

The hydrogen evolution reaction in an acid medium on nickel electrodeposited with $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ from electrolytes of various anionic compositions

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Nickel was electrodeposited from baths based mainly on dilute aqueous solutions of nickel chloride, sulphate or acetate containing $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ anions. Each bath contained one of the ions. The other chemical constituents of the solutions were the same in all of the baths. It was shown that improvement in the overpotential (η) and in the exchange current density (i_0) of the electrodes depends both on the composition of the deposition bath and on deposition time. The h.e.r. electrocatalytic activity of the electrodeposits was then analysed and related to their chemical composition. The results show that some extremely active electrocatalysts are produced when combinations of nickel-tungsten (Ni-W) or nickel-molybdenum (Ni-Mo) are formed. The discussion is extended to include typical hypo-hyper-d-electronic transition metals, and it is concluded that alloying these metals significantly increases electrocatalytic activity.

1. Introduction

The work done to date relevant to the analysis of the hydrogen evolution reaction (h.e.r.) on electromodified electrodes may be summarized briefly as follows. Studies have been made of the electrocatalytic properties of electrodes the surfaces of which have been modified by heteropolyacids (HPAs) [1-5]. The basic concepts of the Brewer theory of intermetallic phases have been described [6-8] 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 [9]. 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 [10]. 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 [11-14], we have shown that electrodeposited nickel electrodes that have been modified by heteropolyacids (HPAs) provide good electrocatalytic properties for the h.e.r. in an acid medium. In this case, the basic electrolyte for the electrodeposition was formulated as follows: 1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 1 M H_3BO_3 , 10^{-4} M dodecyl sodium sulphate and 0.01 M HCl. 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 $\text{PW}_{12}\text{O}_{40}^{3-}$ was found to be a better electrocatalyst than platinum for the h.e.r. in an acid medium [11]. 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 silicon and lead impurities in the nickel significantly alter the characteristics of the electrode. The effect of the concentration of $\text{SiW}_{12}\text{O}_{40}^{4-}$ on the electrocatalytic properties of these deposits and its influence on the h.e.r. has also been investigated. Nickel electrodeposited with a concentration of 8 g dm^{-3} of $\text{SiW}_{12}\text{O}_{40}^{4-}$ was, in fact, found to exhibit the best electrocatalytic parameters for this reaction [13].

This report deals with the electrocatalytic behaviour of nickel electrodeposited on a stainless steel cathode from baths containing either $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$. The electrolyte in each of the baths contained the same chemical constituents except for the anion. How these different anions affect the electrocatalytic parameters of the electrodes was analysed.

2. Experimental details

2.1. Electrodeposition

All the chemicals used were reagent grade (Fisher Scientific, BDH or Anachemia) except for the H_3BO_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and the dodecyl sodium sulphate. The

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Table 1. Composition of the electrodeposition baths

Compound	Concentration (g dm ⁻³) of compound in the baths			
	Chloride (a)	Chloride (b)	Sulphate	Acetate
pH	0.5	3.5	3.6	5.3
NiCl ₂ · 6H ₂ O	212	21.2	—	—
Dodecylsulphate	0.66	0.66	0.66	0.66
H ₃ BO ₃	60	60	60	60
H ₄ SiW ₁₂ O ₄₀	8	8	8	8
H ₄ SiMo ₁₂ O ₄₀	8	8	8	8
NH ₄ Cl	—	12.30	—	—
NaCl	—	4.09	—	—
NiSO ₄ · 6H ₂ O	—	—	22.7	—
(NH ₄) ₂ · SO ₄	—	—	31.3	—
Ni(OOCH ₃) · 4H ₂ O	—	—	—	13.4
CH ₃ CoONH ₄	—	—	—	17.73
CH ₃ CoONa · 3H ₂ O	—	—	—	9.53
HCl 37%	10	—	—	—
Na ₂ SO ₄ · 10H ₂ O	—	—	9.9	—

cathode used in the electrodeposition process was 316 stainless steel (Firth Brown Inox Ltd) with a 1 cm × 1 cm surface area and the anode was a sheet of nickel (99%) with a 5 cm × 5 cm surface area.

