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Effect of Different Substrates on the Electrochemical Behavior of Ni-Mo-Fe-Co-S Composite Film in Alkali Solutions

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A composite Ni-Mo-Fe-Co-S film galvanostatically coated on different substrates like Pt/Si, graphite, nickel, stainless steel and steel was studied for its electrochemical behavior in alkali solutions. The main aim of this investigation is to identify and understand the effect of substrate on the overall electrochemical behavior of the film that has been coated on different substrates. The composite films were characterized by SEM-EDAX and linear scan voltammetry. Linear scan voltammetric studies showed a noticeable difference in over potentials for hydrogen and oxygen evolutions for the coated and uncoated substrates.

Keywords: Ni-Mo-Fe-Co-S composite film; Different substrates; Galvanostatic deposition; Linear scan voltammetry; Catalytic behavior

1. INTRODUCTION

Research on hydrogen production from water electrolysis has attracted a rejuvenated interest and continues unabated due to the recognition arising from the fact that hydrogen would be the fuel of the future. Large scale production of hydrogen from water electrolysis is hampered by the high energy consumption required for the process arising due to the overvoltages associated with hydrogen and oxygen gas evolutions. From a purely technological standpoint, the cost of electrolytic hydrogen is directly dependent on the voltage used to operate the electrolyzer at significant current densities. Meanwhile, the operational voltage depends on the overpotentials for the cathodic and anodic reactions, and on the internal resistance of the cell. Minimizing anodic and cathodic overpotentials is a problem of electrocatalysis, while the ohmic drop is in principle a problem of electrolysis, although the two quantities are often interrelated. One of the most effective ways of minimizing the energy consumption is to reduce the hydrogen evolution potential (HER) of the cathode and oxygen evolution potential (OER) of the anode in the electrolysis.

For water electrolysis, nickel based composite electrodes have been electrodeposited on stainless steel or copper substrates and studied for application as cathodes for industrial electrochemical production for hydrogen. Composite coated Raney nickel and thermally coated Ni/Mo coating electrodes were shown to exhibit higher electrocatalytic activities for hydrogen evolution reaction (HER) in alkaline solution but they were deactivated after two weeks due to power interruptions [1-3]. Ni based binary composite coatings like Ni-Mo, Ni-Zn, Ni-Co, Ni-W, Ni-Fe and Ni-Cr were tried for hydrogen electrodes; out of these electrodes, Ni-Mo was found to be best and most stable electrode with an overpotential of 0.18 V in 6 M KOH solutions [4]. A series of ternary Ni composites such as Ni-Mo-Fe, Ni-Mo-Cu, Ni-Mo-Zn, Ni-Mo-W, Ni-Mo-Co and Ni-Mo-Cr were studied for hydrogen evolution and the authors reported that the best and most stable cathode was Ni-Mo-Fe [5-7]. High stability of amorphous Ni-Mo-Fe electrode was confirmed by other authors who tested the electrode with current interruptions [8]. Recently, electrodeposited cathode coatings like Ni-S, Ni-Mo, Ni-Ti, Ni-Mo-Si, and Ni-Fe-Mo-Zn were tailored and studied for hydrogen production [9-16]. Addition of cobalt was shown to improve the electrocatalytic property for oxygen evolution while the sulphur added helps to activate the hydrogen evolution in alkali solutions [17-19]. Alloying nickel with left transition metals (W, Mo and Fe) was shown to increase the intrinsic electrocatalytic activity in the HER compared to pure nickel [20]. The combined effect of these metals was explained by a synergy model which is based on the known dynamics of adsorbed hydrogen over such metals together with demonstrable electrocatalytic behavior [21].

The present work deals with the preparation of a catalytic film on different substrates so that the effect of substrate on the electrochemical activity of the film can be studied. Based on the above mentioned facts, a composite film consisting of Ni, Mo, Fe, Co and S was coated galvanostatically on the substrates of nickel, graphite, stainless steel, steel and Pt/Si and the film composition was characterized by EDAX. Morphology of the composite film was done by SEM. Electrochemical characterization was done by linear scan voltammetry.

