

Synergetic effect of electrode activation on the h.e.r. in alkaline medium on Pt, Pd, Ni and Cu electrodes

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Platinum, palladium, nickel and copper surfaces were modified from acid baths containing $\text{SiW}_{12}\text{O}_{40}^{4-}$ and different concentrations of Cu^{2+} . It was shown that improvement in the overpotential (η) and in the exchange current density (i_0) of the hydrogen evolution reaction (h.e.r.) on the electrodes, in alkaline medium, depends on the concentration of Cu^{2+} . The copper concentration displaying the best electrocatalytic behaviour for the h.e.r. was determined for the different electrodes. The h.e.r. electrocatalytic activity was then analysed and related to the chemical composition of their surface deposits. The performance of the modified electrodes was also checked through potentiostatic experiments. This showed that the improvement in the electrocatalytic properties was attributable, not to an increase in the surface area of the electrode, but to the chemical composition of the surface deposits.

1. Introduction

The work done to date relating to the analysis of the hydrogen evolution reaction (h.e.r.) on electromodified electrodes may be summarized briefly as follows. Early on, the hydrogen evolution reaction was performed with Chevrel-type cluster compounds [1]. Remixed cluster compounds were found to be the best electrodes for this reaction (both the intermetallic systems of the hypo-hyper-d-electronic metal combinations and the cluster materials were prepared thermally). Recently, attention has turned to the use of oxide electrodes as the activated cathodes for hydrogen evolution [2–5]. RuO_2 has proved to be a suitable cathode, even for long-term performances. Spinel [6] and NiO [7] have been investigated; however, it has been found that an agent is needed in these cases in order to minimize the reduction rate of the oxide layer and thereby ensure stability. *In situ* activation of a nickel cathode with sodium molybdate during the h.e.r. in a basic medium has also been studied [8]. In this case, the hydrogen discharge at 100 mA cm^{-2} in 30% by weight KOH containing 4 mM sodium molybdate largely attenuates the deactivation process owing to the adsorption of hydrogen. H.e.r. analysis in basic medium with electrodes coated with Ni–Mo–Cd [9] shows that these electrodes give excellent low hydrogen polarization performance in alkaline water electrolysis at elevated temperatures, i.e. 70–90°C. *In situ* electrocatalytic activation of noble metals for hydrogen evolution has also been studied [10], and the individual (Co-tris complex) and synergetic (Co–Mo) electrocatalytic effects for hydrogen evolution on substrates of noble metals (Au, Pt, Pd, Re, Ir and Rh) have been demonstrated and

theoretically explained. More recently, studies have been carried out on the modification of electrode surfaces by oxometalates [11–15]. It has been shown that various electrodes can be modified by these species yielding an improvement in their electrocatalytic properties for the h.e.r. in acid medium. It has also been shown that the presence of metal ions, such as Ti^{3+} , Ni^{2+} , Fe^{3+} , Pb^{2+} or Cu^{2+} , in the electrolytic bath has a beneficial effect on the electrocatalytic activity of the h.e.r. on electrodes modified by dodecaphosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) [16]. The Cu^{2+} ions, however, have the most pronounced effect on the h.e.r. These results were obtained on electrodes modified *in situ* with the same concentrations of $\text{PW}_{12}\text{O}_{40}^{3-}$ and of the metal ion in the electrolytic bath.

This paper describes the electrocatalytic behaviour of platinum modified from acid baths containing $2 \times 10^{-3} \text{ M SiW}_{12}\text{O}_{40}^{4-}$ and different concentrations of Cu^{2+} . The copper concentration displaying the best electrocatalytic properties for the h.e.r. was used to activate other electrodes, such as Pd, Ni and Cu. The electrocatalytic parameters of these electrodes in 30% KOH were also determined, as well as the limiting parameter (real surface area or chemical composition) of the electrodes defining their electrocatalytic properties. The stability of the electrodes was also determined.

