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Electro Oxidation of Methanol on Ni/Ni-Co Coated SS Mesh Electrode

N. Durgadevi*, M. Sunitha, S. Asha*, S. Guhan and T. Ramachandran

Department of Sciences, Amrita School of Engineering, Amrita Vishwa Vidyapeetham, Ettimadai – 641112, Coimbatore, India; s_asha@cb.amrita.edu, sashaamrita@gmail.com, n_durgadevi@cb.amrita.edu, m_sunitha@cb.amrita.edu, s_guhan@cb.amrita.edu, t_ramachandran@cb.amrita.edu

Abstract

In this work, the oxidation of methanol was carried out using Ni and Ni-Co alloy electrodeposited on stainless steel mesh substrate with a view to replace expensive and sensitive platinum and platinum alloy catalysts. The performance of electrode was assessed through cyclic voltammetry in alkaline media. The operating conditions of the electrode were optimized.

Keywords: Alkaline Medium, Catalyst, Electro Oxidation, Methanol, Ni/Ni-Co alloy

1. Introduction

Direct Methanol Fuel Cell (DMFC) is claimed to be the most dominant power source in future due to its low operating temperature, high energy density, easy handling, light weight and availability of the fuel in plenty[1]. The electro catalytic activity of methanol is important for the development of DMFC in both acidic and alkaline media[2,3]. In both types, the transformation of methanol into carbon dioxide and hydrogen is slow and incomplete and thus catalyst is required to improve the efficiency of oxidation of methanol. Prabhuram J et al.[4] used Pt-Ru nanoparticle of size 2-3nm on the multi-walled carbon nano tubes at the anode of the DMFC. The results proved that the Pt-Ru/MWCNT yielded higher performance than the commercial E-TEK Pt Ru/C catalyst. Pt/MnO_2/carbon nano tube (CNT) and Pt-Ru/MnO_2/CNT nano composites were synthesized and used as anode catalysts by Chunmei Zhou et al.[5]. They reported that the existence of MnO_2 on the surface of CNTs effectively increases the proton conductivity and remarkably improves the performance of the catalyst on methanol electro oxidation. Loffler MS et al.[6] synthesized Pt – Ru alloy electrodes by electrochemical deposition of nano crystalline Pt- Ru particles of about 8nm on glassy carbon discs for direct methanol fuel cell and reported binary alloy electrodes are more active towards methanol oxidation. Ye Lin et al.[7] synthesized Pt-SnO_2/CNTs for methanol electro oxidation.

Yu et al.[8] used platinized mesh anodes in DMFC. The results showed that catalytic activity of methanol is higher than conventional Pt/C electrodes due to the open area of the mesh and also reduces the mass transport resistance. Raguram Chetty et al.[9] prepared binary and ternary catalysts by thermal decomposition on titanium mesh. The results showed that the mesh based electrodes exhibit competitive performance in comparison to the conventional carbon based anodes. $PtRuO_2$ catalyst thermally formed on Titanium mesh were prepared and showed higher catalytic activity than the conventional Pt Ru /C electrode by Yang et al.[10].

2. Experimental

2.1 Reagents

$NiSO_4.7H_2O$, $CoSO_4.8H_2O$, H_3BO_3, NaOH and Methanol were procured from Merck (Bangalore, India). All these chemicals are of analytical grade and used as received.

**Author for correspondence*

Solutions are prepared with double distilled water. Stainless Steel (SS) mesh was purchased from Alfa Aesar of grade 304.

2.2 Instrumentation

Electrochemical experiments were carried out using CHI608d workstation (CH instrument, USA). The electrochemical cell used in this work was a conventional three electrode cell. SS mesh coated with Ni or Ni-Co alloy was taken as the working electrode, Ag/AgCl (Satd. KCl) was taken as the reference electrode and Pt foil was taken as the counter electrode. All the potential measurements in this work were referenced to the Ag/AgCl (Satd. KCl) electrode. The modified electrodes were characterized by using a scanning electron microscope (SEM, Quanta200, SEI instrument) coupled with an energy dispersive X-ray analysis.

2.3 Electrode Fabrication

SS mesh of size 0.5x0.5 cm^2 was taken as the substrate material and cleaned well and was coated with Ni or Ni-Co. Nickel bath solution was prepared by taking 240g/L of $NiSO_4.7H_2O$ and 30g/L of H_3BO_3 and the pH of the bath was maintained at 3. Electro deposition of Ni was done over the SS mesh by galvanostatic method, maintaining the constant current of -0.02A. The Ni-Co bath solution was prepared in various ratios. The concentration of the Ni is kept constant and Co concentration alone was increased in the ratios 1:1, 1:2, 1:3 and 1:4. The deposition was carried out in the same manner as Ni deposition. After deposition the modified electrodes were rinsed in water thoroughly and used further. Freshly prepared electrodes were used throughout the studies.