2. EXPERIMENTAL PART

2.1. Galvanostatic deposition of Ni-Mo-Fe-Co-S film

Prior to electro deposition, the substrate sufaces (Cu, Ni, steel and stainless steel) were polished with fine emery paper, degreased with acetone and subsequently in an alkaline solution and afterwards pickled in a 3 M sulphuric acid. The films were galvanostatically deposited on the substrates by applying a constant current of 500 mA (250 mA/cm^2) for a period of 100 seconds. The geometric area exposed for coating was 1 cm^2 on each side (2 cm^2 in total). The composition of the plating bath was as follows: $NiSO_4.7H_2O$ (30 g/l); $NiCl_2.6H_2O$ (10 g/l); Na_2MoO_4. $2H_2O$ (10 g/l); $CoCl_2.6H_2O$ (10 gl^{-1});

$FeSO_4.7H_2O$ (10 g/l); Boric acid (20 g/l); $(NH_4)_2S$ (20 g/l). The pH of the plating solution was 7 and the deposition was carried out at room temperature (298 K) with continuous stirring.

2.2. Instrumentation

The semi-quantitative elemental composition of the film was determined using energy dispersive X-ray (EDAX) analysis using horida-ex-200, Japan, with spatial resolution of 134 eV. Surface morphological studies were carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340 F, Jeol, Japan). Linear scan voltammograms (LSVs) were carried out in a conventional three electrode assembly using a potentiostat/galvanostat (EG&G Princeton Applied Research, Model 273A) interfaced with a computer. An Ag/AgCl electrode was used as the reference electrode and a large Pt foil was employed as the counter electrode.

3. RESULTS AND DISCUSSION

3.1. SEM images

Fig. 1 shows the morphology of Ni-Mo-Fe-Co-S as-deposited coatings on ITO substrate in different magnifications. The thickness of the composite film was ~ 8.8 μm. Fig. 1 A shows the morphology at low magnification (6.0 μm). The film has lot of cracks.

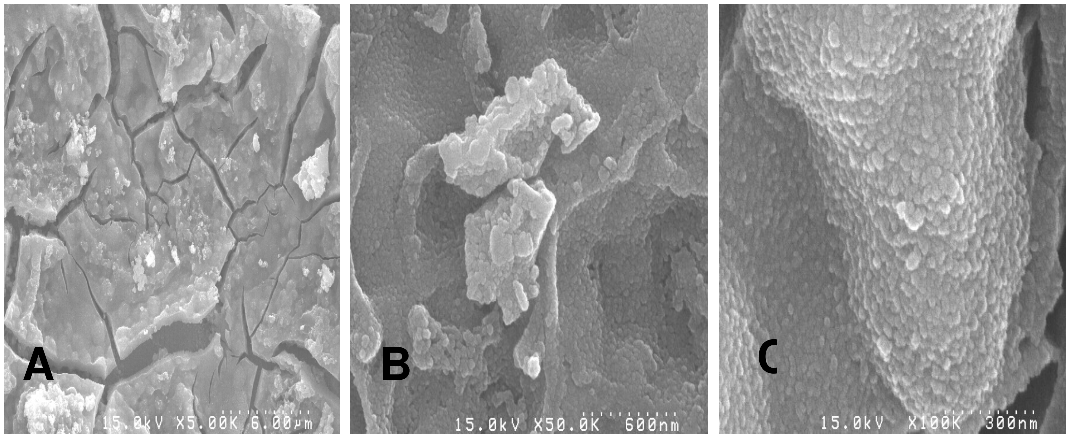

Figure 1. SEM images of Ni-Mo-Fe-Co-S composite film in different magnifications; (A) 6 μm (B) 600 nm (C) 300 nm

The cracks were not uniform in size but the formation of these cracks was vital for the higher utilization of the active material. In fact, some authors tend to leach the coatings to get this type of cracks so that the activity can be enhanced. Because these crack when filled with electrolyte, render a greater part of the internal surface area of the composite film, which can be accessible to electrochemical gas evolution. Numerous cracks are beneficial as they lead to sufficiently short diffusion paths of dissolved hydrogen, for the fastest release off the gas and for avoiding excessive gas accumulation and concentration polarization in the micropores. The presence of cracks also increases invariably the surface area which tend to lower the over voltage for hydrogen evolution [22, 23]. Fig. 1 B and C shows the morphology of the composite film at still higher magnifications. In these magnifications, one could identify the shape of the particles. The shape of the particles was almost spherical and found to be in the range of 13.2 to 35.3 nm with micropores engorging between them.