2. Experimental details

2.1. Electrode modification

All the electrodes were modified under potentiostatic conditions and at room temperature. A constant potential of -1 V/SCE was applied to the electrodes immersed in a derivatization bath composed of 0.5 M

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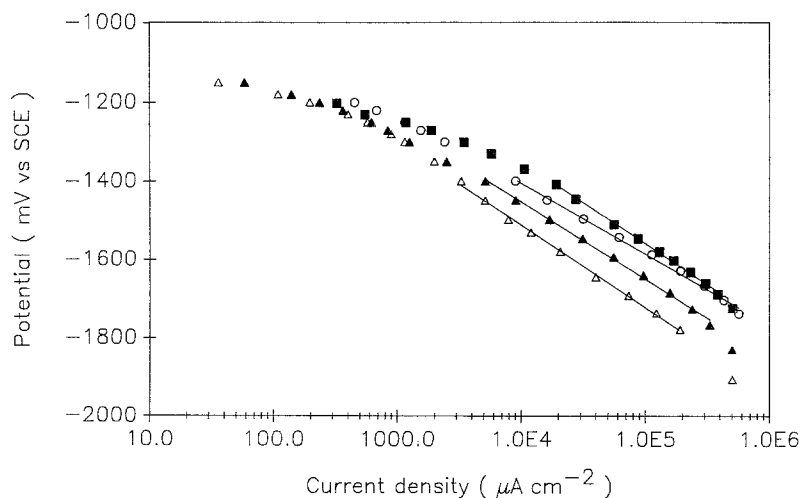


Fig. 1. Cathodic polarization curves for h.e.r. on Pt electrodes modified with $\text{SiW}_{12}\text{O}_{40}^{4-}$ and different $[\text{Cu}^{2+}]$ concentrations in 30% KOH. Key: (■) PtSiWCu-2, (○) PtSiWCu-3, (▲) PtSiWCu-4, and (△) PtSiWCu-5.

H_2SO_4 , 2×10^{-3} M $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and different concentrations of CuSO_4 . Concentrations of 2×10^{-5} , 2×10^{-4} , 2×10^{-3} and 2×10^{-2} M of Cu^{2+} were used. The platinum modified electrodes were labelled PtSiWCu(-5), PtSiWCu(-4), PtSiWCu(-3) and PtSiWCu(-2), respectively. The palladium, copper and nickel electrodes modified with 2×10^{-3} M $\text{SiW}_{12}\text{O}_{40}^{4-}$ containing 2×10^{-3} M Cu^{2+} were identified as PdSiWCu(-3), CuSiWCu(-3) and NiSiWCu(-3), respectively. During the modification process, there is a change in the hydrogen evolution and, consequently, in the measured current. With a Cu^{2+} concentration of 2×10^{-5} M, the current density decreases very quickly at the beginning of the process and then stabilizes. On the other hand, for Cu^{2+} concentrations of up to 2×10^{-4} M, an increase in the current density with the polarization time is observed at the beginning of the modification process. The modification time was determined after the stabilization of the activation current, and found to be 30 min.

2.2. Electrochemical equipment and methods

Potentiodynamic and potentiostatic measurements were taken using a PAR (Model 273) potentiostat monitored by PAR Universal Programmer software (Model 342). Modification and characterization of the electrodes were carried out using a three-compartment cell with a platinum gauze of large surface area as a counter electrode and a saturated calomel electrode (Fischer Scientific) as a reference electrode. All solutions were prepared from reagent-grade chemicals and bidistilled water. The platinum, palladium, nickel and

copper were obtained from Johnson Matthey Limited. The geometric area of the working electrodes was 0.4 cm^2 for both modified and non-modified electrodes. All experimental results were referred to these apparent geometric surface areas, which possibly differed to some extent from the real surface areas.

3. Results and discussion

3.1. Effect of Cu^{2+} ion concentration on the modification performance of Pt

Figure 1 shows the polarization curves of the modified electrodes in 30% KOH. The various kinetic parameters calculated from these curves are summarized in Table 1. These parameters and, consequently, the catalytic activity are affected by the concentration of the Cu^{2+} ions in the derivatization bath. The Tafel slope (b) and the overpotential at a current density of 0.5 A cm^{-2} ($\eta_{0.5}$) reach a minimum at a Cu^{2+} concentration of 2×10^{-3} M (which is the same as the $\text{SiW}_{12}\text{O}_{40}^{4-}$ concentration), whereas the highest exchange current density (i_0) is obtained when the Cu^{2+} concentration is 2×10^{-2} M. A comparison of these results indicates that PtSiWCu(-3) yields the most improved electrocatalytic properties.

