

PREPARATION OF ELECTROLESS NICKEL DEPOSITION ON ELECTROLYTIC MANGANESE DIOXIDE

Suhaila M.Sanip, Madzlan Aziz,
Jamil Yusof and Raizul Azita A. Rashid

*Department of Chemistry,
Faculty of science, Universiti Teknologi Malaysia
81310, Skudai, Johor*

Email: suhaila@kimia.fs.utm.my

ABSTRACT

Electrolytic manganese dioxide (EMD) is one of the active materials in an alkaline manganese dioxide cell. Several researchers have looked upon to further enhance the rechargeability and cycle life of EMD. This study will look into the optimization of nickel deposition on EMD to further improve the conductivity of EMD. Electroless nickel deposition technique was employed for this purpose. This technique utilizes a plating bath consisting of solutions of sodium hypophosphite and sodium pyrophosphate as the reducing agent, nickel sulphate as the nickel source, tin chloride as a nucleating agent and catalysed by palladium chloride in an ultrasonic bath. The concentration of nickel sulphate, tin chloride and palladium chloride were varied to optimize the percentage of nickel doped. The resultant samples of nickel doped EMD were analyzed using SEM and EDAX techniques. It was found that variation of the concentration of the plating solutions greatly influenced the amount of nickel being doped.

INTRODUCTION

Manganese dioxide exists in several different phases, and the most common are γ -MnO₂ and β -MnO₂ [1]. Manganese dioxide is also known to be a semi-conductor with the specific conductivity ranging from 10^{-6} to 10^{-3} (Ω cm)⁻¹ [2]. The manganese dioxide for rechargeable alkaline battery system is the electrochemically produced γ -MnO₂ or better known as electrolytic manganese dioxide, EMD [3]. EMD is one of the major compound in the cathode of RAM batteries. The current RAM batteries has limitation to the extent of its rechargeability. Thus much work have been directed to introduce dopants into EMD using various methods. Brent, *et al.*, [2] have studied the effect of doping Li⁺, Th⁴⁺ and Cr³⁺ onto pyrolytic β -MnO₂ and found an increase in its conductivity. Other researchers have doped EMD with Bi, Pb, Ti(IV) and Ti(OBu)₄ ions and found an increase in the rechargeability of the EMD [4]. Ilicai, *et al.* [5] and Klien [6] both have shown that a larger capacity was obtained by deposition of nickel on the surface of nickel hydroxide electrodes in the nickel-metal hydride battery system.

Therefore the objective of this study is to improve the rechargeability of EMD by providing a conductive layer of nickel on the surface of EMD. Nickel metal was doped onto the EMD using the electroless plating technique. This electroless nickel coating layer will enhance the

electronic transfer from the current collector to the active materials in the cathode and help to minimize the internal cell resistance [7]. This technique via electroless plating was chosen because it will provide a uniform deposition to an irregular substrate such as EMD powder [8].

In this paper, we will look into the preparation of EMD via electroless deposition of nickel and optimized the concentration of tin salt, palladium salt and nickel salt. It is expected that the active surface area will have less internal resistance and thus enhanced the rechargeability of RAM batteries.

EXPERIMENTAL

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. The most common reducing agent being sodium hypophosphite.

The EMD surface was first sensitized using a tin salt and nucleating sites activated with palladium salt before applying nickel via electroless method and in an ultrasonic environment. 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 agent, PdCl_2/HCl solution. The chemical composition and operating conditions of the electroless nickel ultrasonic bath are as Table 1 [6]

Table 1

Composition	Content (g/L)
NiSO_4	42
NaH_2PO_4	42
$\text{Na}_4\text{P}_2\text{O}_7$	84

pH = 10, temperature = 60 – 70°C

After plating, the powder was thoroughly washed with deionized water and filtered. The powder was dried and the percentage of nickel evaluated using the Energy Dispersive X-Ray Analysis (EDAX). Their surface morphology was characterized by Scanning Electron Microscopy (SEM) on a Philips XL40 scanning electron microscope. The specific resistivity, ρ , were done using the Van Der Pauw method [8]. The conductivity, σ , was then calculated as $1/\rho$. Table 2 gives the composition ratios of the plating bath.