3.2. Film composition

The composition of the as prepared Ni-Mo-Fe-Co-S film was determined by EDAX analysis (wt. %) as: Ni, 26.5; Mo, 2.29; Fe, 4.6; Co, 5.51; S, 8.7 and (At. %) Ni, 10.77 ; Mo, 0.57; Fe, 1.97; Co, 2.23; S, 6.47 (cf. Fig. 2).

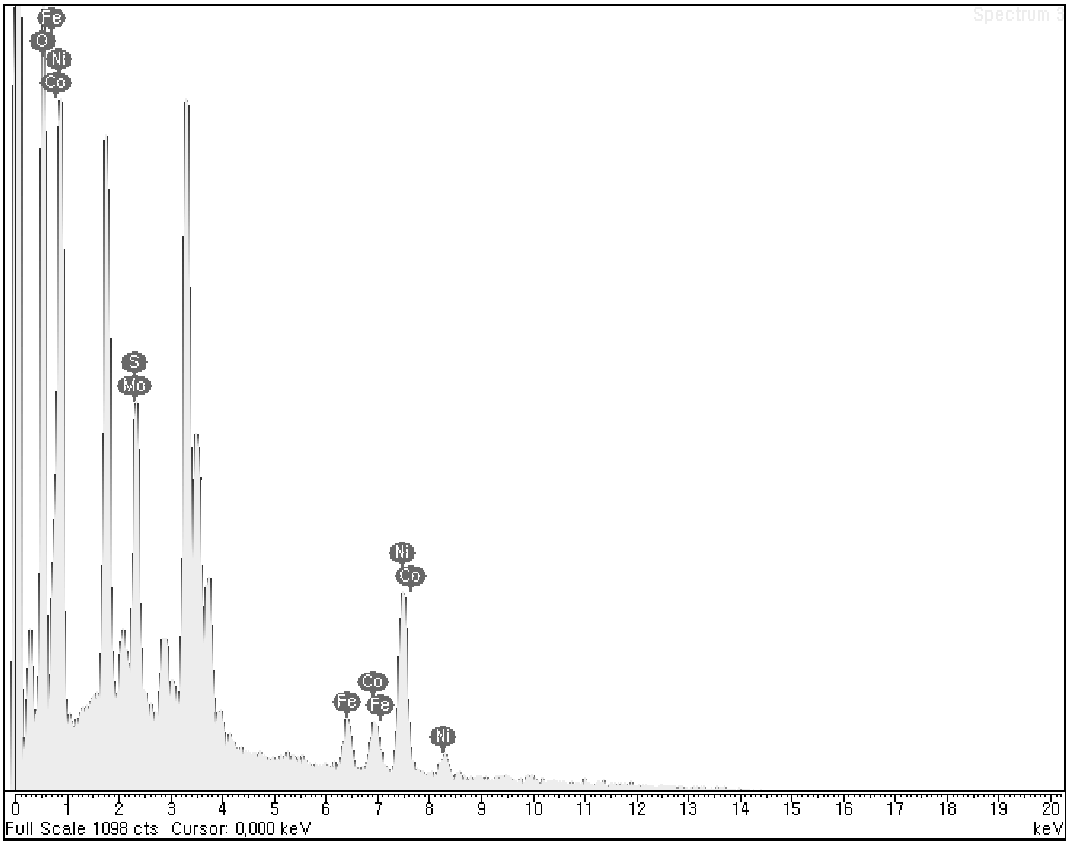

Figure 2. EDAX image of Ni-Mo-Fe-Co-S composite film

3.3. Linear scan voltammetric studies

Figs. 3-7 show the linear scan voaltammograms (LSVs) of uncoated and film coated substrates recorded in 1.0 M NaOH solution; the substrates were nickel, steel, Pt/Si, stainless steel and graphite respectively. Table 1 presents the hydrogen/ oxygen evolution potentials determined from the rising/declining portion of the curve. For the uncoated nickel substrate, the hydrogen evolution started at -1.375 V but on the film substrate, this potential shifted to -1.293 V (cf. Fig. 3). There is a shift of 82 mV in the positive direction which could be attributed to catalytic effect of the composite film. One could visualize the effect from the LSVs of both substrates; in the case of film substrate, the current starts rising rather sharply in both gas evolutions [24]. The oxygen evolution started at 0.386 V in the uncoated nickel substrate but shifted to 0.244 V in the film coated nickel substrate. In this case, the oxygen evolution occurred at more negative potentials on the film than the plain substrate which suggests that this composite film cannot act as a catalyst for oxygen evolution as well.