Prior to the electrodeposition, the electrodes were degreased and cleaned with acetone and HNO₃. They were then activated by anodic electrochemical polishing for 20 min in 1 M H₂SO₄ at a current density of 35 mA cm⁻² using a Hewlett Packard (Model HP6266B) power supply.

The deposition of the electrodes was performed using the same power supply (HP6266B) at a cathodic current density of 35 mA cm⁻². The baths were prepared with distilled water. The anion concentration was within the optimum range previously used in the successful electrodeposition of nickel from chloride baths [11–14]. The compounds making up the various baths and their concentrations are listed in Table 1. The reproducibility of the process was checked at least ten times for each electrode, and 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 reproducibility of the electrodeposition process.

2.2. Electrochemical equipment and electrodes

The cathodic polarization of the electrodeposited electrodes was measured using a PAR (Model 273) potentiostat and monitored by PAR Universal Programmer software (Model 342). For the cathodic polarization studies of the h.e.r., reagent grade H₂SO₄ was used. The solutions were de-aerated 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 with a large

surface area and the working electrode was an electrodeposited electrode with a geometric area of 1 cm². All experimental results are referred to this apparent geometric surface area, which may differ from the real surface area of the samples. As other researchers have pointed out [15], 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 not considered. 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 four times.

3. Results and discussion

Figure 1 shows typical quasi-steady-state polarization curves obtained on electrodeposited nickel with different electrodes under potentiodynamic conditions at the low sweep rate of 2 mV s⁻¹. As may be seen from these curves, at a constant potential in the region of the hydrogen evolution reaction, the current density (*i_c*) of the nickel deposited with SiW₁₂O₄₀⁴⁻ or SiMo₁₂O₄₀⁴⁻ is higher than that of the nickel electrodeposited without SiW₁₂₄₀⁴⁻. It may also be seen that in a large domain of this region, the curves exhibit typical Tafel behaviour:

$$\eta = b \log \left(\frac{i_c}{i_o} \right)$$

where *i_c* is the cathodic current, *i_o* is the overall h.e.r. exchange current density, *b* is the Tafel slope in mV dec⁻¹ and η is the hydrogen overvoltage. The Tafel lines for the h.e.r. indicate that the electrocatalytic activity of the nickel electrodeposited in baths containing SiW₁₂O₄₀⁴⁻ or SiMo₁₂O₄₀⁴⁻ is much better than that of the electrodes electrodeposited

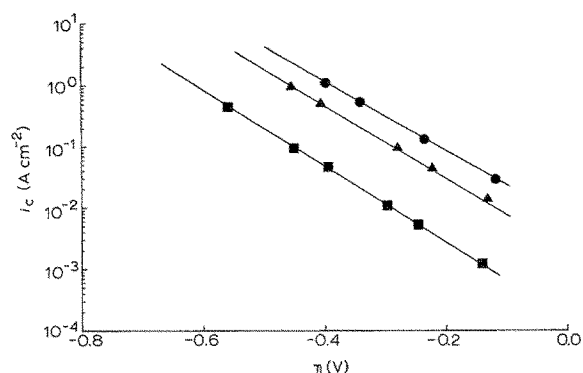


Fig. 1. Some quasi-steady state polarization curves for the h.e.r. obtained under potentiodynamic conditions at a low sweep rate of 2 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ on nickel electrodeposited from different baths. (■) chloride a, (▲) chloride a + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$, and (●) acetate + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$.

without these species. For a given electrodeposition bath, the results show that the i_0 values on the electrodes electrodeposited with $\text{SiW}_{12}\text{O}_{40}^{4-}$ are greater than those of nickel electrodeposited without $\text{SiW}_{12}\text{O}_{40}^{4-}$ (Table 2). Thus, the increase in the i_0 value may be related to the effect of $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$. In fact, for the same electrodeposition bath, the electrocatalytic properties of the nickel electrodeposited with $\text{SiMo}_{12}\text{O}_{40}^{4-}$ are superior to those fabricated with $\text{SiW}_{12}\text{O}_{40}^{4-}$ (see Fig. 1). The results shown in Fig. 1 and Table 2 were obtained with electrodes electrodeposited for a period of 6 h to study the effect of the electrodeposition time on electrocatalytic properties. As an example, variation of the overvoltage with the electrodeposition time is shown in Fig. 2 with the electrode fabricated in a sulphate bath with and without $\text{SiW}_{12}\text{O}_{40}^{4-}$. As may be seen, the h.e.r. overvoltage of