3. Results and Discussion

3.1 Electro Catalytic Activity of Nickel Catalyst

SEM image and the EDX analysis confirms the uniform deposition and the presence of Ni catalyst on the electrode surface (Figure 1.(a),(b)). The fabricated electrode was activated in 0.5M NaOH at a scan rate of 0.1V/s from -1.0V to 0.7V for 50cycles. During activation two anodic peakswere observed (Figure 2(a)). First peak indicates the formation of $Ni(OH)_2$ at a negative potential of around 0.58V and the second peak corresponds to the transition of $Ni(OH)_2$ to NiOOH at a potential around 0.56V. This can be explained based on the following equations[11].

$$Ni + 2OH^- \leftrightarrow Ni(OH)_2 + 2e^- \quad (1)$$

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (2)$$

The corresponding cathodic peak was observed for the reduction of Ni^{3+} to Ni^{2+} around 0.47V. In the activation process it is observed that the current gets increased as the number of cycle gets increased due to the intensified formation of NiOOH.

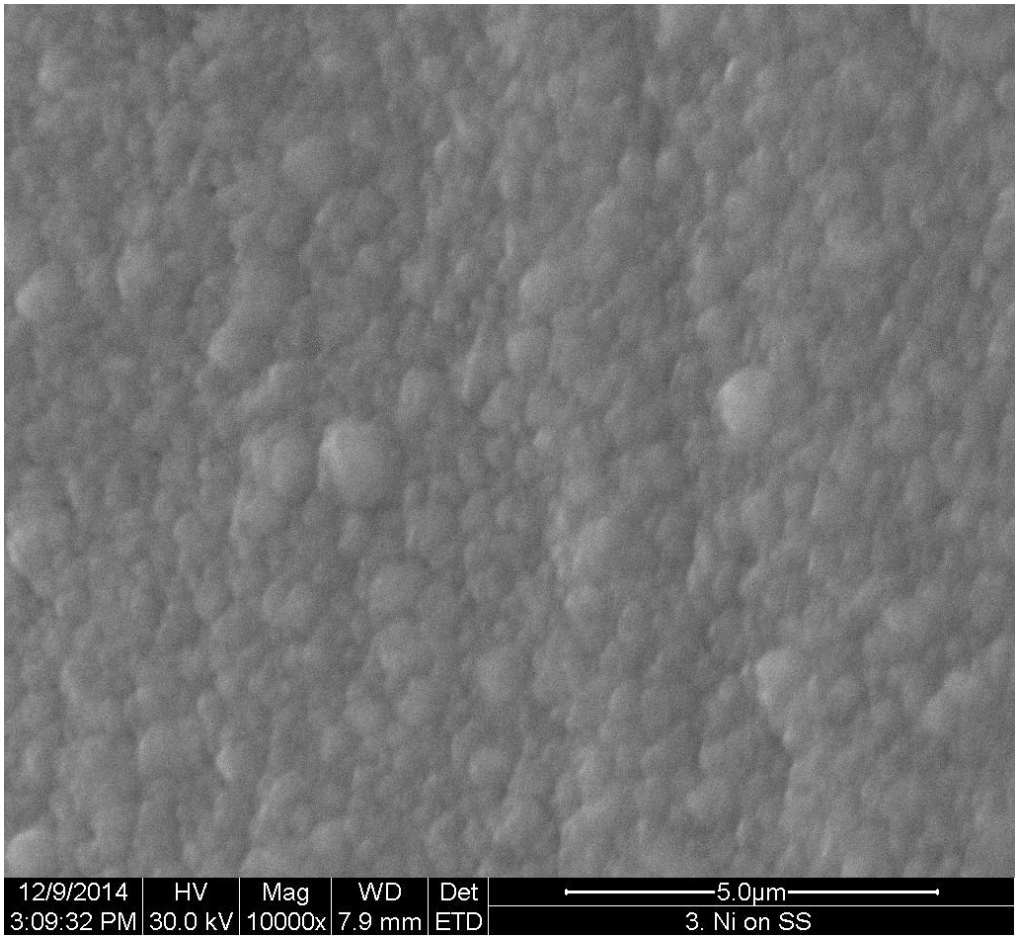
The activated electrode was tested for methanol oxidation by varying the concentration of methanol from 0.1mL to 0.5mL in the potential range -0.8V to 0.7V at a scan rate of 0.1V/s. From the voltammogram it is noted that the electrode responds to the addition of methanol and there is variation in the oxidation peak at 0.46V (Figure 2b). It is depicted from the figure, as the methanol concentration increases peak current also gets increased, due to the increase in oxidation of methanol. The response of the electrode got stagnant upon increasing the concentration beyond 0.5mL addition of methanol. This is due to the hindrance of the catalyst surface by the adsorbed oxidation products and also due to the insufficient anodic area available for the reaction[12].