The performance of the modified electrodes was also checked through potentiostatic experiments. The electrodes were polarized at a constant potential of -2 V/SCE and the corresponding current densities after stabilization of the current were determined (Table 2). The current efficiency of the h.e.r. on the various different electrodes was found to be 100%. In

Table 1. Kinetic parameters for the h.e.r. at modified Pt electrodes in 30% KOH. The Tafel slopes are for high current densities

Electrode	i_0 (A cm^{-2})	b (mV decade^{-1})	$\Delta\eta^*$ (at 0.5 A cm^{-2}) (mV)
PtSiWCu(-5)	3.5×10^{-4}	210	4
PtSiWCu(-4)	5.4×10^{-4}	197	74
PtSiWCu(-3)	8.4×10^{-4}	181	191
PtSiWCu(-2)	2.1×10^{-3}	210	180
Smooth Pt	5.8×10^{-4}	235	-

* $\Delta\eta$: overpotential decrease with respect to the smooth Pt.

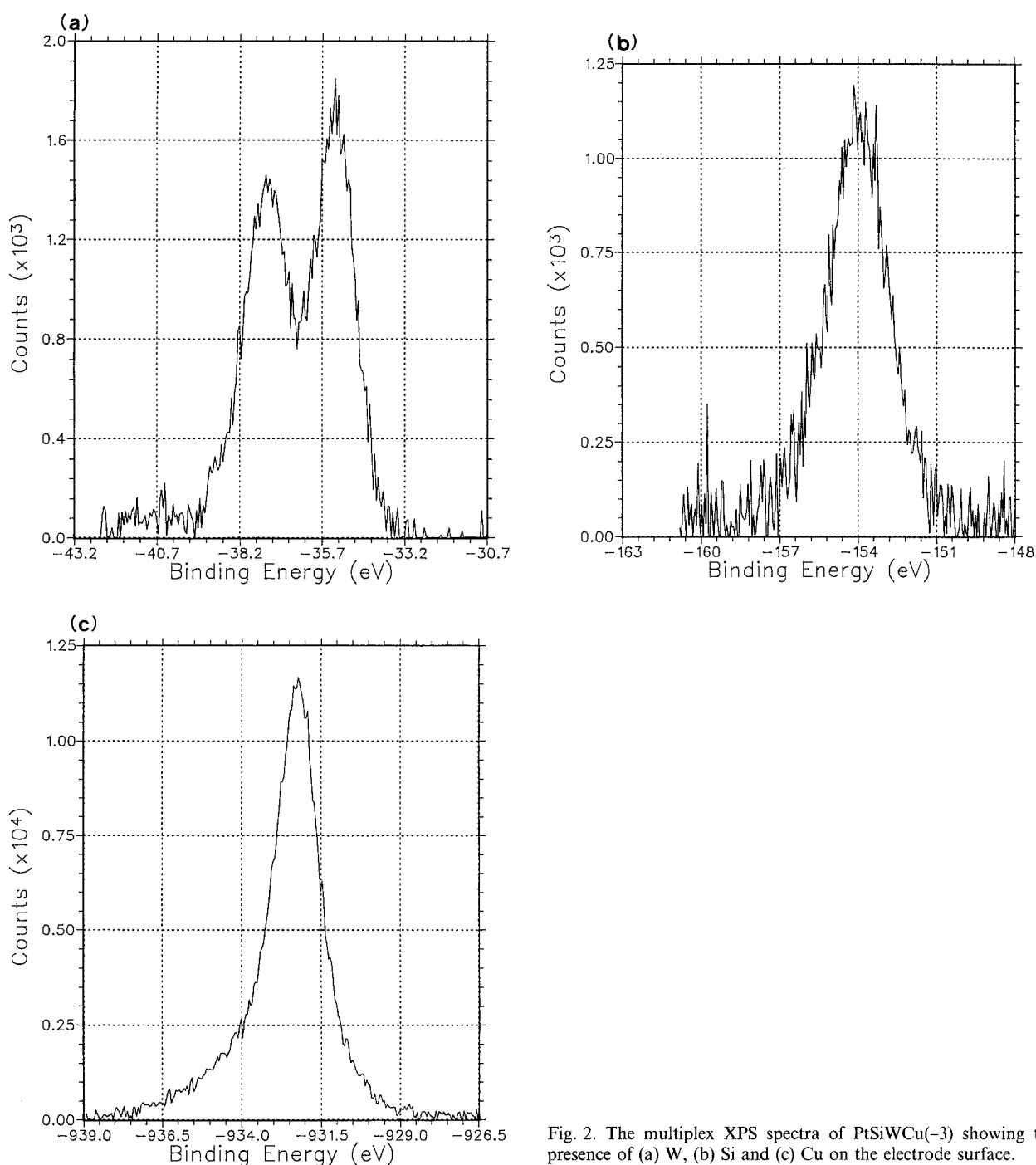


Fig. 2. The multiplex XPS spectra of PtSiWCu(-3) showing the presence of (a) W, (b) Si and (c) Cu on the electrode surface.

