JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 437–442

The hydrogen evolution reaction in basic medium on iron electrodeposited with heteropolyacids

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Received 8 March 1991; revised 20 July 1991

Iron was electrodeposited from dilute aqueous solutions of iron sulphate, containing $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$ or MoO_4^{2-} ions. It was shown that improvement in the overpotential and in the exchange current density of the hydrogen evolution reaction (h.e.r.) on the electrodes depends on the nature of the heteropolyacid of the deposition bath. The h.e.r. electrocatalytic activity of the electrodeposits was then analysed and related to their chemical composition. The results show that some active electrocatalysts are produced when combinations of $Fe(SiW_{12})$ or $Fe(PMo_{12})$ are formed. The influence of the type of the heteropolyacid in the electrolyte on the electrocatalytic properties of these deposits for the h.e.r. was investigated. The best electrocatalytic properties for the h.e.r. are obtained with electrodes electrodeposited with $2\,g\,dm^{-3}$ of $PMo_{12}O_{40}^{3-}$. The effect of $[PMoO_{40}^{3-}]$ in the deposition bath on the electrocatalytic properties of the h.e.r. of the electrodes was determined.

1. Introduction

The work done to date relevant to the analysis of the hydrogen evolution reaction (h.e.r.) on electromodified electrodes has been summarized briefly in [1] and references therein. The basic concepts of the Brewer theory of intermetallic phases have been described [2–4] and typical issues arising from the electrocatalytic activity achieved as a function of the composition of hypo-hyper–d-electronic transition metals have been presented in [5]. It has been shown that the bulk properties of these intermetallic phases determine their electrocatalytic activity for the h.e.r. This reaction has also been performed with Chevrel-type cluster compounds [6]. The re-mixed cluster compounds were found to be the best electrodes for the h.e.r. (Both intermetallic systems of hypo-hyper–d-electronic metal combinations and cluster materials were prepared thermally.)

In previous papers [7–11], we have shown that electrodeposited nickel electrodes modified by heteropolyacids (HPAs) provide good electrocatalytic properties for the h.e.r. in an acid medium. A detailed study was carried out to investigate how HPAs influence the electrocatalytic properties of the electrodeposited electrodes for the h.e.r. A significant decrease in overpotential (η) and an increase in exchange current density (i_0) were observed. A nickel electrode prepared with $SiMo_{12}O_{40}^{4-}$ in an acetate bath was found to be a better electrocatalyst than platinum for the h.e.r. in an acid medium [11]. This may be attributed to the production of an extremely active Ni–Mo electrocatalyst when a synergetic activation d-metal (Ni) is combined with a reactivity-inductive d-metal (Mo). It was also found that the HPA-modified electrodeposited nickel electrode is less sensitive than platinum to impurity effects for the h.e.r., while tin and lead impurities in the nickel significantly alter the characteristics of the electrode [9]. The effect of the concentration of $SiW_{12}O_{40}^{4-}$ on the elecrocatalytic properties of these deposits and its influence on the h.e.r. have also been investigated. Nickel electrodeposited with a concentration of $8\,g\,dm^{-3}$ of $SiW_{12}O_{40}^{4-}$ was, in fact, found to exhibit the best electrocatalytic parameters for this reaction [9, 11].

This report deals with the electrocatalytic behaviour in basic medium of iron electrodeposited on a stainless steel cathode from baths containing either $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$ or MoO_{40}^{2-}. The electrolyte in each of the baths contained the same chemical constituents except for the heteropolyacid. How these different heteropolyacids affect the electrocatalytic parameters of the electrodes was analysed.

2. Experimental procedure

2.1. *Electrodeposition*

All the chemicals used were reagent grade (Fisher Scientific, BDH or Anachemia). The base electrolyte was composed of $248\,g\,dm^{-3}$ of $FeSO_4$, $30\,g\,dm^{-3}$ of $FeCl_2$ and $22.3\,g\,dm^{-3}$ of NH_4Cl. The cathode used in the electrodeposition process was 316 stainless steel (Firth Brown Inox Ltd) with a 1 cm × 2 cm surface area, and the anode was a sheet of nickel (99%) with a 5 cm × 5 cm surface area.

