

Full Paper

Development of MnO₂ Incorporated Ni-P Electrode for Ethanol Sensing

S. M. A. Shibli¹ and N. D. Suma^{2,*}

¹*Department of Chemistry, University of Kerala, Kariavattom Campus, Thiruvananthapuram-695 581, India*

²*Department of chemistry and Polymer chemistry, KSM Devaswom Board College, Sasthamcotta Kollam P.O - 690 521, India*

*Corresponding Author, Tel.: 9947157749

E-Mail: sumagirish81@gmail.com

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Abstract- MnO₂ incorporated Ni-P electrodes were prepared by electroless deposition from a solution containing MnO₂ particle suspended by stirring. The electrocatalytic activity of the electrode towards ethanol oxidation found to vary with concentrations of MnO₂ particles. The electrode with 10 g/L MnO₂ particles exhibited maximum electrocatalytic activity. The optimized electrode had a response time of 14 s and a sensitivity of 8.6 $\mu\text{A/ppm cm}^2$. The electrochemical characterization for the catalytic activity was explained by cyclic voltammetry, chronoamperometry. The sensing behavior of the electrode was studied in 0.2 M NaOH solution containing ethanol using impedance spectroscopy. The maximum rate of ethanol oxidation was observed at its sensing potential.

Keywords- Electroless plating, MnO₂ incorporation, Ethanol sensing, Chronoamperometry, Electrochemical sensor, Ni-P coating

1. INTRODUCTION

Ethanol sensors are widely used for determining the concentration of ethanol in food, fermentation, cosmetic industries and alcohol beverages [1-5]. In recent years the researchers have showed increased interest in the development of ethanol sensors and sensing

technologies. Ethanol determinations have been accomplished using different approaches such as chromatography, refractometry, near infra-red spectroscopy, biosensors and chemo sensors [6-9]. Some of these approaches present disadvantages such as poor stability, relatively high unit cost and low storage temperature [10,11]. Amperometric method is a versatile method for the determination of alcohol concentration due to their convenience, simplicity and accuracy [12]. The direct determination of alcohol in aqueous solution by electrochemical method using conventional electrode material is virtually impossible [13-15]. This is because oxidation potential of alcohol is much larger than that of water. This result in interference by simultaneous oxidation of other species present in the sample system [16,17]. In the electrochemical oxidation of alcohol the electrode material is clearly an important parameter where a high efficient electrocatalyst must be required.

Metal or metal oxide modified electrodes have been developed for sensing ethanol. The most commonly used electrode materials for amperometric detection of polar organic compounds are Pt, Au, Ni and Cu [18,19]. While using metal electrode material such as Pt, Au and Co in the direct current mode however losses its electro catalytic activity, which can be ascribed to the fouling of the electrode by reactant/product adsorption effects [20]. Nickel has been reported to make good electrodes for oxidation of various organic compounds [21-23]. The ethanol oxidation mechanism at the nickel electrode in alkaline medium has been proposed by Fleischmann et al [21] Robertson [24] and Lo and Hwang.

In our previous study [25] we observed that the electrocatalytic activity of catalytic metal oxide incorporated Ni-P alloy electrodes were more efficient than pure Ni-P electrode for ethanol electrooxidation. Olivi [26] and Xin [27] have reported, respectively, that addition of SnO₂ can promote the catalytic activity for methanol and ethanol oxidation. ZrO₂ [28] CeO₂ [29] and MgO [30] IrO₂ [31] RuO₂ [32] are also studied and found that they can improve the catalytic activity for ethanol electro oxidation. In this context we select MnO₂ catalyst as composite for incorporation with N-P coating. In the present study we have developed MnO₂ reinforced Ni-P coating using electroless deposition. The MnO₂ modified electrodes have been used as electrodes for oxygen and hydrogen electro reduction due to its lower cost and higher catalytic activity [33]. MnO₂ catalyst also shows a certain extent of electrochemical activity for carbohydrate oxidation [34]. Here we have studied both the sensing performance and electrocatalytic action of MnO₂ incorporated Ni-P electrode for ethanol sensing and the results are discussed in this paper.