the case of smooth Pt, the current density decreased very quickly from a value of 0.9 to a stabilized value of 0.355 A cm⁻², as indicated in other published data [7]. This can probably be attributed to penetration of atomic hydrogen into the metal, but not to the surface

Table 2. Current densities at modified Pt electrodes in 30% KOH at -2 V/SCE after 1800 s of polarization

Electrode	Current density (A cm ⁻²)
PtSiWCu(-5)	0.627
PtSiWCu(-4)	0.954
PtSiWCu(-3)	1.200
PtSiWCu(-2)	1.023
Smooth Pt	0.355
PtCu(-3)	0.545

poisoning. In fact, it was found that the influence of the metallic impurities on the deactivation process is not significant, at least during the first 10⁴ s [8]. By contrast, in the case of the modified electrodes, no variation in current densities with time was observed. This indicates that the stability of these electrodes with respect to the smooth Pt electrode is good. Table 2 also shows that the current densities varied with the Cu²⁺ concentration, and that a maximum was obtained with 2 × 10⁻³ M of Cu²⁺. The increase in the current density may be attributed mainly to the catalytic effect of the modified electrodes, and not to an increase in the surface area of the electrodes. In effect, the BET analysis in the case of the Pt and Ni electrodes modified with SiW₁₂O₄₀⁴⁻ has shown that the increase in the electrocatalytic activity is not due to the increase in the real surface area, but to the presence of the catalyst on