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Prior to electrodeposition, the electrodes were degreased and cleaned with acetone and HNO_3. They were then activated by anodic electrochemical polishing for 20 min in 1 M H_2SO_4 at a current density of 35 mA cm^{-2} using a Hewlett Packard (Model HP6266B) power supply.

The electrodeposition of the electrodes was performed using the same power supply (HP6266B) with different heteropolyacids. The electrodeposition baths were prepared with distilled water. The heteropolyacid concentration was within the optimum range previously used in the successful electrodeposition of nickel from chloride baths [7-11]. Various concentrations of $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$ and MoO_4^{2-} in grams per dm^{-3} (x) of base electrolyte were used. The iron electrodes electrodeposited with $PW_{12}O_{40}^{3-}$, $PMo_{12}O_{40}^{3-}$ or MoO_4^{2-} were identified respectively as Fe(xPW$_{12}$), Fe(xPMo$_{12}$) and Fe(xMo). The electrodeposition process lasted 6 h. The results were found to be completely reproducible. The reproducibility of the electrocatalytic parameters (h.e.r. exchange current density, Tafel slope and hydrogen overvoltage) of the electrodes was also checked in assessing the overall reproducibility of the electrodeposition process. The reproducibility of the process was checked at least ten times for each electrode, and the results were found to be completely reproducible.

2.2. *Electrochemical equipment and electrodes*

The cathode polarization of the electrodeposited electrodes was measured using a PAR (Model 273) potentiostat and monitored by PAR Universal Programmer software (Model 342). Reagent grade KOH was used for the cathodic polarization studies of the h.e.r. The solutions were de-oxygenated thoroughly with nitrogen, and kept under a positive pressure with this gas throughout the experiment. The polarization curves were obtained using a single-compartment cell with a standard three-electrode configuration. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was platinum gauze of large surface area and the working electrode was an electrodeposited electrode of geometric area 2 cm^2. All experimental results were referenced to this apparent geometric surface area, which may possibly differ to some extent from the real surface area of the samples. As other authors have pointed out [16] the real surface area on an "atomic level", particularly in the case of porous or rough electrodes (like the electrode investigated here), cannot be determined experimentally with certainty. Therefore, a discussion of electrocatalytic effects based on the real surface area was considered after the BET surface determination. Since some measurements on rotating disc electrodes do not show any convection effects on the polarization curves, all the results presented here were obtained using stationary electrodes. In order to ensure the reproducibility of the results, each experiment was performed at least three times.

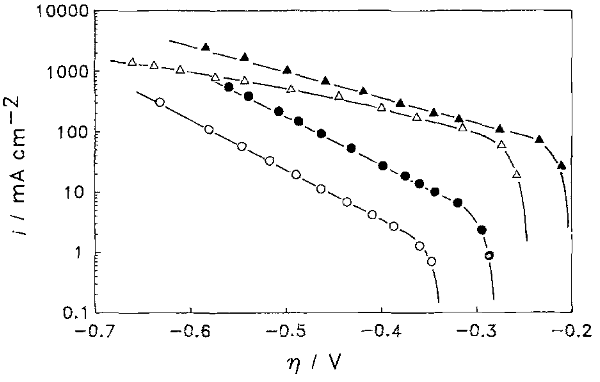

Fig. 1. Quasi-steady state polarization curves for the h.e.r. obtained under potentiodynamic conditions at a low sweep rate of 2 mV s^{-1} in 3 M KOH at 298 K for (○) Fe, (●) Fe(2PW$_{12}$), (△) Fe(2PMo$_{12}$) and (▲) Fe(2Mo).