3.2 Electro Catalytic Activity of Ni-Co Catalyst

Ni-Co alloy coating was obtained from bath containing Ni and Co in the ratios 1:1, 1:2, 1:3 and 1:4. SEM image of the electrode fabricated using 1:1 Ni-Co solution (Figure 3a). The EDX spectra confirms the presence of Co and Ni on the electrode (Figure 3b).

The above prepared electrodes were tested for electro catalytic activity through CV by varying the methanol concentration and the results were compared. Modified electrode from 1:1 Ni-Co solution showed best electro catalytic activity towards methanol oxidation with less oxidation potential around 0.3075V (Figure 4). And the data are tabulated (Table 1). Therefore, further studies were carried out using 1:1 Ni-Co solution.

The alloy deposit obtained from bath containing mixture in the ratio 1:1 show better electro catalytic performance for MOR rendered by oxidation at lower potentials. The catalytic performance of Ni-Co alloy gives good oxidation current with very less potential when compared to Ni catalyst (Figure 5). Mehdi Asgari, et al.[13] reported that



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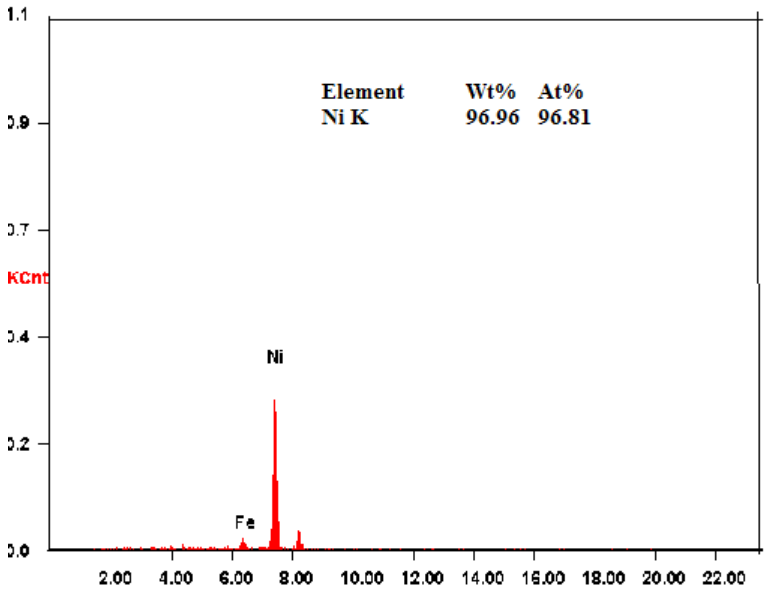
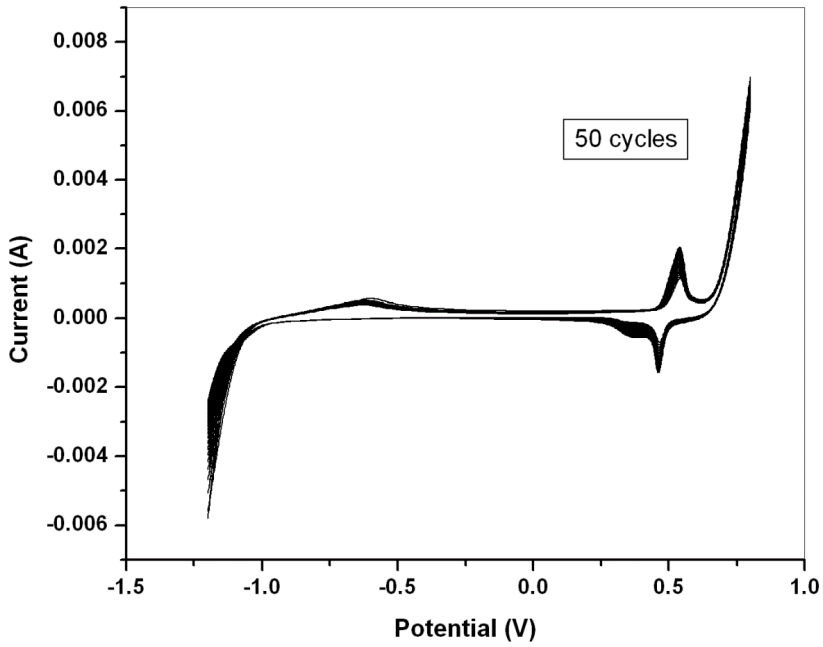


(b)

Figure 1. **(a)** SEM image of the Ni coated substrate for 10 minutes. **(b)** EDX spectra of the Ni coated substrate for 10 minutes.