2. EXPERIMENTAL DETAILS

2.1. Fabrication of MnO₂ incorporated Ni-P electrode

Mild steel coupons were purchased from steel market at Trivandrum town having the composition in percentage as follows C - 0.09, Mn - 0.034, P - 0.036, Si - 0.0480 and

Al- 0.024. These coupons were then cut into small pieces (5 cm×6 cm×0.4 cm) and used for all experimental analysis. Mild steel coupons were subjected to pretreatment before electroless plating process. After mechanical cleaning, the impurities adhere on the surface of the plate was removed by using NaOH (5%) solution [ASTM B 656]. For maximum deposition of the coating, the removal of all traces of oxide from the surface is essential. Hence, the coupons were then subjected to acid pickling in 3% HCl solution for 5 min [ASTM B 656]. The treated coupons were then sensitized in a solution of 10 g/L SnCl₂ in 40 mL/L HCl (37%). After sensitization the surface was activated in a solution of 1 g/L PdCl₂ in 10 mL/L HCl (37%). Subsequent to sensitization and activation the substrates were introduced into the electroless plating bath. The electroless bath had the composition of 30 g/L nickel sulphate, 25 g/L succinic acid, 25 g/L sodium hypophosphite. The chemicals used in these experiments were all AR grade (Merck). The ammonia solution was added to the electroless bath for adjusting the pH to 4.5. MnO₂ material (Merck, India) incorporated Ni-P electrodes were prepared by adding different concentration of MnO₂ powder in the electroless bath during plating process. The whole plating process continued for 2 h at 80 °C.

2.2. Physico-chemical characterization

Physical performance of the MnO₂ added coupons were characterized by measuring hardness, thickness and porosity of the coatings. The hardness of the coatings was measured using Vickers micro indentation hardness (ASTM E 384-99) with a 100 g load and indentation time was 12 s. Porosity of the coatings was tested by using ferroxyl reagent test [35]. A solution of potassium ferricyanide, sodium chloride and agar-agar in hot water was used as the ferroxyl reagent. Coatings after immersing into the reagent for 5 minutes were inspected for any appearance of Prussian blue color.

2.3. Electrochemical characterization

Electro catalytic nature of the coatings was studied by taking cyclic voltammogram in 0.2 M NaOH solution containing ethanol at a scan rate of the 10 mV/s using BAS (USA). The surface area of the working electrode used in CV was 0.3 cm² and the remaining portion of the electrode was covered with Teflon. The counter electrode used was Pt and the reference electrode was silver electrode. Chronoamperometric analysis was employed to detect the performance of the electrode. An impedance spectrometer AUTOLAB PGSTAT with FRA 2 software of FRA version 4.9 was used to study sensing behavior at a potential of 407 V. The measurements were made in the frequency range from 1 MHz to 0.1 Hz.

The ethanol detection system consisted of an electrochemical cell containing working, counter and reference electrodes. MnO₂ incorporated Ni-P electrode with geometric area of 0.3 cm² was used as working electrode. The exposed area was polished with emery paper

and rinsed with deionized water prior to use. A Pt electrode (4 cm²) and the Ag/AgCl electrode were used as counter and reference electrode respectively. A 0.2 M NaOH solution was used as base electrolyte. The response current was noted after adding desired concentration of ethanol to the NaOH solution. It is noted that total concentration of the solution in the cell become 100 ppm after each addition of ethanol solution. A calibration curve of ethanol concentration of the response current was plotted. The sensitivity of the electrode was calculated using the formula $S = \Delta I / \Delta C$ A, where S is the sensitivity ($\mu\text{A/ppm cm}^2$), ΔI is current response (μA), ΔC the change in ethanol concentration and A is the surface area of the sensing electrode (cm^2).