3. Results and discussion

3.1. *Effect of the heteropolyacid*

Figure 1 shows the typical quasi-steady-state polarization curves obtained on electrodeposited iron with different heteropolyacid under potentiodynamic conditions at the low sweep rate of 2 mV s^{-1}. As may be seen, at a constant potential in the region of the hydrogen evolution reaction (h.e.r.), the current density (i_0) of the iron electrodeposited with heteropolyacid is more significant than that of the iron electrodeposited without heteropolyacid. It may also be seen that in a large domain of this region (h.e.r.), the curves exhibit typical Tafel behaviour. The results obtained in iron electrodeposited without HPA are similar to those obtained in other published data [13, 14].

The Tafel lines for the h.e.r. indicate that the electrocatalytic activity of the iron electrodeposited with different heteropolyacid is much better than that of the electrodes electrodeposited without heteropolyacid. The variation of i_0 with heteropolyacid is reported in Table 1. As can be seen, there is a remarkable variation in the exchange current density of the h.e.r. of iron with heteropolyacid. The results show that the i_0 values of the h.e.r. on the electrodes electrodeposited with HPAs are greater than the i_0 value of the h.e.r. on iron electrodeposited without these species (see Table 1). In particular, the maximum values of i_0 are obtained for Fe(2PMo$_{12}$). Thus, the increase in i_0 value is related to the effect of heteropolyacid. On the other hand, the h.e.r. overvoltage changes with the

Table 1. Variation of the exchange current density of the hydrogen evolution reaction (i_0) and the hydrogen overvoltage in 3 M KOH at 298 K of iron electrodeposited at 35 mA cm^{-2} with different heteropolyacids

Electrodes	*Fe*	*Fe(2PW$_{12}$)*	*Fe(2PMo$_{12}$)*	*Fe(2Mo)*
i_0/mA cm^{-2}	10^{-2}	5	80	20
$\lvert\eta\rvert$/V at 0.1 (A cm^{-2})	0.58	0.48	0.220	0.28
b/mV decade^{-1}	120	140	250	180