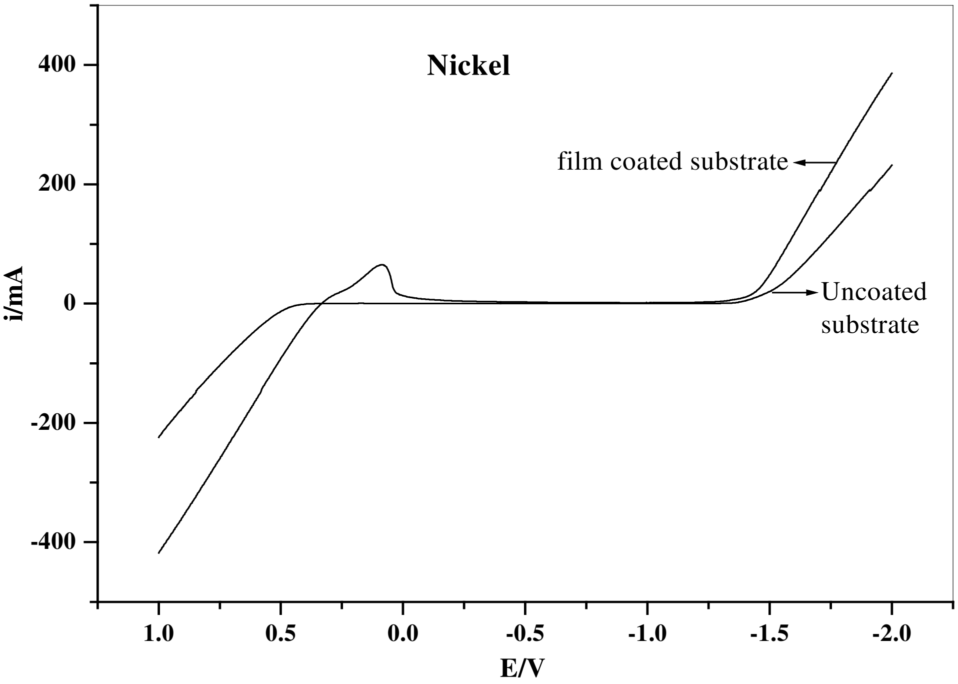

Figure 3. Linear scan voltammograms of uncoated and film coated nickel substrate in 1. 0 M NaOH solution; scan rate = 20 mVs^{-1}.

Table 1. Hydrogen and oxygen evolution potentials determined from the linear scan voltammograms for the coated and uncoated substrates in alkali soltuion

Substrate	Uncoated substrate (V)		Film coated substrate (V)	
	H_2	O_2	H_2	O_2
Pt/Si	-1.178	0.674	-1.329	0.244
Graphite	-1.599	0.518	-1.252	0.244
Nickel	-1.375	0.386	-1.293	0.244
Steel	-1.476	0.477	-1.320	0.248
Stainless steel	-1.531	0.372	-1.430	0.299