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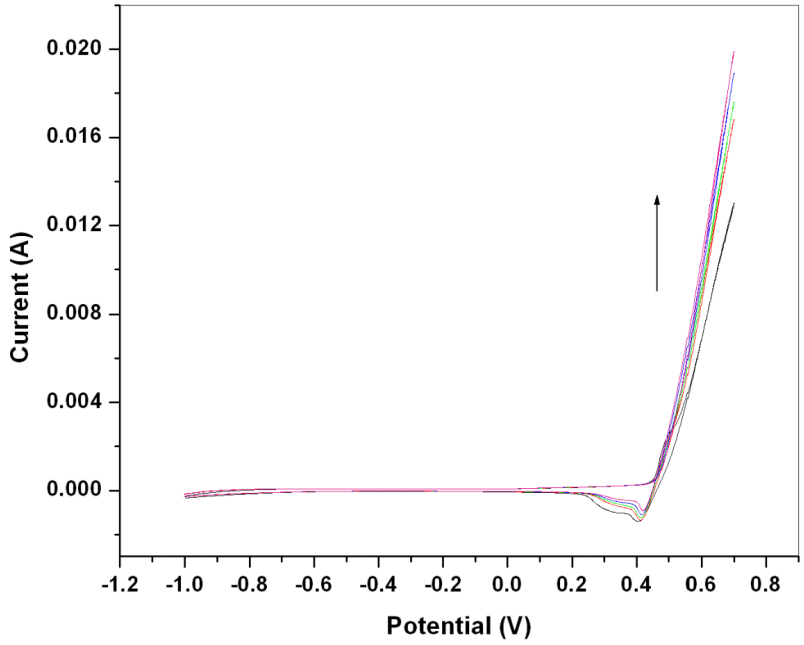
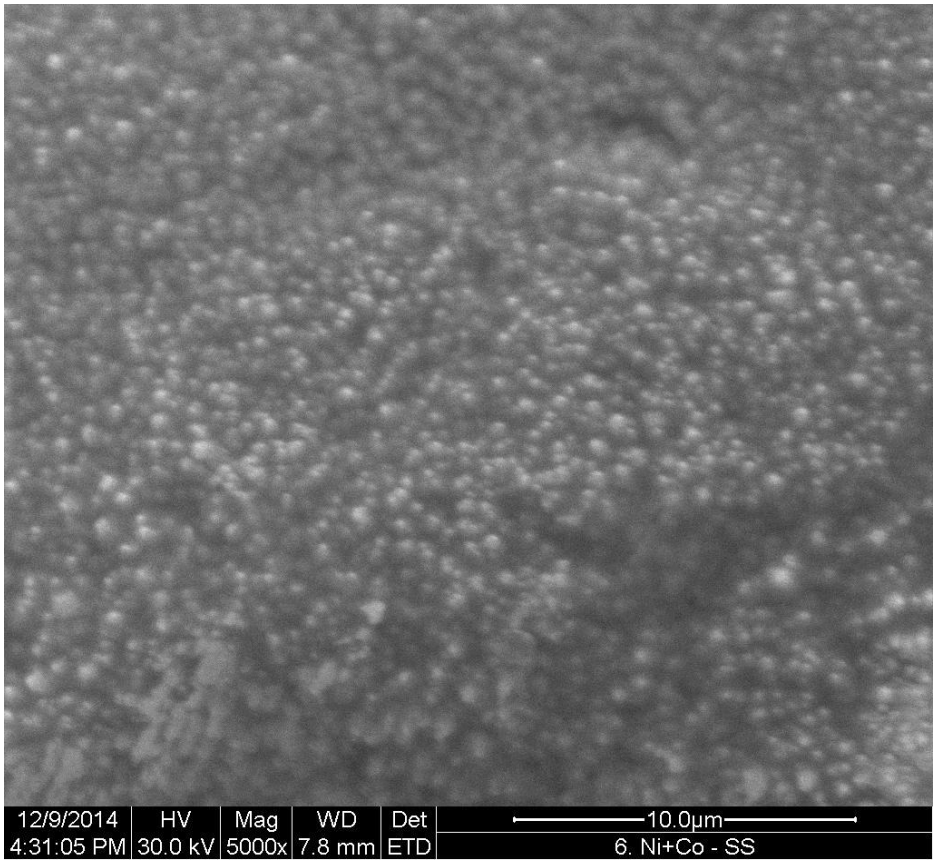


(b)

Figure 2. **(a)** Activation of Ni coated electrode in 0.5M NaOH solution at the scan rate of 0.1V/s. **(b)** Oxidation of methanol in 0.5M NaOH/(0.1mL to 0.5mL)methanol at the scan rate of 0.1V/s .