Table 2 Composition Ratios of Plating Baths

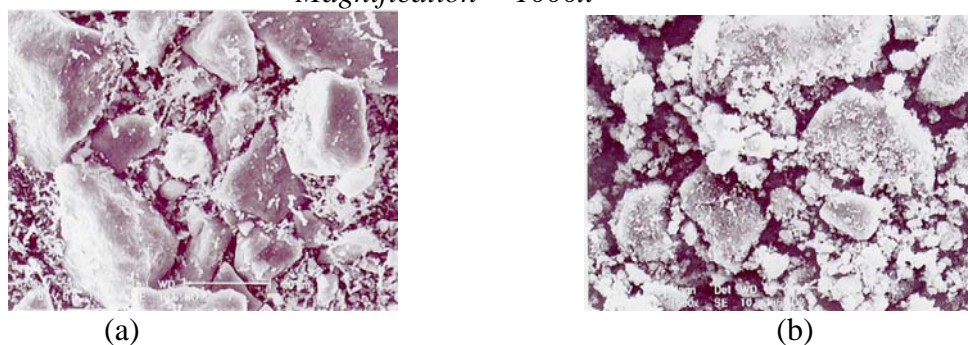
Samples	Composition Ratio SnCl ₂ :PdCl ₂ :NiSO ₄	Sample Identification
EMD-Ni	1:1:1	EMD-Ni 1
EMD-Ni (SnCl ₂)	1:1:4.0	EMD-Ni 2
	1:1:2.0	EMD-Ni 3
	1:1:1.6	EMD-Ni 4
	1:1:1.4	EMD-Ni 5
	1:1:1.2	EMD-Ni 6
	EMD-Ni (PdCl ₂)	1:1.40:1
1:0.84:1		EMD-Ni 8
1:0.68:1		EMD-Ni 9
1:0.54:1		EMD-Ni 10
1:0.36:1		EMD-Ni 11
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
	1:1:0.67	EMD-Ni 15
Ni	-	Ni

RESULTS AND DISCUSSION

Figure 1 shows nickel was coated onto the EMD from SEM micrographs of EMD and nickel coated EMD.

Figure 1 SEM Micrographs of a) EMD and b) nickel coated EMD

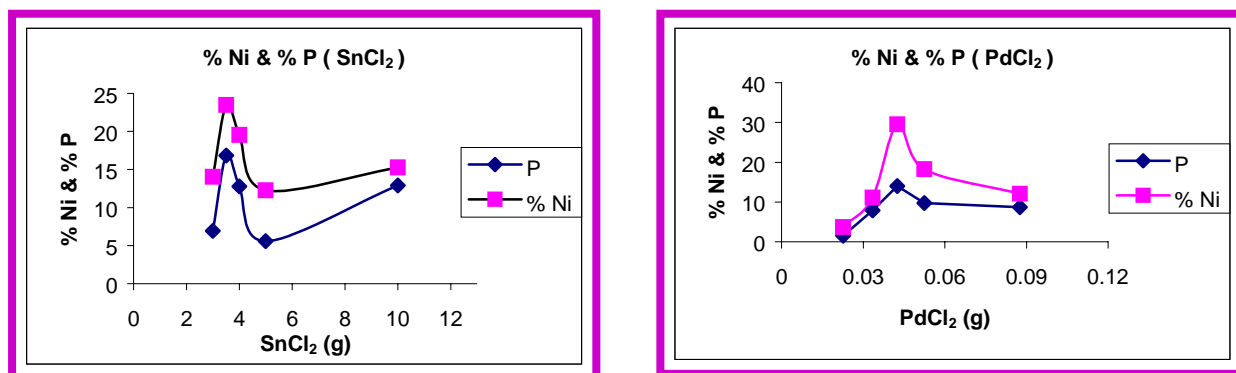
Magnification = 1000x



The amount of nickel coated, however were dependent upon the concentration of plating compounds. Table 3 gave the results of the percentage of nickel and phosphorus from EDAX analysis for the electroless plating. EMD-Ni represented the standard concentration of plating bath based on the reference [6].

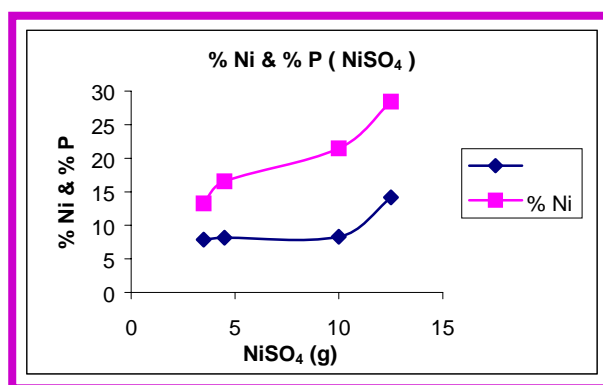
Table 3: Percentage of Nickel and Phosphorus for EMD-Ni samples after plating