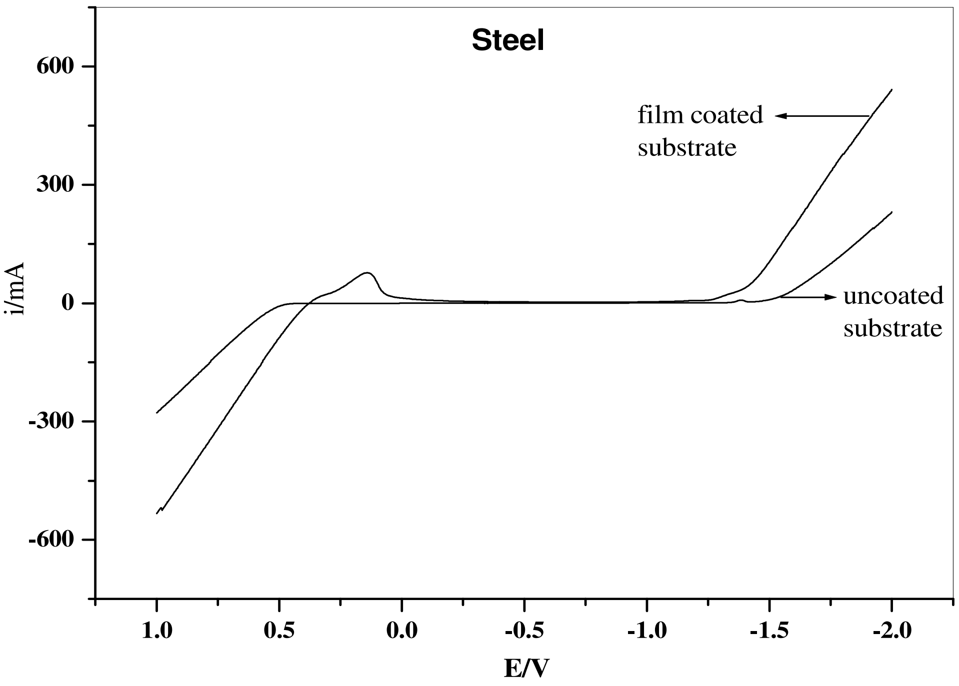

Figure 4. Linear scan voltammograms of uncoated and film coated steel substrate in 1. 0 M NaOH solution; scan rate = 20 mVs^{-1}.

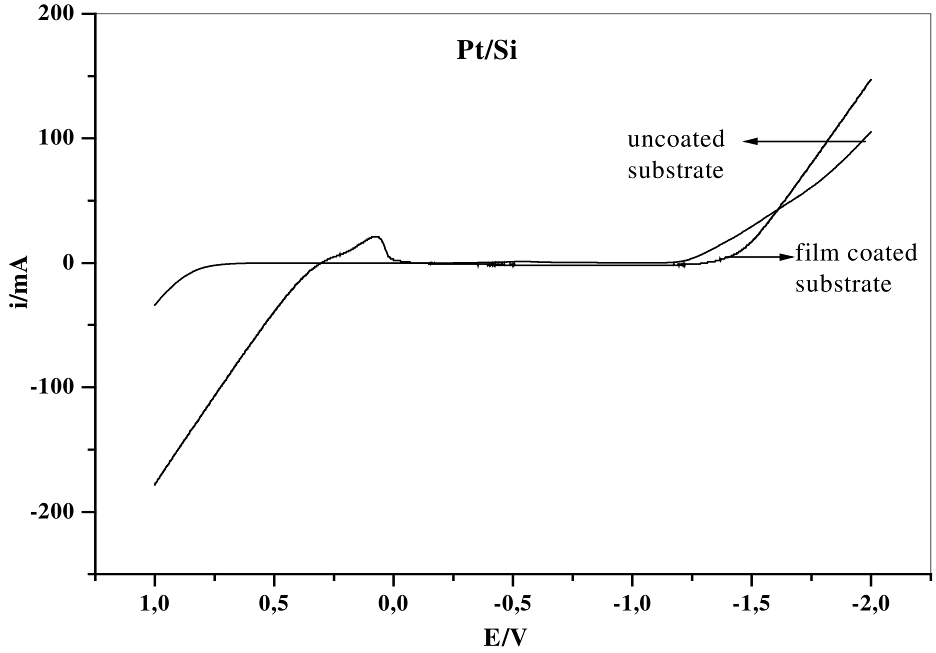

Figure 5. Linear scan voltammograms of uncoated and film coated Pt/Si substrate in 1. 0 M NaOH solution; scan rate = 20 mVs^{-1}.

Fig. 4 shows the LSVs obtained for the uncoated and film coated steel substrate between the hydrogen and oxygen evolution potentials. The hydrogen evolution potential was -1.476 V for the uncoated steel substrate; on the film coated substrate, this potential shifted to more positive potentials of -1.32 V. The catalytic behavior of the composite film was more significant on the steel surface as against the nickel surface and the positive shift in potential was 156 mV. Similarly, the oxygen evolution potential of the uncoated steel substrate was 477 mV while for the film coated substrate, this potential shifted to more negative potentials of 248 mV which indicates that this film coated on steel substrate is not catalytic towards oxygen evolution.