3. RESULTS AND DISCUSSION

3.1. Physico-chemical characterization

The physical properties of the MnO₂ incorporated Ni-P electrodes are compared in Table 1.

Table 1. Elemental composition and hardness values of the Ni-P electrodes with MnO₂ incorporation

MnO ₂ composition (%)	Coating composition (%)		Hardness (HVN)
	P	Mn	
0	10.2	0	380
0.5	9.35	0.45	420
1	10.85	0.61	425
2	10.4	0.81	436

The hardness value of the MnO₂ incorporated electrode has been found to be higher than that of the pure Ni-P electrode [36]. The maximum hardness attained was 436 HVN for Ni-P alloy coating with 2% MnO₂. A Prussian blue coloration observed for the MnO₂ incorporated Ni-P electrode during ferroxyl reagent test was a clear indication of porous nature of the electrode. The percentage compositions of the elements present in the coating determined by Energy Dispersive Spectroscopic analysis and it is given in Table 1. Phosphorous content was found to be in the range of 9-11 wt %. Ni-P alloy with intermediate phosphorus content has been described as fine dispersion of microcrystalline nickel in an amorphous matrix [37].

3.2. Voltammetric analysis

The electrochemical characterization of conductive metallic oxide electrode is generally accomplished through cyclic voltammetry. The typical CV curves for ethanol electro

oxidation on MnO₂ incorporated Ni-P electrode and pure Ni-P electrode are shown in Fig. 1. The potential was varied between rest potential to 500 mV with a scanning rate of 10 mV/s. When pure Ni-P electrode was immersed in alkaline medium two different structures of nickel hydroxide were formed.

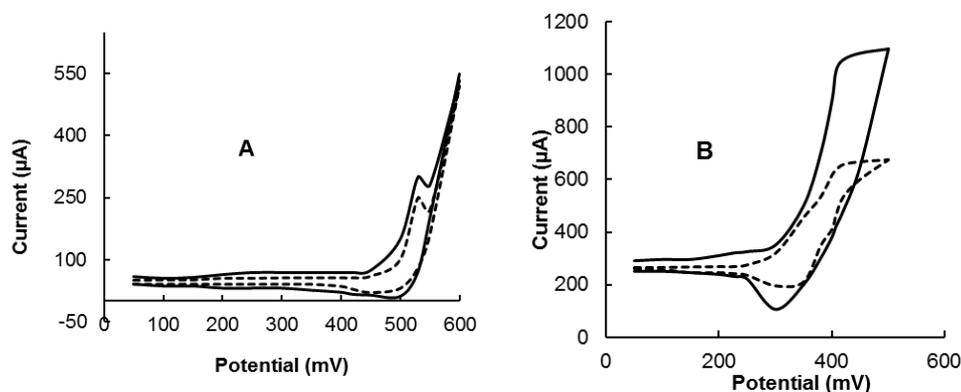


Fig. 1. The cyclic voltammograms recorded for A) Pure Ni-P electrode; B) Ni-P electrode incorporated with 1% MnO₂ [Dotted lines corresponds to 0.2 M NaOH solution, solid line corresponds to 0.2 M NaOH+1000 ppm EtOH solution, scan rate: 10 mV/s, temp: 32 °C]

