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THE HYDROGEN EVOLUTION REACTION ON NICKEL BASED ELECTRODEPOSITS

Because of its importance in fundamental electrochemistry and electrochemical tecnology, the hydrogen evolution reaction has received much attention. Hydrogen is presently seen as a fuel that may help greatly in solving the serious environmental problems produced by the burning of fossil fuels. The production of hydrogen by water electrolysis is the preferred method of production, but it is necessary to lower the cost of the product. The production of adequate cathode materials with good electrocatalytic properties, and a cost compatible with the technology, is necessary to allow electrolysers to work at lower overpotentials. An understanding of the properties of these materials and of the kinetics and mechanistic aspects of the HER is essential to design materials with the desired properties. This work describes several nickel based electrodeposits, including nickel alloys and nickel with incorporated sulphides, that present low overpotentials for the HER. It also stresses and demonstrates the use of impedance spectroscopy to gain a deep knowledge of the kinetics and mechanism of the reaction on these materials.

The hydrogen evolution reaction (HER) is one of the most studied electrochemical processes. Experimental studies of the HER at the beginning of the century by Tafel [1], and the many studies that followed, contributed substantially to establish the foundations of modern electrochemical kinetics. Today, fundamental studies of this reaction are still important, as shown, for example, by studies of the dependence of the kinetics of the HER on the orientation of single crystal gold electrodes [2]. At the same time, the HER has an enormous importance in electrochemical technology. The pure hydrogen produced in electrolytic processes has recognised applications in the food industry, metal refining, etc. Furthermore, today there is a global concern because of the degradation of the environment due to the combustion of fossil fuels, a problem that could be minimised by the clean combustion of hydrogen in fuel cells. For this, it is necessary to produce hydrogen at competitive prices. The cheapest way of producing hydrogen is by vapour reforming of fossil fuels but, obviously, this is no solution because fossil fuels are still used and the production of CO_2 remains the same. Furthermore, vapour reforming produces a rather impure hydrogen which can be used in oil refineries or in the production of ammonia, but for other applications it may involve costly purifying procedures. The best alternative is electrolytic hydrogen but, with present technologies, this product is more expensive. It has been demonstrated that the cost of electrolytic hydrogen, apart from other components, is directly proportional to the operational voltage of the electrolyser [3]. This magnitude can be expressed by the relation

$$V_{op} = V_{i=0} + \eta_c(i) + \eta_a(i) + iR$$

where $\eta_c(i)$ is the cathodic and $\eta_a(i)$ the anodic overpotential, both dependent on current, and iR is the voltage drop due to the various resistances in the circuit, including the electrolyte resistance. Proper choice of the cell design and of the electrolyte can minimise this last contribution. The most common cathode materials used in commercial alkaline electrolysers are carbon (or mild) steel in unipolar and nickel (or nickel plated steel) in bipolar electrolysers. These materials work in 28% KOH solutions at around 80°C where the electrolyte conductivity is maximum. Under operational current densities, the overvoltages of these cathodes may be over 350 mV. Considering an equivalent value for the overvoltage of the anode, the sum represents about 1/3 of the operational voltage of the electrolyser. Therefore, there is much interest in reducing those values. Because of the dependence of overvoltage on current density, an obvious approach is the use of electrodes with large effective areas. This involves the production of rough surfaces or codeposits from which one of the elements is chemically removed, leaving a high surface area material. On the other hand, the reduction of overpotential can be promoted by using suitable electrode materials with good electrocatalytic activity. In the search for these materials, it must be taken into account that the cost must be compatible with the cost of the technology as a whole, so the use of precious metals is discarded. It must be pointed out that the HER is of importance in the large chlor/alkali industry, where the overpotential of this reaction is also important in determining the production costs.

For a long time it has been observed that although nickel has a higher overpotential than carbon steel, nickel alloys with transition metals or nickel surfaces modified by the introduction of non–metals present much lower overpotentials than nickel itself. Suitable theories exist to explain the effect of alloying nickel with transition metals [4], but most of the search for new materials has been tentative, for lack of a detailed knowledge of the kinetics and mechanism of the HER on a given material. Earlier studies of the HER involved the recording of Tafel slopes and the dependence of the

exchange current density and of a given potential on pH. These values were then compared with mechanistic values derived theoretically [5,6], and a mechanism was determined after guessing whether the hydrogen coverage was either low or high. Not surprisingly, this approach led to tentative and ambiguous results. The situation changed qualitatively when impedance spectroscopy was introduced as a technique that allowed the determination of rate constants and hydrogen coverages [7,8], which led to a much better specific knowledge of the HER on specific materials.

This work describes several studies of the HER, involving kinetic and mechanistic aspects, on electrodeposits of nickel alloys or nickel composites that present overpotentials low enough to make them attractive in electrochemical technology.

EXPERIMENTAL APPROACH

In order to work under conditions as near as possible as those of the electrolyser and, at the same time, maintain rigorous control on the surface of the electrode, it is necessary to adopt adequate procedures in the preparation of electrodes and the purification of solutions.