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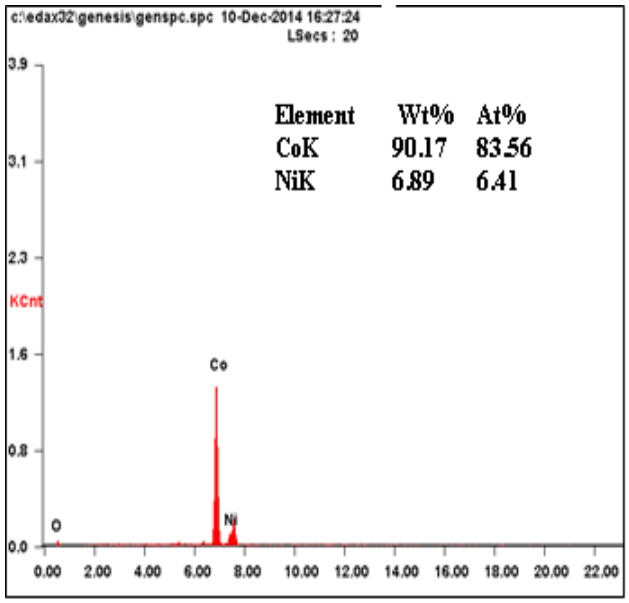


(b)

Figure 3. **(a)** SEM image of the electrode after deposition of Ni-Co catalyst using 1:1 solution. **(b)** EDX analysis of the same electrode.

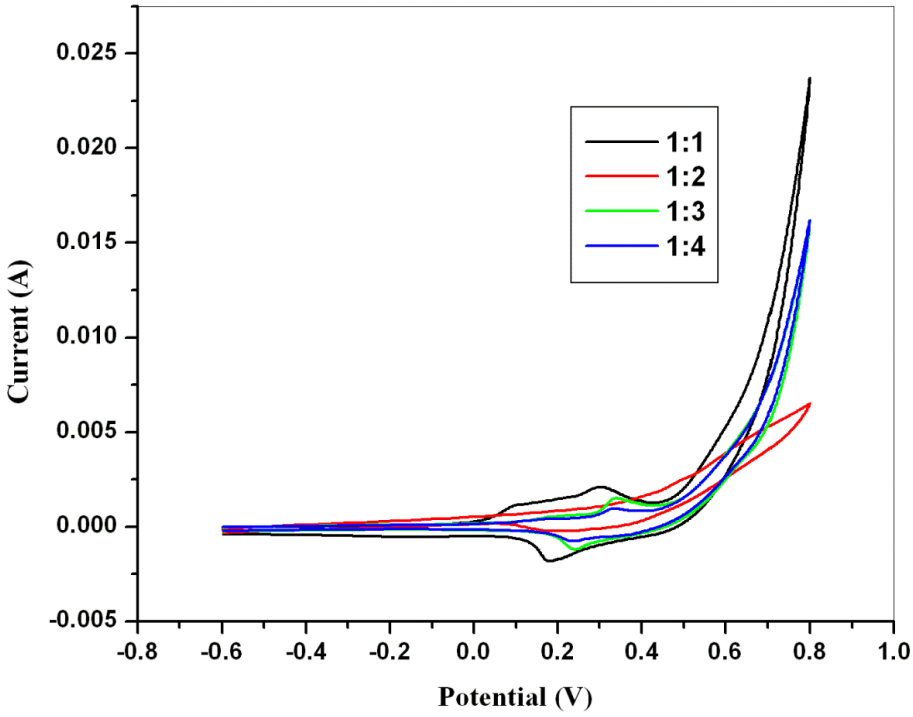


Figure 4. Comparative cyclic voltammogram of the electrodes coated with various composition of Ni-Co solution containing 0.5mL methanol in 0.5M NaOH at a scan rate of 0.1V/s.