Table 2. H.e.r. Tafel slope (b), hydrogen exchange current density (i_0) and hydrogen overvoltage (η at 0.1 A cm^{-2}) for nickel electrodeposited from baths with and without $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$

Electrodeposition bath	b (mV decade^{-1})	i_0 (A cm^{-2})	$ \eta $ (V)
Chloride (a)	140	2.0×10^{-4}	0.50
Chloride (a) + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	155	3.0×10^{-3}	0.27
Chloride (a) + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	150	4.0×10^{-2}	0.17
Acetate	140	1.7×10^{-3}	0.41
Acetate + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	150	6.4×10^{-3}	0.16
Acetate + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	155	7.0×10^{-2}	0.06
Chloride (b)	135	8×10^{-4}	0.36
Chloride (b) + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	135	6.4×10^{-3}	0.16
Chloride (b) + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	140	6.0×10^{-2}	0.07
Sulphate	140	2.7×10^{-3}	0.38
Sulphate + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	155	6.8×10^{-3}	0.15
Sulphate + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	150	8×10^{-2}	0.05

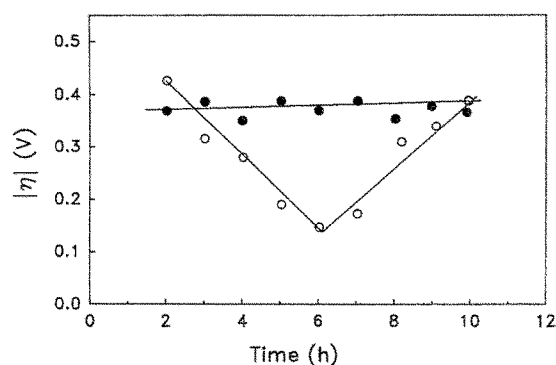


Fig. 2. Variation of the hydrogen overvoltage (η) in $1 \text{ M H}_2\text{SO}_4$ with the electrodeposition time for nickel electrodeposited from sulphate (●) without $\text{SiW}_{12}\text{O}_{40}^{4-}$; (○) with $\text{SiW}_{12}\text{O}_{40}^{4-}$.

nickel electrodeposited without $\text{SiW}_{12}\text{O}_{40}^{4-}$ does not change with electrodeposition time. On the other hand, the lowest h.e.r. overvoltage is obtained on electrodes produced over a period of 6 h in the presence of $\text{SiW}_{12}\text{O}_{40}^{4-}$. For other deposition times, an increase of η is observed. Analogous results are obtained on nickel electrodeposited with and without $\text{SiMo}_{12}\text{O}_{40}^{4-}$ (see Fig. 3).

These different results may be related to the chemical composition of the electrodes. The electrode chemical composition obtained by fluorescence spectroscopy analysis is shown in Table 3 for nickel electrodeposited with $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ (labelled Ni-W and Ni-Mo respectively) over different lengths of time. As indicated, silicon is only detected on the electrodes, produced over 2, 4, 8 and 10 h. Tungsten and silicon are detected on nickel electrodeposited with $\text{SiW}_{12}\text{O}_{40}^{4-}$ over 6 h, while molybdenum and silicon are detected on electrodes produced with $\text{SiMo}_{12}\text{O}_{40}^{4-}$ over 6 h. These latter electrodes exhibited the lowest h.e.r. overvoltage and the best exchange current density. Accordingly, the best electrocatalytic properties are obtained if Si and Mo are detected in the electrode. This conclusion is illustrated by the correlation of the chemical composition of the electrodes fabricated from the various baths to their electrocatalytic properties for the h.e.r. presented in Table 4. This table shows that silicon and tungsten or silicon and molybdenum are detected only in the electrodes with the best electrocatalytic parameters. In

