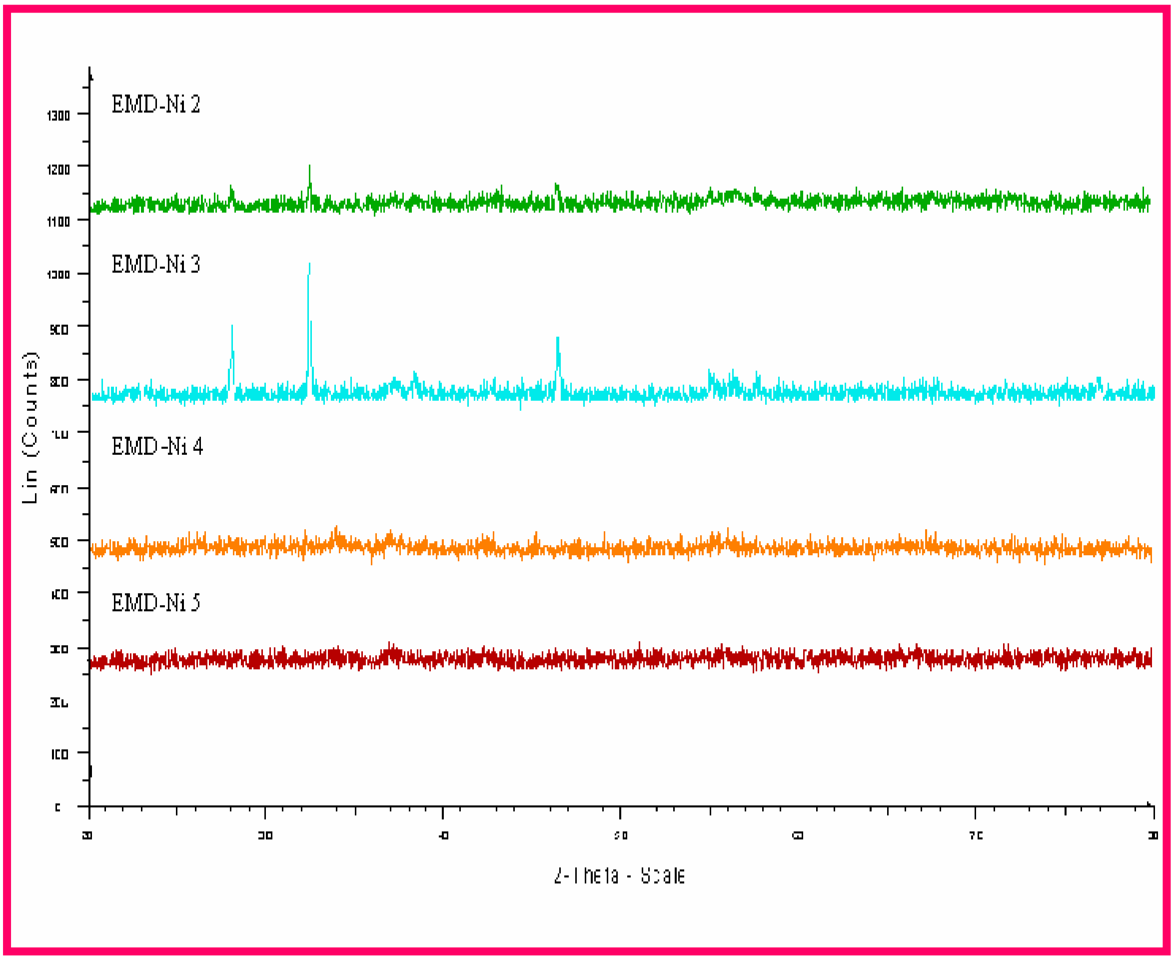

Figure 1: X-ray diffractograms of nickel plated EMD for different $SnCl_2$ (sensitizer) compositions.