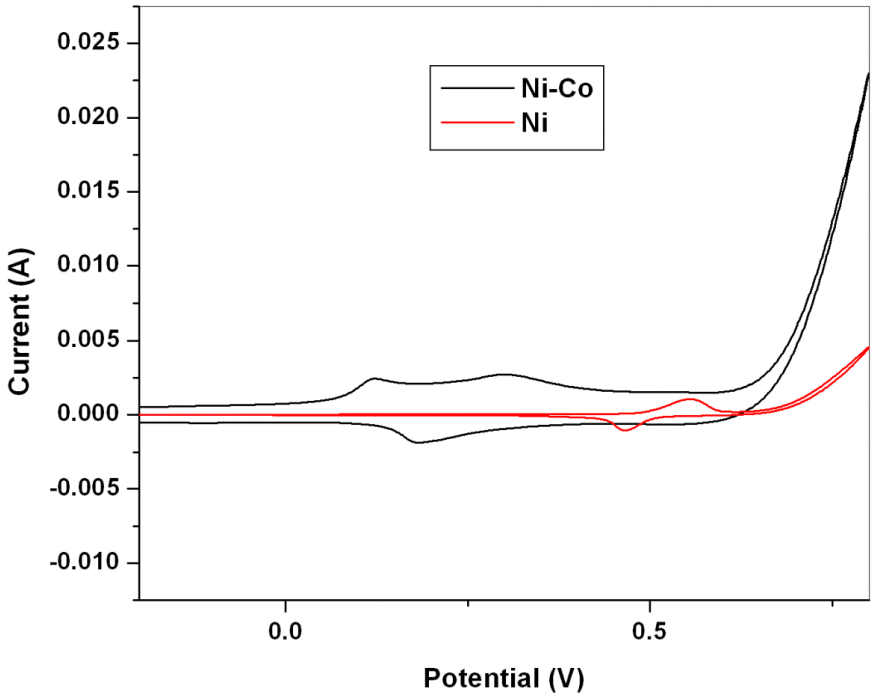


Figure 5. The catalytic action of Ni and Ni-Co coated electrode for the MOR containing 0.5mL methanol in 0.5M NaOH medium at a scan rate of 0.1V/s.

Table 1. The Peak potential and current for the MOR on Ni-Co electrode in 0.5M NaOH/0.5mL methanol

Ni-Co ratio	Potential (V)	Current(mA)
1:0	0.458	0.045
1:1	0.3075	1.87
1:2	0.3459	2.1
1:3	0.3577	1.9
1:4	0.3697	1.7

this is due to the formation of $Co(OH)_2$ during the oxidation process which increases the charge acceptance ratio of Ni and also inhibit the formation of γ- NiOOH, which deactivates the catalytic property of Ni.

3.3 Thickness Studies

The thickness of the catalytic layer was varied by varying the time of deposition. The electrode was coated with 1:1 Ni-Co solution for various time intervals and its methanol oxidation property was studied (Figure 6). Electrode coated for 10 and 20 minutes posses similar electro catalytic property with a small increase in the anodic current of about 1.53mA. Further on increasing the coating time to 30 and 40 minutes the thickness of the deposit gets increased. On increasing the thickness of electro catalytic layer, the resistance offered by the catalyst gets increased to a large extent due to the increase in Co content. Increase in Co content will diminish the recorded methanol oxidation current and their potential slightly shifts towards more positive potentials, X. Tarrus, et al.[14]. Thereby the activity of the electrode gets degraded and it is not preferred.

3.4 Effect of Medium

The influence of alkaline medium in MOR is studied by varying the concentration of NaOH. On increasing the hydroxyl ion concentration from 0.3M to 0.7M there is no remarkable change in the basic cyclic voltammogram. The presence of more hydroxyl ions improves the

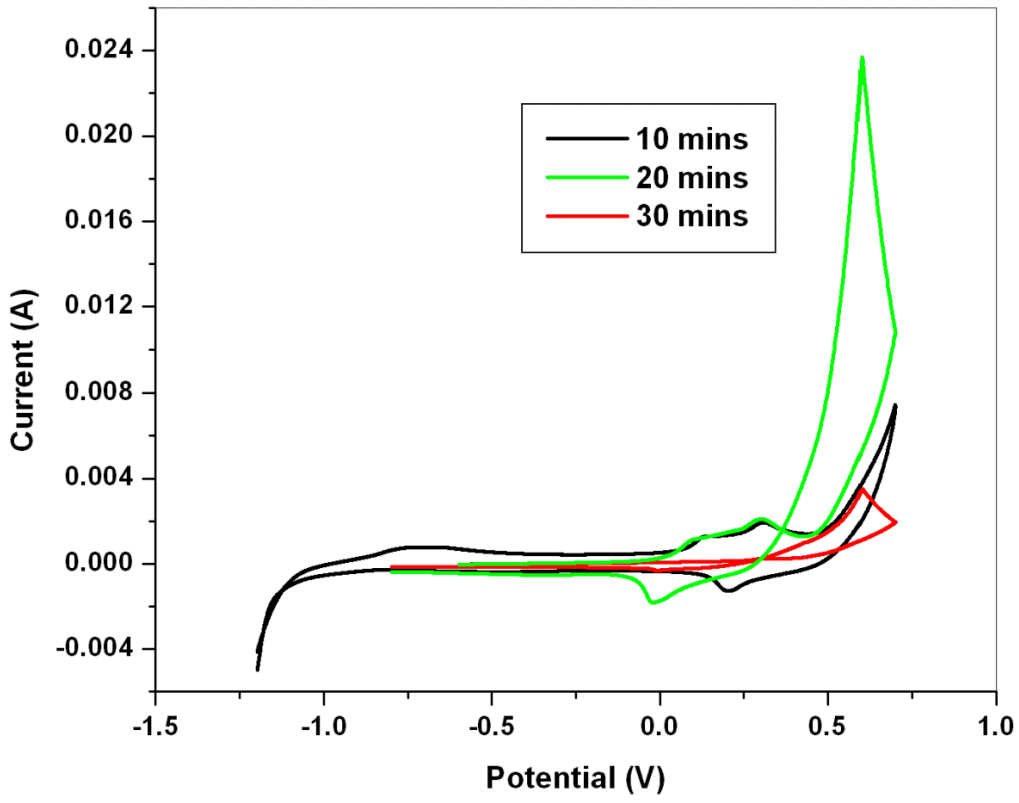


Figure 6. Electro catalytic activity of Ni-Co coated electrode for 10, 20 and 30 mins in presence of 0.5mL methanol/ 0.5M NaOH at a scan rate of 0.1V/s.