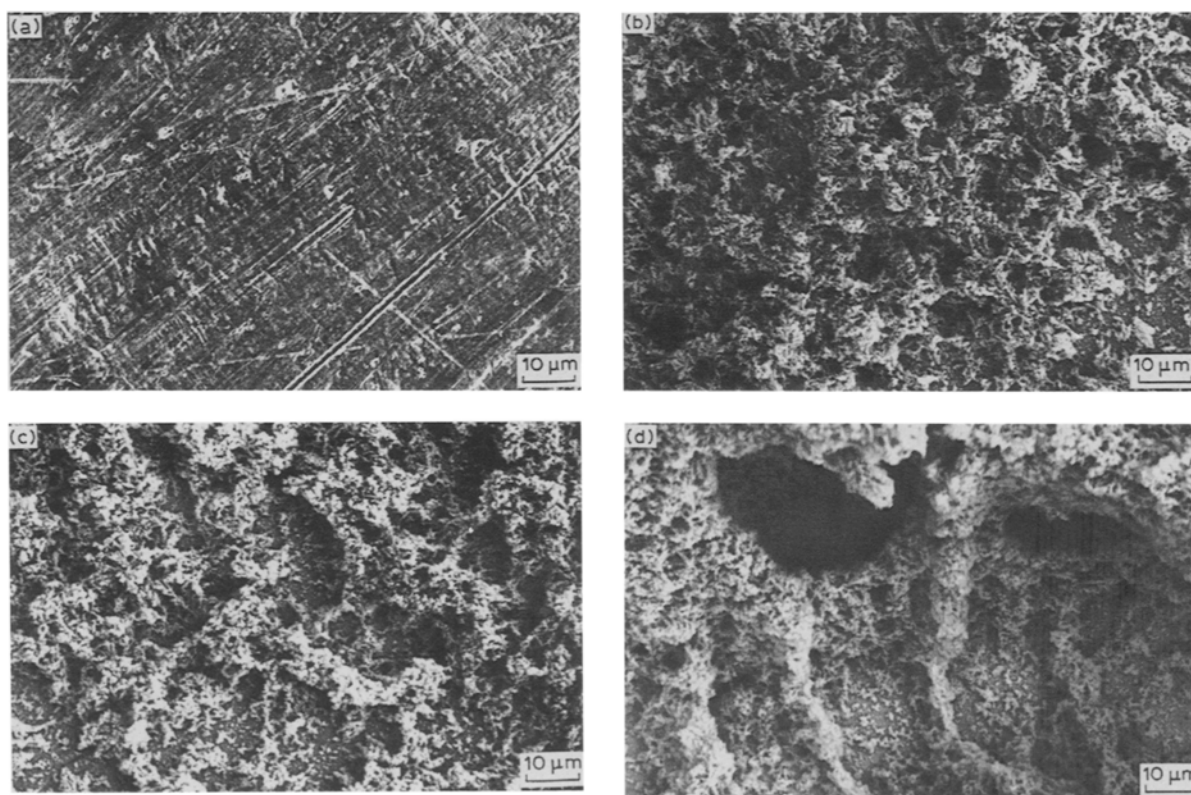


Fig. 3. SEMs of Pt electrodes modified with 2×10^{-3} M of $\text{SiW}_{12}\text{O}_{40}^{4-}$ and the following concentrations of Cu^{2+} : (a) 2×10^{-5} M, (b) 2×10^{-4} M, (c) 2×10^{-3} M, and (d) 2×10^{-2} M.

the electrode surface [19]. Support for this conclusion may be obtained by determining the current density for the h.e.r. at -2 V/SCE for the Pt electrode modified only with 2×10^{-3} M Cu^{2+} and for the Pt electrode modified with 2×10^{-3} M Cu^{2+} and $\text{SiW}_{12}\text{O}_{40}^{4-}$. As indicated in Table 2, the electrode modified with $\text{SiW}_{12}\text{O}_{40}^{4-}$ and Cu^{2+} had a higher current density (1.2 A cm^{-2}) than the electrode modified with Cu^{2+} only (0.545 A cm^{-2}).

The experimental results also show that if the electrodes modified with $\text{SiW}_{12}\text{O}_{40}^{4-}$ and Cu^{2+} are transferred to a sulphuric acid solution, there is a gradual dissolution of the electrode surface. Further, no significant improvement in the h.e.r. in an acid medium was obtained with any of these electrodes. This result differs from the results previously obtained with Pt and Pd electrodes [20] modified only with $\text{SiW}_{12}\text{O}_{40}^{4-}$, which showed good stability in H_2SO_4 1 M and an improvement in the h.e.r. However, the results presented here differ from those published elsewhere [16], where the stability of the platinum electrode modified with $\text{PW}_{12}\text{O}_{40}^{3-}$ and Cu^{2+} was good if the electrodes were kept in an acid electrolysis bath containing $\text{PW}_{12}\text{O}_{40}^{3-}$ and Cu^{2+} ions. This may be attributed to the change in the chemical composition of the electrode surface. Figure 2 shows the XPS spectra of a modified platinum electrode before the electrochemical characterization. These spectra reveal that W, Si and Cu were detected on the electrode surface. From the position of the W peaks, we may conclude that this element was presumably bound to several atoms of oxygen. Similar analyses were performed on the elec-

trodes after determination of the h.e.r. parameters in H_2SO_4 1 M, H_2SO_4 1 M containing $\text{SiW}_{12}\text{O}_{40}\text{H}_4$ and Cu^{2+} , and 30% KOH, respectively. A significant change in the chemical composition of the electrode surface was observed in the case of the electrode characterized in H_2SO_4 1 M. The atomic concentrations of the various elements detected on the electrode surface before and after characterization in H_2SO_4 1 M, are listed in Table 3. These figures show that the concentration of W decreases significantly after electrode characterization in acid solution. On the other hand, before and after electrode characterization in 30% KOH, no decrease in the W concentration was observed. The results in a basic medium are not shown. Also, there was no change in the concentration of copper or silicon before or after electrode characterization in an acid or a basic medium. Accordingly, it can be concluded that the improvement in the h.e.r. on the modified electrodes is related mainly to the presence of W. Dissolution of this element from the

Table 3. Atomic concentrations of the different elements calculated from the XPS analysis at $\text{PtSiWCu}(-3)$ surface (a) before, and (b) after characterization in H_2SO_4 1 M

Element	Atomic concentration %	
	(a)	(b)
W	1.31	0.61
Si	1.98	3.5
Cu	64.7	58.4
O	32.1	37.49