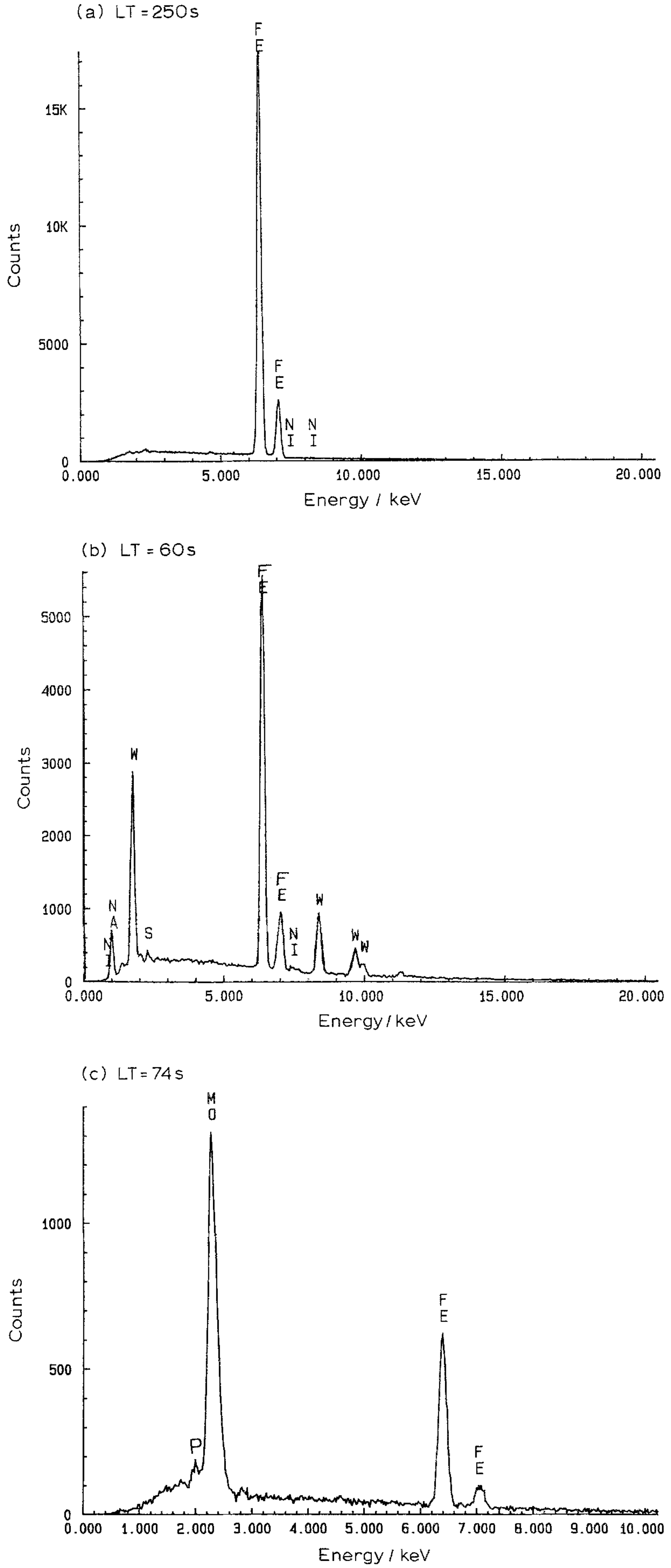

Fig. 2. X-ray fluorescence spectroscopy (XRFS) analysis of the electrodes: (a) electrodeposited iron, (b) electrodeposited iron with $PW_{12}O_{40}^{3-}$, (c) electrodeposited iron with $PMo_{12}O_{40}^{3-}$ and (d) electrodeposited iron with MoO_4^{2-}.

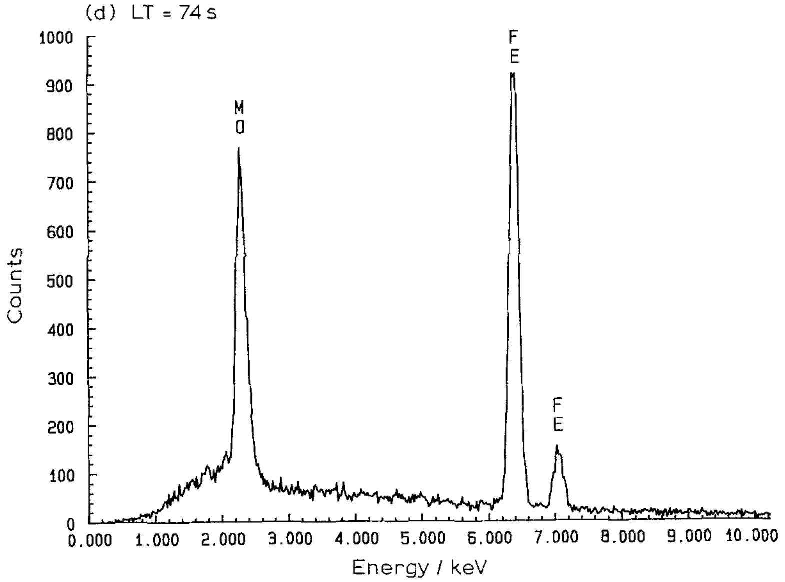

Fig. 2. (continued).