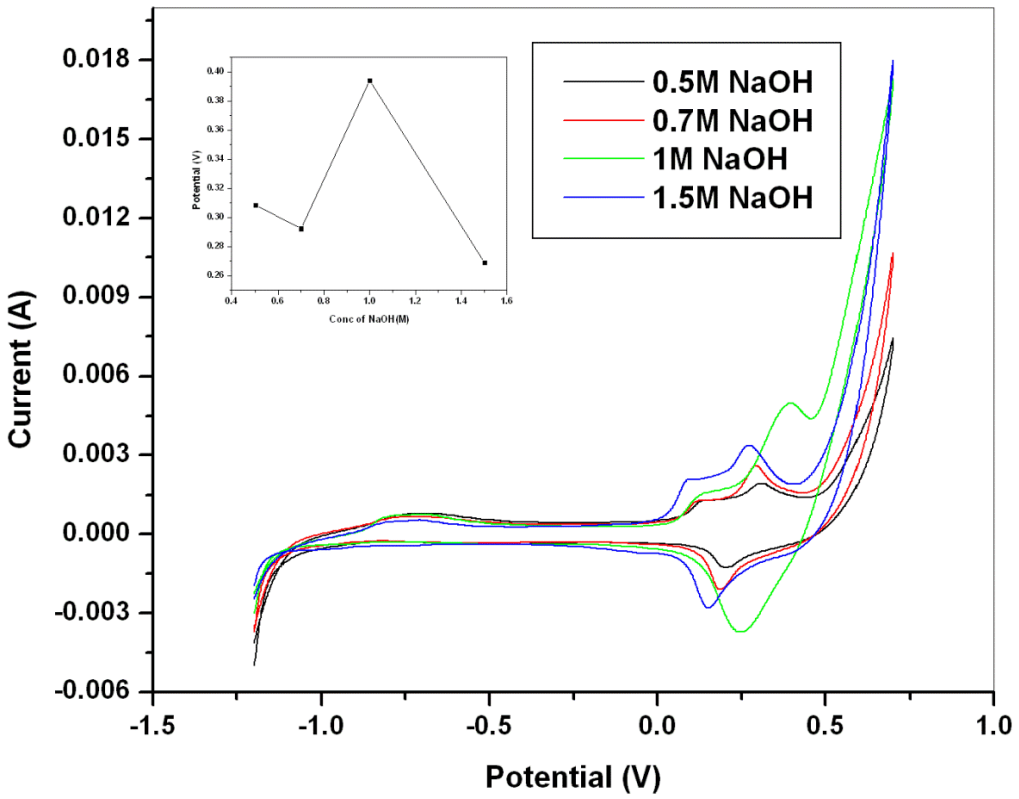


Figure7. Effect of hydroxyl ion concentration for methanol oxidation in presence of 0.5mL methanol at a scan rate of 0.1V/s.