Parameter	Samples	Ni (%)	P (%)
	EMD-Ni 1	18.53	-
	EMD-Ni 2	14.06	6.95
SnCl₂	EMD-Ni 3	23.46	16.83
	EMD-Ni 4	19.54	12.79
	EMD-Ni 5	12.26	5.59
	EMD-Ni 6	15.28	12.92
	EMD-Ni 7	3.74	1.52
PdCl₂	EMD-Ni 8	11.11	7.91
	EMD-Ni 9	29.53	14.03
	EMD-Ni 10	18.26	9.71
	EMD-Ni 11	12.10	8.66
	EMD-Ni 12	13.25	7.89
NiSO₄	EMD-Ni 13	16.56	8.15
	EMD-Ni 14	21.46	8.29
	EMD-Ni 15	28.43	14.16



(a) SnCl₂ parameter

(b) PdCl₂ parameter



(c) NiSO₄ parameter

Figure 2: Graphs of variation of percentage of nickel and phosphorus for different composition of plating baths

From the above observation, it can be deduced that there exist an optimum percentage of the nickel coated, Figure 2 (a, b, c) at which the conductivity of the electroless nickel coated layer will be enhanced. M.S. Wu, *et. al.*, found that an increase in the thickness of the nickel coating will reduce the efficiency of transport of the ion species. [5]. This would also result in an improvement of the conductivity but will result in a decrease in the surface area of the active sites of EMD. Therefore, this will consequently affect the capacity of the cathode system by increasing the charge transfer resistance. The decrease in the capacity could also be due to the instability of the nickel deposit in KOH electrolyte of the battery system. During the charge-discharge cycles, the nickel coated layer is being oxidized to nickel hydroxide [5].

The possible presence of phosphorus in the coated layer, was attributed from the reducing agent, sodium hypophosphite [8]. Studies have shown that an increase in the phosphorus content 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 [8].

Table 4: Conductivity results for the optimum parameter

Parameter	Sample	% Nickel	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$) x 10^{-5}
SnCl ₂	EMD-Ni 3	1226	6.634
PdCl ₂	EMD-Ni 8	29.53	6.748
NiSO ₄	EMD-Ni 15	13.25	6.970
Optimum	EMD-Ni (opt)	10.25	5.855
Standard (US Patent) [6]	EMD-Ni 1	18.53	5.495

A varying amount of nickel was found coated onto the EMD. Samples EMD-Ni 3 with 23.46 % nickel was found to be the optimum condition for the varying concentration of SnCl₂. Conductivity tests were then carried out and gave comparable readings with the reference sample EMD-Ni 1. For the varying concentration of PdCl₂, sample EMD-Ni 8 was found to be the optimum based upon the results of its conductivity, although the amount of nickel deposited was only 11.11 %. A change in the concentration of NiSO₄ concentration has resulted in an optimum condition for EMD-Ni 15, whereby the percentage of nickel deposited was 28.43 %. Using the optimum parameters, a plating bath was then prepared and the sample EMD-Ni (opt) was analysed and the resultant gave conductivity results comparable with the standard sample.

CONCLUSION

The optimum condition for the plating bath depends upon the concentration of the three major compounds, SnCl₂, PdCl₂ and NiSO₄. The optimum ratio obtained from the studies was SnCl₂ : PdCl₂ : NiSO₄ – 5.0g : 0.0425g : 3.5g by weight ratio with 10.25 % nickel. However, two forms of nickel were found deposited through this electroless technique and their conductivity results were greatly influenced by this. A highly crystalline nickel with high conductivity values are most preferred for enhancing the rechargeability of EMD in RAM batteries.

ACKNOWLEDGEMENT

This research work has been funded by Industrial Grant Scheme (IGS) in collaboration between Grand Battery Technologies Sdn. Bhd., Senai, Johor and Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, Skudai, Johor.

REFERENCES

- [1] Shen, Yuwei, *PhD Thesis*, Technical University of Graz, Austria, 1997, pp. 23-24
- [2] Suqui D. Desai, Julio B. Fernandes and V. N. Kamat Dalal, *Journal of Power Sources*, 16, 1985, pp. 1-43
- [3] R. Andreaus and L. Binder, *Electrochemical Soc. Proc.*, Vol. 96-16, pp. 23-34
- [4] L. Binder, W. Jautscher, D. A. Fielder and K. Kordesch, *Electrochemical Soc. Proc.*, Vol. 97-18, pp. 583-591
- [5] M.S.Wu, C.M. Huang, Y.Y. Wang, C.C. Wan, 1999, *Electrochimica Acta*, 44, pp. 4007-4016
- [6] M. Klien, US Patent No: 5,611,823 (1997)
- [7] M. Klien, *38th Power Sources Conference*, Proc., 1998, pp. 106-109
- [8] R. Parkinson, *Nickel Development Institute*, NiDI Tech Series No. 10 081
- [9] L.J. Van der Pauw, *Philips Research Report*, 1958, Report No 13, pp 1-9