heteropolyacid (see Table 1). The lowest overvoltage is obtained with an electrode fabricated with 2 g dm^{-3} of $PMo_{12}O_{40}^{3-}$. It has also been observed that the highest Tafel slope is obtained when the electrodes were produced with 2 g dm^{-3} of [$PMo_{12}O_{40}^{3-}$] whereas the Tafel slopes on the others electrodes are similar. This indicates that the h.e.r. mechanism in Fe(2PMo_{12}) may be different than the mechanism of the h.e.r. process on the other electrodes, e.g. Fe(2PW_{12}) and Fe(2Mo) (see Table 1). The different results also indicate that the electrode electrodeposited with 2 g dm^{-3} of $PMo_{12}O_{40}^{3-}$ is a better electrocatalyst for the h.e.r. than these other electrodes. This may be attributed to the electrocatalytic activation of the proton reduction by the heteropolyacid species in the electro-deposited iron electrode. In particular, the change in the electrocatalytic properties for the electrodeposited iron with different heteropolyacids can be linked to the nature of the reduced compounds of $PMo_{12}O_{40}^{3-}$ produced during the electrodeposition process. Support for this conclusion may be found by determining the chemical composition of the electrodes. Figure 2 shows the X-ray fluorescence spectroscopy (XRFS) analysis of the electrodes. Iron plus molybdenun or tungsten are detected in electrodes having the best electrocatalytic properties, e.g. Fe(2PMo_{12}), Fe(2Mo) or Fe(2PW_{12}), while iron with and without phosphorous are only detected in the other electrodes. Thus, the decrease in the hydrogen overvoltage and the increase in the h.e.r. exchange current density for the electrodeposited iron with different concentrations of $PMo_{12}O_{40}^{3-}$ can be linked to the presence of tungsten or molybdenum in the electrodes. The non-variation of the surface area ($\sim$ 0.08 m^2 g^{-1} determined by BET) of the electrode with different heteropolyacids is in agreement with this interpretation. The differences in performance of the electrodes fabricated with tungsten and molybdenum could be related to the number of d-electron of W(5d^4) and Mo(4d^5). It is well known that the catalytic effect increases with the number of d-electrons ([5] and references therein). Further tungsten electrode is less performant than the molybdenum one.

These results may be attributed to the formation of an electrocatalytic active hypo-hyper–d-electronic composite transition metal, as has been pointed out by Jaksic [2–5]. Furthermore, extremely active electrocatalysts are produced when a synergetic activation d-metal (Fe) is combined with a reactivity–inductive d-metal (Mo, W), as has been predicted by the Brewer theory [15, 16]. In fact, electrocatalytic activity increases sharply if the amount of Mo or W in the electrocatalysts is increased. Good electrocatalytic electrodes for the h.e.r. are obtained when a significant amount of molybdenum or tungsten is detected in the electrocatalyst. In particular, these results may be attributed to an increase of the d-electronic density of the states at the material Fermi level. This interpretation agrees well with other published data [17, 18]. Work is currently underway to study the correlation between the h.e.r. activity of the electrodes, their stoichiometric Laves phases and their Mo content. It has been further shown that the improvement in the electrocatalytic properties for the h.e.r. on the iron electrodeposited with $PMo_{12}O_{40}^{3-}$, $PW_{12}O_{40}^{3-}$ or MoO_4^{2-} is mainly related to their chemical composition and not to an increase in surface area. These results are different from those obtained classically on Raney-nickel electrodes where an improvement in the h.e.r. is generally attributed to an increase of the electrode surface area ([17] and references therein).

3.2. *Effect of* [$PMo_{12}O_{40}^{3-}$], [$PW_{12}O_{40}^{3-}$] *or* MoO_4^{2-}

The experimental results have also shown that quasi-steady state polarization curves obtained on iron electrodeposited with different concentrations of [$PMo_{12}O_{40}^{3-}$] exhibit typical Tafel behaviour. The Tafel lines for the h.e.r. indicate that the electrocatalytic activity of the iron electrodeposited with different concentrations of $PMo_{12}O_{40}^{3-}$ is much better than the