The LSVs recorded for uncoated and the composite Ni-Mo-Fe-Co-S film coated Pt/Si susbtrate were shown in Fig. 5. The results were singularly interesting. The hydrogen evolution on the uncoated substrate started at -1.178 V which was more positive than the potentials noticed for other plain substrates. This is not surprising as the Pt electrode is well known for its catalytic properties, especially for hydrogen evolution in alkali solutions. It is legendary that Pt metal is the best electrocatalyst for hydrogen evolution as the reaction in essence is thermoneutral i.e the rate of adsorption of protons on the surface is almost equal to the rate of desorption or recombination to form hydrogen gas ($\Delta G = -0.1$ eV). Next ideal metal is Ni ($\Delta G = -0.28$ eV) followed by Mo ($\Delta G = -0.36$ eV) [25]. However on the film coated Pt/Si substrate, the hydrogen evolution started at -1.329 V, a potential more negative than observed on the plain substrate which suggests that this film coated substrate does not possess any catalytic properties for hydrogen evolution. For oxygen evolution also, the uncoated substrate gave the best results. The onset potential for oxygen evolution was 0.674 V on the uncoated Pt/Si substrate (Table 1) while it shifted to more negative potentials of 0.244 V on the film coated substrate.

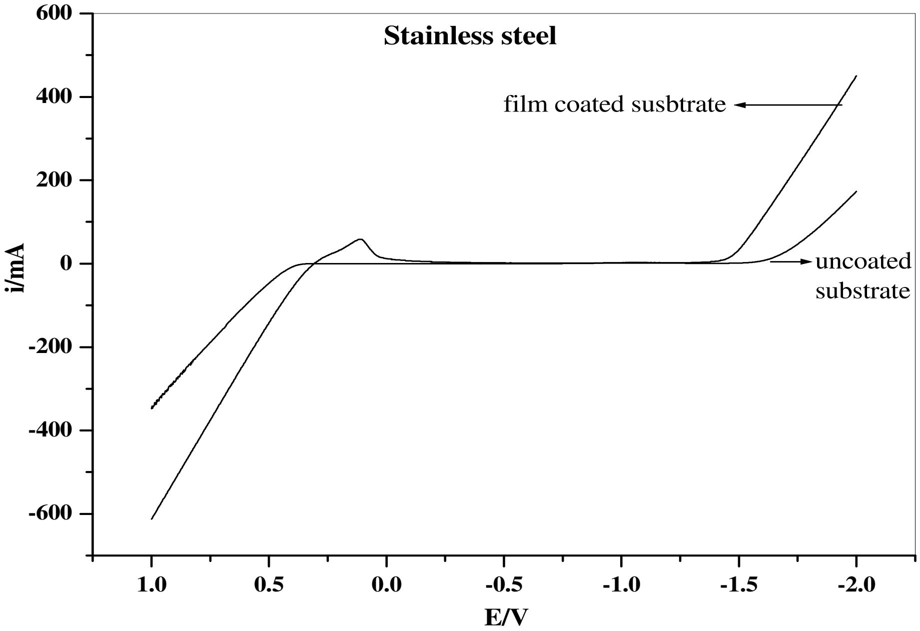

Figure 6. Linear scan voltammograms of uncoated and film coated stainless steel substrate in 1. 0 M NaOH solution; scan rate = 20 mVs^{-1}.

Fig. 6 shows the LSVs obtained from the uncoated and the film coated stainless steel substrate for both gas evolutions. On the uncoated substrate, the hydrogen evolution started at -1.531 V whereas it shifted to a positive potential of -1.43 V on the film coated surface. A potential shift of 101 mV in the positive direction confirms the catalytic nature of the film on this substrate. However, the reverse was found to be true for oxygen evolution. The uncoated substrate had the oxygen evolution started at 372 mV while on the film coated substrate, the oxygen evolution potential shifted to 299 mV; in the case of oxygen evolution, the result was found to be the same for all the substrates i.e uncoated substrates were better catalysts than the coated ones.

The LSVs recorded for uncoated and the composite film coated graphite substrate were shown in Fig. 7. The onset potential for hydrogen evolution on the uncoated graphite substrate was the most negative of the other substrates; it was -1599 V. On the film surface, this potential was more positive by 347 mV i.e the gas evolution potential was -1.252 V. Significantly, the catalytic property of the composite film is more pronounced on the graphite substrate as evident by the enormous positive shift of over potential. The electrochemical behavior of graphite substrate to oxygen evolution remained similar to other substrates; the onset potential was 518 mV for the uncoated substrate and 244 mV for the film coated substrate.