The extent of phosphorus content in the Ni-P electrode seem to decide the formation of α Ni(OH)₂ during cyclic voltammetric studies in alkali solution. A.M. Fundo and L.M. Abrantes showed that the cyclic voltammetric response of Ni-P electrode with low phosphorous content was similar to that of pure Ni electrode [38]. In the present work phosphorus content was in the range of 8-11 at %. In general anodic oxidation peak of β Ni(OH)₂ is more positive than α Ni(OH)₂ and the oxidation state of γ NiOOH is higher than that of β NiOOH [39]. The form of nickel hydroxide has a higher reversible redox potential compared to the β form. Therefore, α Ni(OH)₂ is expected to be a better electro active material for oxidation of ethanol [40]. An anodic peak potential of 530 mV was recorded in NaOH solution. The anodic peak corresponds to α Ni(OH)₂ to γ NiOOH [41]. The composite added coating gave an anodic peak potential of 407 mV (vs. Ag/AgCl). The anodic peak potential was found to less positive on composite incorporated Ni-P electrode. Upon addition of ethanol to the base electrolyte cyclic voltammogram gave higher oxidation current and reached a maximum value at a potential of 407 mV. In the presence of ethanol optimum concentration of MnO₂ added coupon showed higher anodic current density of 1000 $\mu\text{A}/\text{cm}^2$. Thus the increased oxidation current at the MnO₂ incorporated Ni-P electrode resulted from the electro catalytic oxidation of ethanol. The main species involved in ethanol oxidation appear to be Ni(OH)₂/NiOOH. This redox mediator acted as an electron transfer mediator and showed the synergistic effect for ethanol oxidation.

The onset potential value for ethanol oxidation showed interesting differences. The onset potential of ethanol oxidation for optimum concentration of composite incorporated Ni-P

electrode (196 mV) occurred at lower potential than that of pure Ni-P electrode (360 mV). Electro catalytic efficiency of MnO₂ incorporated Ni-P electrode is defined as the ratio of the anodic catalytic current to the anodic peak current relative to the blank. The electro catalytic efficiency (ECE) for ethanol oxidation reached a maximum of 1.61 for 10 (g/L) MnO₂ incorporated Ni-P electrode. For Ni-P electrode, ECE was found to be 0.95. These observations indicated that composite incorporated Ni-P electrodes have higher catalytic activity and better stability for ethanol oxidation than pure Ni-P electrode because of the incorporation of MnO₂ into the Ni-P electrode.

Sensing performance of the electrode

3.3. Response time and sensitivity of the electrode

The current-time response of the MnO₂ incorporated Ni-P electrode was studied by using amperometric detection at a potential of 407 mV. Fig. 2 shows the amperometric response for successive addition of the ethanol to 0.2 M NaOH solution. The total ethanol concentration after each addition in to the cell increased by 100 ppm. Response time Ni-P electrode was found to be 25 s.

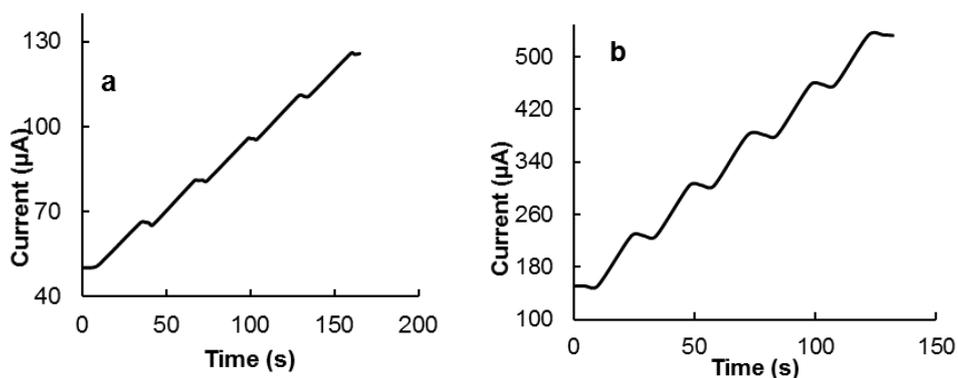


Fig. 2. Amperometric response of Ni-P electrode with and without MnO₂ incorporation (a) incorporated with (1%) MnO₂; (b) pure Ni-P electrode [Base electrolyte: 0.2 M NaOH solution, ethanol concentration after each addition increased by 100 ppm, applied potential: 407 mV, temp: 32 °C]

The MnO₂ incorporated Ni-P electrode achieved steady state current within 14 s. At lower applied potential the sensor exhibited lower signals and lower stability. The reason is that the potential is too low to reoxidise all the manganese ions back to the higher oxidation state [42]. In the case of Ni-P electrode the low response may be related to slowness of the diffusion-migration process occurring at the electrode-solution interface. The steady state values of the response current in Fig. 2 were plotted against the concentration of ethanol was shown in Fig. 3. It was observed that MnO₂ incorporated Ni-P coating exhibited well defined

current response observed a broad concentration range. An optimum concentration of MnO_2 (10g/L) composite would accelerate the electron transfer reaction between electrode and ethanol solution, which in turn improves the sensitivity and reproducibility of the coating.