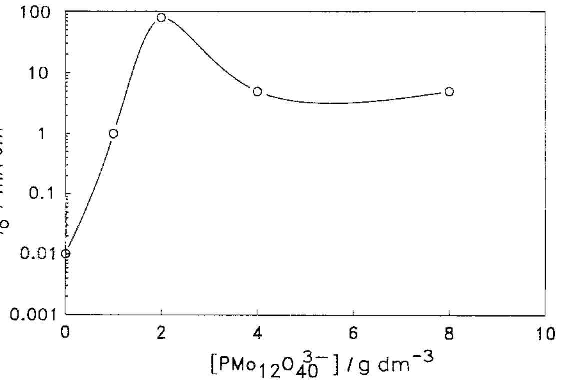

Fig. 3. Variation of the exchange current density of the hydrogen evolution reaction (i_0) in 3 M KOH at 298 K of iron electrodeposited at 35 mA cm^{-2} with [$PMo_{12}O_{40}^{3-}$].

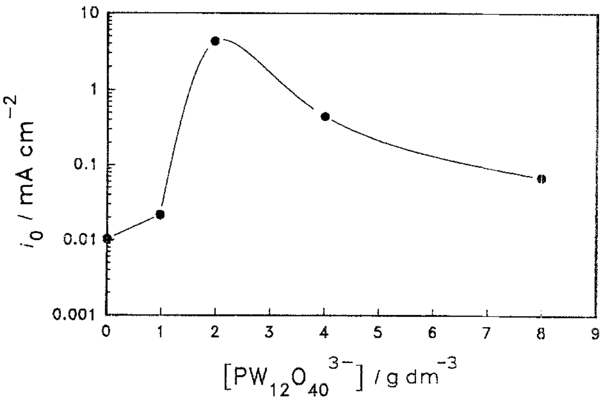

Fig. 5. Variation of the exchange current density of the h.e.r. (i_0) in 3 M KOH at 298 K of iron electrodeposited at 35 mA cm^{-2} with [$PW_{12}O_{40}^{3-}$].

electrodes electrodeposited without heteropolyacid. The variation of i_0 with [$PMo_{12}O_{40}^{3-}$] is shown in Fig. 3. As can be seen, there is a remarkable variation in the exchange current density of the h.e.r. with [$PMo_{12}O_{40}^{3-}$]. The results show that the i_0 values of the h.e.r. on the electrodes electrodeposited with $PMo_{12}O_{40}^{3-}$ are greater than the i_0 value of the h.e.r. on iron electrodeposited without these species. In particular, the maximum values of i_0 are obtained for Fe(2PMo$_{12}$). Thus, the increase in i_0 value is related to the chemical composition of the electrode. The non-variation of the surface area (~0.08 m^2 g^{-1} determined by BET) of the electrode with [$PMo_{12}O_{40}^{3-}$] is in agreement with this interpretation. The X-ray fluorescence spectroscopy (XRFS) analysis of the electrodes indicated that iron, and molybdenum are detected in the best electrocatalytic electrode e.g, Fe(2PMo$_{12}$), whereas the other electrodes contained only iron and phosphorous. On the other hand, the hydrogen overvoltage changes with [$PMo_{12}O_{40}^{3-}$] (Fig. 4). The lowest overvoltage is obtained with an electrode fabricated with 2 g dm^{-3} of $PMo_{12}O_{40}^{3-}$. It has also been observed that the highest Tafel slope is obtained when the electrodes were produced with 2 g dm^{-3}. Analogous results are obtained on Fe deposited with different concentrations of [$PW_{12}O_{40}^{3-}$] (see Figs 5 and 6). The highest exchange current density and Tafel slope (Fig. 5) and the lowest overvoltage (Fig. 6) are obtained on Fe(2PW$_{12}$). Similar trends are obtained with MoO_4^{2-} where the best electrocatalytic properties were observed on Fe(2Mo). Further, the experimental results obtained on Fe(*x*Mo) are not shown because these are analogous to those of Fe(*x*PMo$_{12}$) or Fe(*x*PW$_{12}$). The remarkable improvement in the hydrogen overvoltage (η) and in the exchange current density on the electrodes electromodified with the heteropolyacids indicate the good electrocatalytic properties of nickel electrodeposited with heteropolyacid as previously shown.