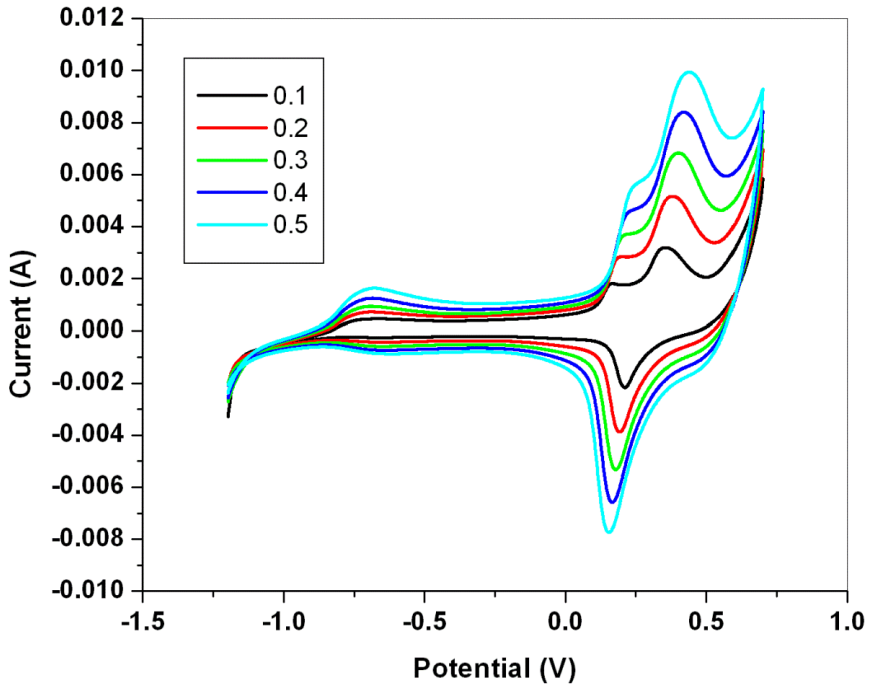
catalytic activity of the electrode that can be inferred by the increase in methanol oxidation current. On further increasing the hydroxyl ion concentration to 1M there was a potential shift towards positive side from 0.294V to 0.395V. This is due to the fact that the highly concentrated hydroxyl ions may get adsorbed on the catalyst surface thereby masking the active catalyst surface area available for MOR[15]. But on further increasing the hydroxyl ion concentration to 1.5M there is increase in the oxidation current and the anodic potential gets reduced (0.395V to 0.274V). Ming Jun Hu, et al.[16] had reported that the surface morphology of the Ni-Co electrode gets changed, at higher NaOH concentration. This leads to the availability of more active sites for the reaction. Apparently, NaOH concentration is the main factor affecting the morphology of the alloy particles[17] (Figure 7).

3.5 Scan Rate Studies

The effect of scan rate on the Ni-Co coated electrode in 0.5M NaOH/0.5mL methanol (Figure 8) was done. On increasing the scan rate gradually from 0.1V/s to 0.5 V/s the magnitude of the anodic and cathodic current also gets increased. The oxidation potential shifts towards the positive values and the reduction potential shifts towards the negative values. This is due to the IR drop generated at higher current density values. From the square root versus current plot it is clearly seen that it is a diffusion controlled and irreversible electrode reaction[14, 18].

4. Conclusions

The electrocatalytic activity of methanol on Ni, Ni-Co modified stainless steel mesh based electrode has been investigated in alkaline medium using cyclic voltammetry. The EDX study reveals the presence of nickel and cobalt on the surface of the electrode. The electrode fabricated using 1:1 Ni-Co solution contains 7wt% of Ni and 90wt% of Co. The performance and working conditions were optimized. The electrode coated for 10 minutes shows good electro catalytic activity towards methanol



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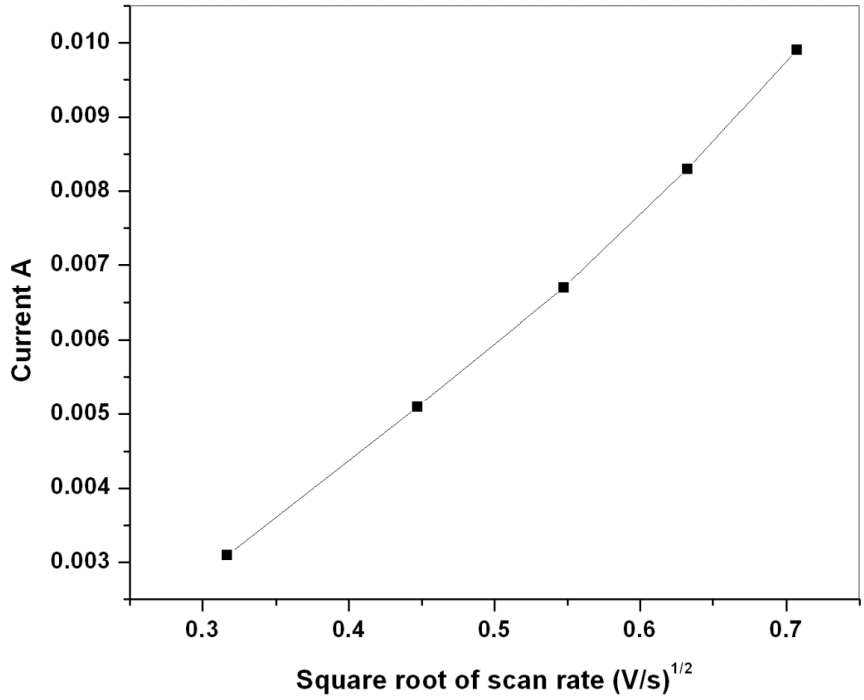

(b)

Figure 8. **(a)** Cyclic voltammogram at different scan rates starting from 0.1V/s to 0.5V/s in 0.5M NaOH/ 0.5mL methanol. **(b)** Plot between current Vs Square root of scan rate.

oxidation in 1.5M NaOH up to 0.5mL addition of methanol. Therefore it has potential to be used as an electrode material in DMFC.

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