The sensitivity of the MnO_2 modified Ni-P electrode was $8.6 \mu\text{A}/\text{ppm cm}^2$ and that of pure Ni-P electrode was found to be $1.5 \mu\text{A}/\text{ppm cm}^2$. The sensitivity was found to be five times higher than that of the pure Ni-P coatings. Fig. 4 showed that under optimal conditions the linear response range of the Ni-P- MnO_2 to ethanol was from 100 ppm to 500 ppm with a detection limit of 12 ppm.

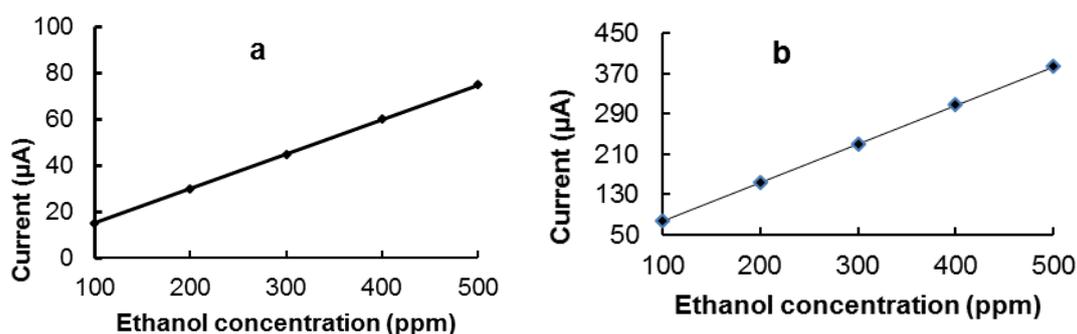


Fig. 3. The calibration plot of the Ni-P electrode with and without MnO_2 (a) (1%) MnO_2 composite incorporated Ni-P electrode, applied potential: 407 mV; (b) Pure Ni-P electrode, applied potential: 510 mV [Base electrolyte: 0.2 M NaOH solution, ethanol concentration after each addition increased by 100 ppm, temp: 32°C]

3.4. Impedance measurement

Fig. 4 shows the Nyquist plots for pure Ni-P and MnO_2 incorporated Ni-P electrodes measured in 0.2 M NaOH solution containing with and without the ethanol at OCP and sensing potential. The equivalent circuit was derived from the simulation of the experimental data. The CNLS program was used for the fitting of experimental results to the equivalent circuit. In this R_s , (R_pC1), ($RC2$), R_s represent uncompensated solution resistance, while the parallel combination of R_p and $C1$ represents ethanol adsorption and subsequent oxidation on the mixed oxide layer. A single semicircle was observed for both electrodes at OCP. In the present study MnO_2 incorporated Ni-P electrode at OCP show a poorly developed semicircle. The origin of this poorly developed semicircle was thought to be associated with porous characteristics of outer surface of MnO_2 incorporated Ni-P coatings.