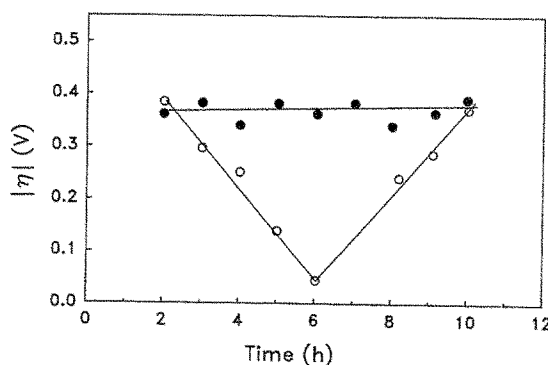


Fig. 3. Variation of the hydrogen overvoltage (η) in $1 \text{ M H}_2\text{SO}_4$ with the electrodeposition time for nickel electrodeposited from sulphate (●) without $\text{SiMo}_{12}\text{O}_{40}^{4-}$; (○) with $\text{SiMo}_{12}\text{O}_{40}^{4-}$.

Table 3. Chemical composition of electrode fabricated at different times from chloride (a) with $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$ or $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$ using X-ray fluorescence spectroscopy: (×) detected; (–) not detected

Electrodeposition time (hour)	Detected elements			
	Ni	Si	W	Mo
2	×	×	–	–
4	×	×	–	–
6	×	×	×	–
6	×	×	–	×
8	×	×	–	–
10	×	×	–	–

those electrodes that are produced with $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ and that provide less interesting electrocatalytic properties, only silicon is detected.

On the other hand, from a comparison of the h.e.r. electrocatalytic properties of the different electrodes described in Table 2, it may be observed that the electrocatalytic activity of the nickel deposited without $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ increases in the sequence chloride (a) < chloride (b) < acetate < sulphate (see Table 1 for the composition of the baths). Furthermore, the electrocatalytic activity is affected considerably by the nature of the electrodeposition bath without $\text{SiW}_{12}\text{O}_{40}^{4-}$. This finding agrees with those published elsewhere in the literature on the relative catalytic activity of nickel powders for the decomposition of a 0.4% H_2O_2 solution [16, 17]. In contrast,

Table 4. List of elements detected by X-ray fluorescence spectroscopy analysis for electrode fabricated over 6 h from different baths: (×) detected; (–) not detected

Electrodes from bath	Detected elements				
	Ni	Si	W	Cl ⁻	Mo
Chloride (a)	×	–	–	–	–
Chloride (a) + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	×	×	×	–	–
Chloride (a) + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	×	×	–	–	×
Acetate	×	–	–	–	–
Acetate + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	×	×	×	–	–
Acetate + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	×	×	–	–	×
Chloride (b)	×	–	–	×	–
Chloride (b) + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	×	×	×	×	–
Chloride (b) + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	×	×	–	–	×
Sulphate	×	–	–	–	–
Sulphate + $8 \text{ g dm}^{-3} \text{ SiW}_{12}\text{O}_{40}^{4-}$	×	×	×	–	–
Sulphate + $8 \text{ g dm}^{-3} \text{ SiMo}_{12}\text{O}_{40}^{4-}$	×	×	–	–	×

the h.e.r. electrocatalytic activity of the nickel electrodeposited with $\text{SiW}_{12}\text{O}_{40}^{4-}$ or $\text{SiMo}_{12}\text{O}_{40}^{4-}$ does not change significantly with the nature of the bath composition. This can be explained in the light of the detection of silicon and tungsten or silicon and molybdenum in these deposits. The presence of silicon and tungsten or silicon and molybdenum favours the activation of the electrode surface which in turn results in an improvement in the h.e.r.

These results may be attributed to the effect on electrocatalytic activity of hypo-hyper-electronic transition metals, as has been pointed out by Jaksic [7, 9]. In fact, electrocatalytic activity increases sharply with the alloying of typical hypo-hyper-d-electronic transition metals. Furthermore, extremely active electrocatalysts are produced when a synergetic activation d-metal (Ni) is combined with a reactivity-inductive d-metal (Mo, W). The good electrocatalytic properties of the h.e.r. on Ni-W and Ni-Mo obtained here are in agreement with these considerations.

Work is currently underway to study h.e.r. activity on electrodes fabricated from nitrate and iodide baths and on electrodes electrodeposited from the various baths with other heteropolyacids. The fabrication of new electrocatalysts based on a combination of other synergetic activation d-metals (Co, Fe, In, Pd and Pt, for example) and reactivity-inductive-d-metals is still being studied.

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