3.3. *Fe and Fe(2PMo$_{12}$) electrocatalyst stability*

Long term electrocatalyst stability was demonstrated using a 2 cm^2 test cathode in 3 M KOH. Electrolysis was carried out at 0.2 A cm^{-2} for more than 160 h at 25° C. The experimental polarization curves before and after 160 h durations at 0.2 A cm^{-2} showed no significant change in characteristics. On the other hand, the variation of the overvoltage at 0.2 A cm^{-2} with time shows no significant change for Fe(PMo$_{12}$) whereas a decrease of the overvoltage with time is observed for coated iron (Fig. 7). Analogous results were obtained when the electrodes were exposed to open circuit conditions. Electrodes were operated for three days at 0.2 A cm^{-2}, then disconnected and allowed to sit at their rest potential in 3 M KOH at 25° C for one week (Fig. 8). As may be seen the rest

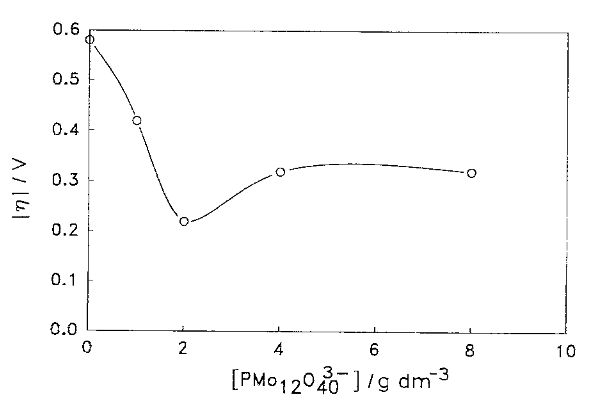

Fig. 4. Variation of the hydrogen overvoltage (η) at 0.1 A cm^{-2} in 3 M KOH at 298 K of iron electrodeposited at 35 mA cm^{-2} with [$PMo_{12}O_{40}^{3-}$].

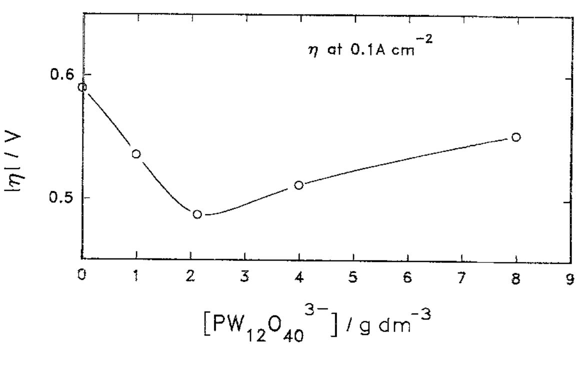

Fig. 6. Variation of the hydrogen overvoltage (η) at 0.1 A cm^{-2} in 3 M KOH at 298 K of iron electrodeposited at 35 mA cm^{-2} with [$PW_{12}O_{40}^{3-}$].

Table 2. Variation of the exchange current density i_0 for Ni, Fe and Fe(2PMo$_{12}$) in 3 M KOH with and without mercury and cadmium as deactivating agents at 298 K

Electrode	i_0 ($A\ cm^{-2}$)		
	without	*with*	*with*
	Cd^{2+} *or* Hg^{2+}	10^{-4} *M* Hg^{2+}	10^{-4} *M Cd*
Fe	10^{-5}	8×10^{-7}	2×10^{-7}
Fe(2PMo$_{12}$)	8×10^{-2}	6×10^{-2}	5×10^{-2}
Ni	9×10^{-5}	10^{-7}	6×10^{-7}