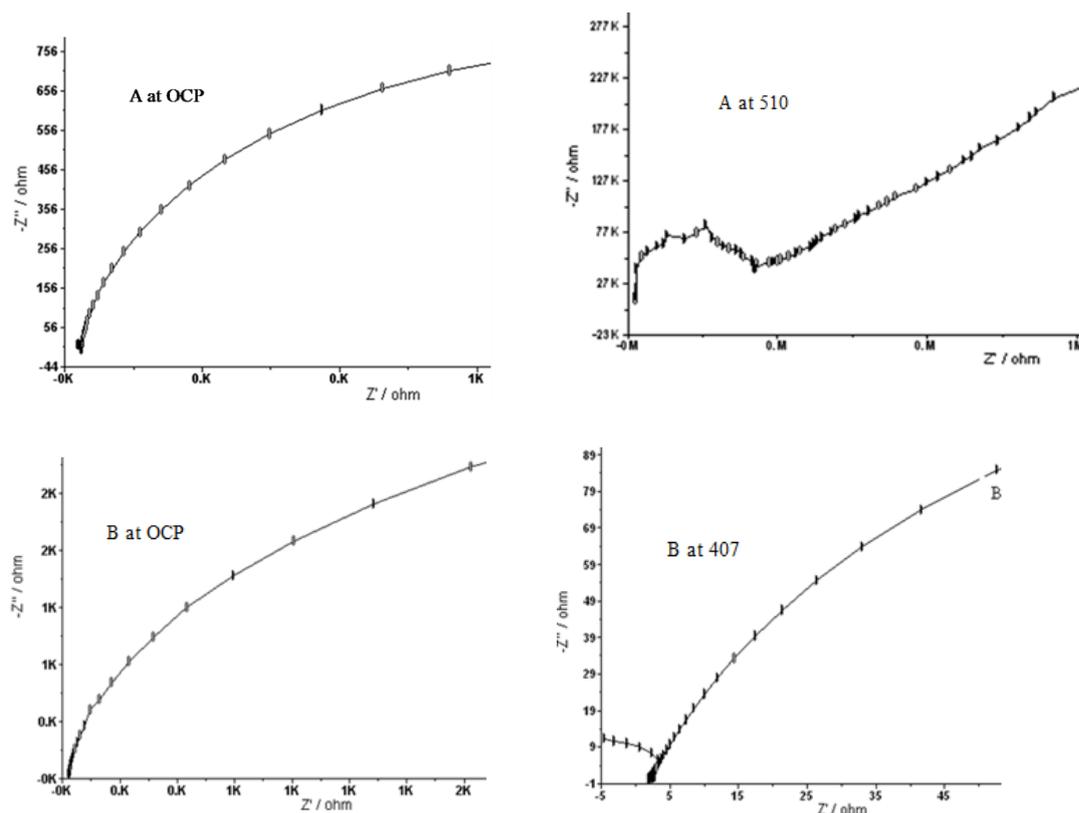


Fig. 4. Nyquist plots for Ni-P electrode with and without MnO_2 incorporation at different potentials A) pure Ni-P electrode B) 1% MnO_2 incorporated Ni-P electrode [Electrolyte: 0.2 M NaOH at OCP, 0.2 M NaOH+1000 ppm ethanol at sensing potential, temp: 32 °C]

The occurrence of single semicircle in the Nyquist plot in the case of pure Ni-P coating indicated that corrosion process involves a single time constant [43]. All the parameters obtained from the simulation is given in Table 2. The MnO_2 incorporated Ni-P coating exhibited an R_p value of 1050 Ω . The high value of polarization resistance (R_p) and low capacitive value corresponding to composite coatings revealed a better corrosion protective ability of the coating than the pure Ni-P coating. The impedance spectra of composite incorporated Ni-P coating consist of two components (semicircle I and semi-circle II). The semicircle II related to the electro oxidation process of ethanol. Composite coatings exhibited lower R_p value at sensing potential than that of pure Ni-P coatings. Maximum rate of ethanol oxidation was observed at minimum R_p value [44]. Ni-P electrode incorporated with 1% MnO_2 exhibited an R_p value of 80.2 Ω . Maximum rate of ethanol oxidation in the case of 1% MnO_2 incorporated Ni-P electrode at a potential of 407 mV was revealed by the observed minimum R_p value. Charge transfer value was found to be lower for composite incorporated Ni-P electrode. Both the capacitance value and CPE have been reported as being directly proportional to the number of an electrodes electrochemically active surface sites, surface roughness and porosity [45]. The capacitive value was found to be higher for Ni-P composite coating. The higher capacitance value exhibited by the MnO_2 incorporated Ni-P electrode in

ethanol solution was in good agreement with the higher CV current response in the ethanol solution. The optimized electrode exhibited high CPE value (3.5×10^{-9}) than that of pure Ni-P electrode. The high CPE value observed for the electrode revealed that the surface structure high roughness. These observations revealed that composite coating enhanced the activity of the Ni-P coating towards the ethanol oxidation.