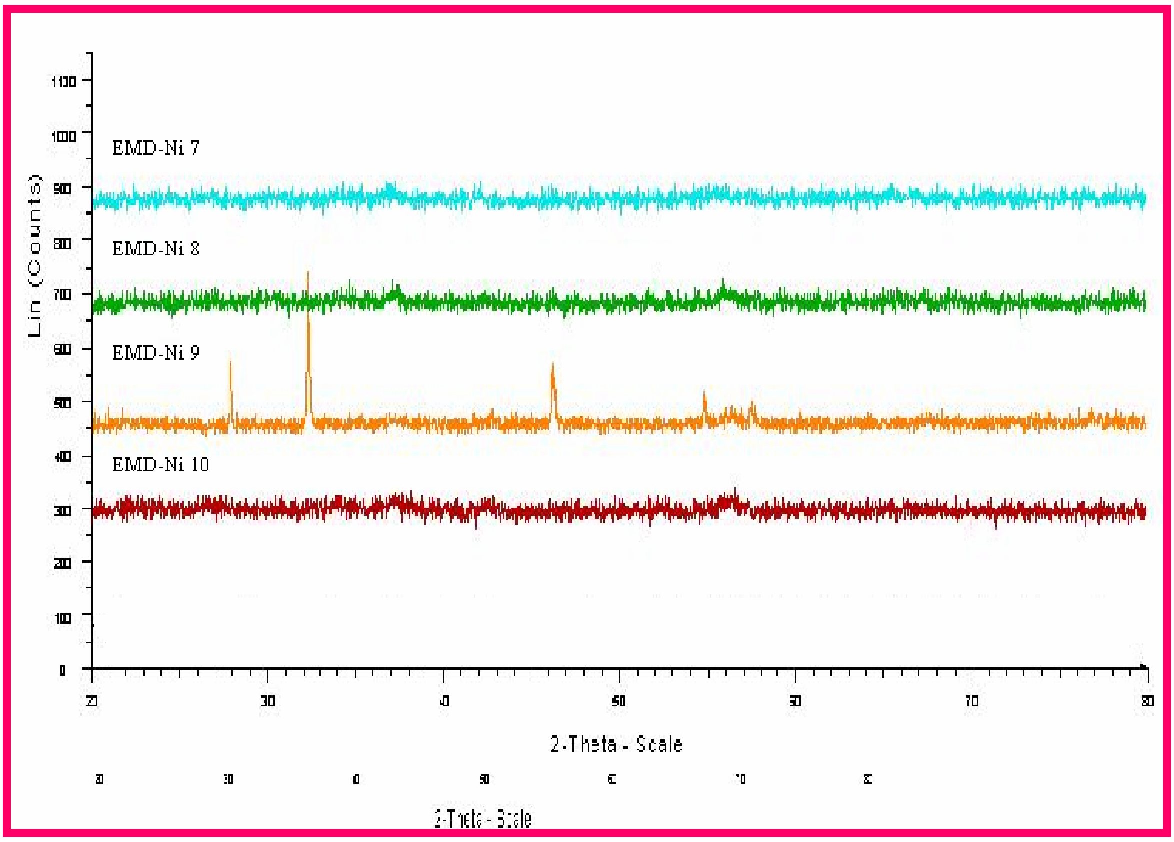

Figure 2: X-ray diffractograms of nickel plated EMD for different $PdCl_2$ (nucleator) compositions.

From Figure 1 and 2, sample EMD-Ni 3 and EMD-Ni 9 exhibit the crystalline structure and both these samples show high conductivity values. Among the two EMD-Ni 9 shows the highest and the diffractogram indicate a higher degree of crystallinity.

CONCLUSION

The electroless deposition process for nickel depends very much on the amount of sensitizer and nucleator and there is an optimum condition for the preferred nickel. Nickel deposited through the electroless technique can appear both in the amorphous and crystalline phases. The nickel to phosphorus ratio is important in depositing crystalline nickel and in this study a ratio of 2.1 is crucial. Higher conductivity is a result of a long range order reflected in the crystallinity of the material and as for the application in battery cathodes this is preferred.

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