potential is practically constant with time for Fe(2PMo$_{12}$), whereas it changes toward anodic values for iron. The electrodes were also tested to determine their resistance to electrocatalyst poisons present as electrolyte contaminants. The experimental results (see Table 2) show that the presence of severe deactivating agents [7; 19; 20] like mercury and cadmium have no significant effect on Fe(2PMo$_{12}$) exchange current density. For comparison the i_0 values of iron and nickel are also reported. As can be seen, the exchange current density decreases remarkably with Hg^{2+} and Cd^{2+} for iron and nickel. This indicates that Fe(2PMo$_{12}$) had a good resistance to severe catalyst poisons. Accordingly Fe and Ni are very sensitive to Hg^{2+} or Cd^{2+}. Further evidence for this conclusion can be found through the measurement of the overvoltage of the electrodes with and without catalyst poisons. It was found that the overvoltage of Fe(2PMo$_{12}$) did not change with Hg^{2+} or Cd^{2+}. In contrast, mercury and cadmium raised the overvoltage of iron under the same conditions of electrolysis for Fe(2PMo$_{12}$). These results confirm the good electrocatalytic properties of Fe(2PMo$_{12}$).

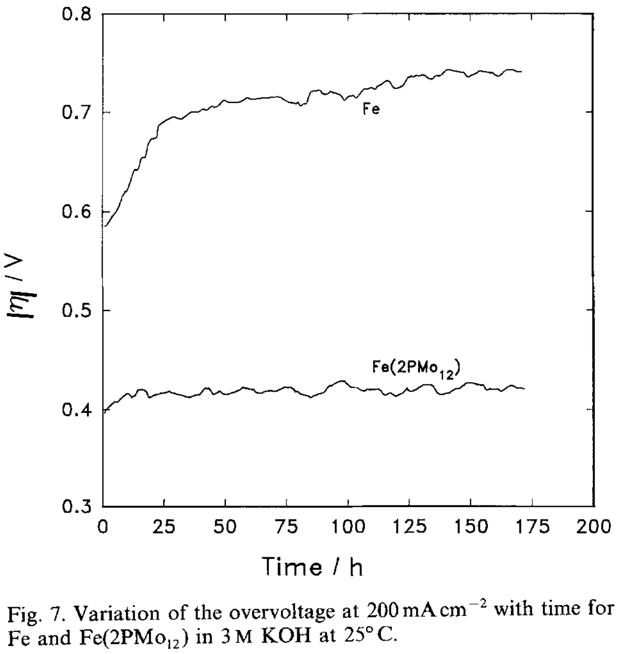

Fig. 7. Variation of the overvoltage at 200 mA cm^{-2} with time for Fe and Fe(2PMo$_{12}$) in 3 M KOH at 25° C.

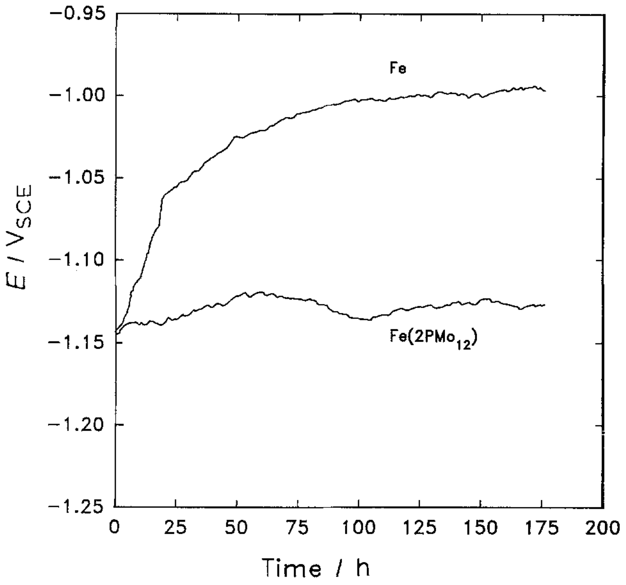

Fig. 8. Variation of the rest potential with time for Fe and Fe(2PMo$_{12}$) in 3 M KOH at 25° C.

Acknowledgements

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada and "Le programme actions structurantes des fonds FCAR du Gouvernement du Québec" for their financial support.

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