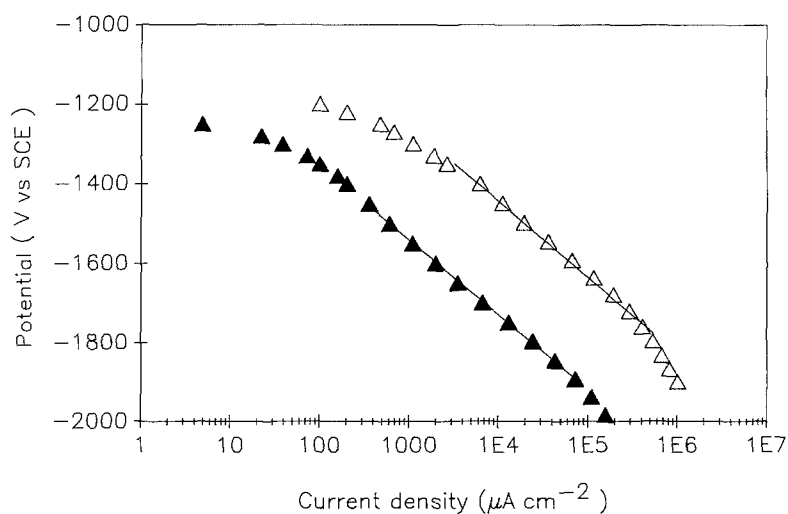


Fig. 4. Cathodic polarization curves for the h.e.r. on modified (Δ) and non-modified (\blacktriangle) Pd electrodes.

electrode surface decreases the electrode performance for the h.e.r.

The morphology of the electrode surface was investigated by scanning electron microscopy (SEM). The SEM images show that the roughness of the electrode surface increases with the Cu^{2+} concentration in the modification bath (see Fig. 3). The most porous surface (and consequently the roughest one) corresponds to a Cu^{2+} concentration of 2×10^{-2} M. However, from the results of the electrochemical measurements on the electrodes, it is clear that the best electrocatalytic properties are not displayed by the electrode with the highest surface roughness. The BET analysis also showed that the real surface area of the electrode modified with Cu^{2+} is similar to that of the electrode modified with $\text{SiW}_{12}\text{O}_{40}^{4-}$ and Cu^{2+} . We may conclude, therefore, that electrocatalytic activity is related to the chemical composition of the electrode rather than to its surface roughness.

3.2. Effect of the modification on other electrode materials

Since, in the case of modified platinum electrodes, a concentration of 2×10^{-3} M of both $\text{SiW}_{12}\text{O}_{40}^{4-}$ and CuSO_4 resulted in the best electrocatalytic activity, the same concentration of these species was used to modify other electrode materials, such as Pd, Cu and Ni. Figure 4 shows the polarization curves of non-modified

and modified Pd in 30% KOH. The results of the potentiostatic and potentiodynamic experiments are listed in Table 4.

In the case of the palladium electrode, the activation resulted in a very substantial improvement in the i_0 and a significant decrease in η (295 mV at 0.1 A cm^{-2}). No change in the Tafel slope was observed. When a constant potential of -2 V/SCE was applied in 30% KOH, the PdSiWCu(-3) electrode showed no variation in the current density after 1800 s of polarization, unlike the palladium electrode which was very sensitive to the deactivation process, and its value was much higher than the initial current density at the palladium electrode. The modification of the copper and nickel electrodes affected the kinetic parameters of these electrodes for the h.e.r. in almost the same way as for palladium, i.e. an increase in i_0 and a decrease in $\eta_{0.1}$. In the case of the nickel electrode, the modification resulted in a decrease in the Tafel slope, which suggests a change in the reaction mechanism.

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Table 4. Kinetic parameters for the h.e.r. in 30% KOH on non-modified and modified Pd, Cu and Ni electrodes. The Tafel slopes are for high current densities

Electrode	i_0 (A cm^{-2})	b (mV decade^{-1})	$\Delta\eta^*$ (at 0.1 A cm^{-2}) (mV)	Current density (A cm^{-2}) at -2 V/SCE after 1800 s
Bare Pd	1.7×10^{-5}	189	—	0.3
PdSiWCu(-3)	6.0×10^{-4}	191	295	1.05
Bare Cu	8.9×10^{-6}	166	—	0.60
CuSiWCu(-3)	6.5×10^{-5}	168	165	1.618
Bare Ni	2.4×10^{-5}	163	—	0.782
NiSiWCu(-3)	2.9×10^{-5}	133	130	1.545

* $\Delta\eta$: overpotential decrease with respect to the non-modified electrode.

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