Table 2. The electrochemical impedance parameters measured at 0.407 V of the Ni-P electrodes incorporated with MnO₂ particles

System	E _{applied} (mV)	R _p (Ωcm ²)	R _p (Ωcm ²)	C1 (μF)	C2 (μF)	n	CPF (F)
Ni-P electrode	OCP	950	450	34.1	278	0.81	5.4×10^{-8}
	510	352	466	1.33	4.11	0.80	1.61×10^{-10}
MnO ₂ incorporated Ni-P electrode	OCP	1050	501	20.01	0.64	1.07	8.34×10^{-10}
	407	80.2	170.3	18.36	0.39	1.02	3.5×10^{-9}

3.5. Surface morphology

The surface morphology of the Ni-P coating with the MnO₂ incorporation is given in Fig.5.

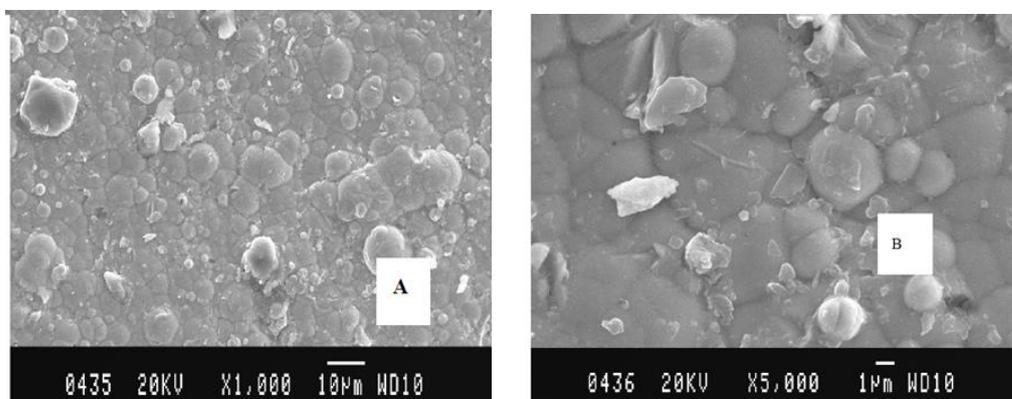


Fig. 5. The scanning electron micrographs of different types of the Ni-P plates (A) 1% MnO₂ incorporated Ni-P plate (x1000magnification), (B) 1% MnO₂ incorporated Ni-P plate(x5000 magnification)

At low magnification (1000), the Ni-P coatings incorporated with MnO₂ composite particles were found to have uniform distribution of the composite particles all over the coating surface. The composite particles made island like structures on the surface of the coating as was viewed at higher magnification (5000). This island structure would be

facilitating the access of the ethanol molecule to the substrate materials during the sensing action.

4. CONCLUSION

We have developed cost effective MnO₂ incorporated Ni-P electrode by electroless method. Physical characteristics of the modified electrode were found to be better than that of pure Ni-P electrode. The presence of MnO₂ particle shifts the onset potential of electrochemical reaction to less positive potential. The amperometric measurement of ethanol at sensing potential on Ni-P electrode incorporated with MnO₂ composite showed fast response time and good linearity in the range of 100-500 ppm. The incorporation of MnO₂ composite reduces the effective metallic area available for corrosion. At sensing potential MnO₂ added electrode gave low R_p value. Composite electrode with low R_p value exhibited maximum rate of ethanol oxidation.

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