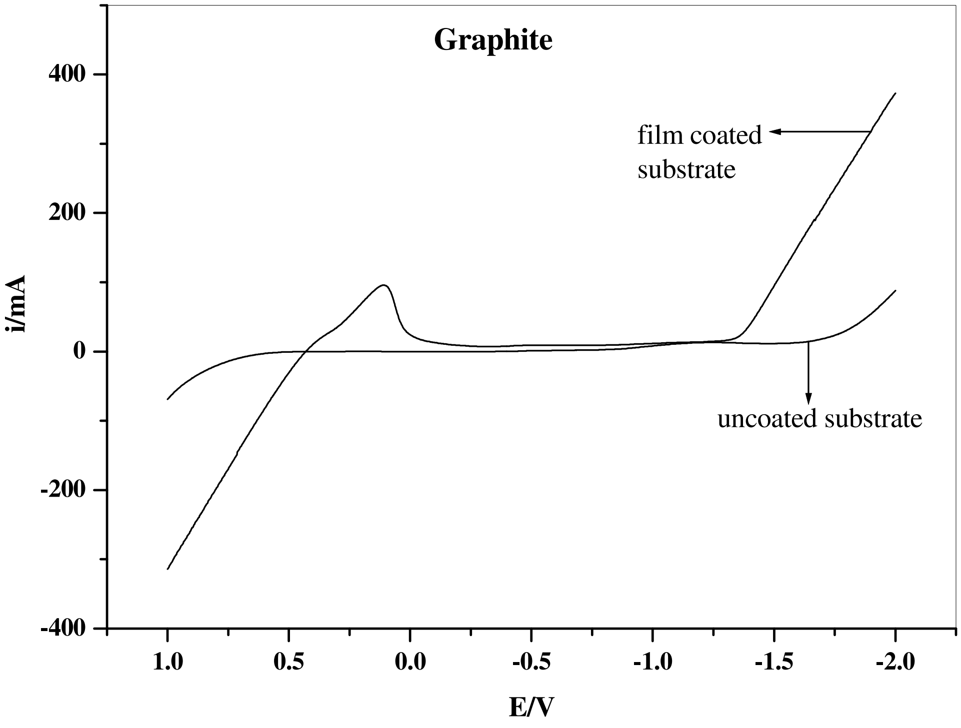

Figure 7. Linear scan voltammograms of uncoated and film coated graphite substrate in 1. 0 M NaOH solution; scan rate = 20 mVs^{-1}.

The above presnted results lead us to the following facts: (1) the onset or the starting potential for hydrogen evolution (as decided from the rising portion of LSVs) varies with the nature of the substrate. This is understandable as the solid surfaces have unsatisfied valencies and that transition metals in such surfaces would present empty d orbitals which can be active in catalysis; (2) the composite Ni-Mo-Fe-Co-S film coated on these substrates gave onset potentials which varied with the nature of substrate. The film was catalytic to hydrogen evolution (except Pt/Si) but the difference in onset potentials confirms the effect of substrate on the catalytic behavior; (3) the same film could not be used for the catalysis of oxygen evolution and a single peak appeared prior to oxygen evolution in the all the LSVs was due to nickel hydroxide formation; (4) the electron transfer for the hydrogen gas formation depends not only on the electric field at the film/solution interface but also on the substrate/film interface. The gradient at this interface differs with different substrates which gets reflected on the onset potential. Detailed investigation could be interesting but regrettably it is not within the scope of the present work.

4. CONCLUSIONS

Ni-Mo-Fe-Co-S composite film coated on graphite, stainless steel, steel and nickel were catalytic to hydrogen evolution in alkali solution. This study confirms the effect of substrate on the catalytic behavior of film coated on different substrates. Of these, film coated graphite was the second best substrate with the lowest over potential for hydrogen evolution. Pt/Si uncoated substrate was shown to be the best as expected. The catalytic behavior was decided by the electric filed gradient at the film/ solution interface as well as the substrate/film interface and this changes the performance of the catalytic film with reference to the substrate. This study confirms that the nature of substrate have a definite say on the electrochemical behavior of catalytic films.

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