Cells. Electrochemical cells were made of pyrex glass. Although it is well known that hot concentrated alkali attacks glass, no influence of impurities coming from glass dissolution were found within the normal time interval for kinetic experiments. However, these impurities may be responsible for a slight potential decay observed in long term operation experiments. Cells were usually immersed in a water thermostat kept at the temperature of the experiment

Solutions. Solutions were made with p.a. grade KOH and water purified in a Milli–Q (Millipore) system. Even the best grade of commercial KOH was found to contain iron as impurity. This produces a non–controlled electrodeposit in the cathode that alters the properties of the surface. Because of this, solutions for kinetic experiments were normally electrolysed for 90 h with either Pt or Ni electrodes under a current density of 1 A cm^{-2}. Although no difference was found in the results with both types of electrodes, the use of Pt should be discouraged because of the possibility of the formation of Pt ions that could eventually deposit on the working cathode and enhance its activity.

Electrodes. The substrates for the electrodes were prepared by embedding a carbon steel foil in epoxy resin, leaving an exposed area of about 0.5 cm^2. Extensive tests demonstrated that the resin is not affected by concentrated hot alkali. Prior to the electrodepositions the surface of the substrate was polished with emery paper down to grade 600 and cleaned with diluted HCl. The electrodeposits were made from adequate modifications of Watts baths for the electrodeposition of nickel and either references or details will be given in each case. The reference

electrode was usually of the type $Hg/HgO/HO^-$, joined to the main compartment with a Luggin capillary, and secondary electrodes were made with Pt foils. Kinetic experimental results were always corrected for the potential drop between the reference and working electrodes.

Experimental measurements. Stationary, galvanostatic current–potential curves and potentiodynamic experiments (cyclic voltammetry) were performed with PAR potentiostats (models 173 and 273). For the impedance measurements a 1250 Solartron Frequency Response Analyser and a Solartron 1286 Electrochemical interface were used. These were cupled to a personal computer for data aquisition.

Evaluation of the electrodeposited electrodes. Before a detailed study of a given material is done it is necessary to demonstrate two important aspects: performance and stability. Performance was usually established first by evaluating the potential of the electrode under a current of 135 mA cm^{-2} (a value normally employed in unipolar electrolysers) in 28 % KOH at 70°C. This potential was then compared with that of carbon steel cathode, under the same conditions. A material may be considered operationally active if its potential is at least 100 mV lower than that of mild steel.

THE STUDY OF THE KINETICS AND THE MECHANISM OF THE HER WITH IMPEDANCE SPECTROSCOPY.
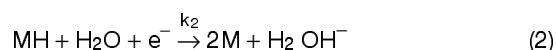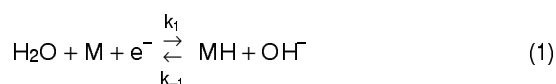
Because of the importance of impedance spectroscopy studies of the HER in the last two decades, and because many of the results of this work were obtained with this technique, a brief description of the technique will be necessary. Theoretical and experimental aspects of the application of impedance spectroscopy to the study of the HER were established by Harrington and Conway [7], Bai et al. [8] and Bai and Conway [9]. The treatment considers that the HER is an electrochemical reaction with an adsorbed intermediate, so the analysis of Armstrong et al. can be applied [10, 11]. Disregarding diffusional effects, the equivalent circuit may be represented by
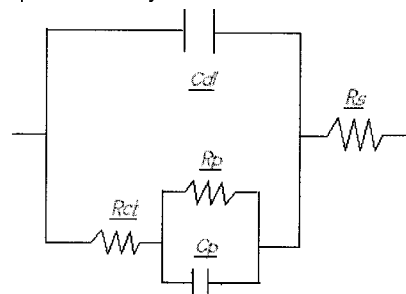
Here C_{dl} is the capacity of the double layer, R_s the resistance of the solution, R_{ct} the charge transfer resistance and the parallel circuit $R_p//C_p$ simulates the adsorption process. Adsorption is generally simulated by a capacitor but, being frequency dependent, a parallel RC circuit is necessary. The expected plot in the

complex impedance plane will depend on the values of the circuit parameters. If the adsorption parallel circuit prevails, it is possible that only one semicircle is observed. On the other hand, if the impedances of the charge transfer and the adsorption processes are comparable, two semicircles are expected. It should be pointed out that an equivalent circuit is not necessary to correctly understand the impedance response of the HER, it only helps to understand the system conceptually. The correct approach is to obtain the impedance from the kinetics of a proposed mechanistic scheme, as a function of frequency, and to compare the predictions with the experimental results. From a suitable set of rate constants the hydrogen coverage can be calculated as a function of overpotential.

The kinetic/mechanistic scheme usually proposed for the HER is

$$H_2O + M + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MH + OH^- \tag{1}$$

$$MH + H_2O + e^- \overset{k_2}{\rightarrow} 2M + H_2\,OH^- \tag{2}$$

$$MH + MH \overset{k_3}{\rightarrow} 2M + H_2 \tag{3}$$

Step (1) represents the first electron transfer and is known as the Volmer reaction. This may be followed by an electrochemical desorption step (2), known as the Heyrovsky reaction or by a chemical recombination step (3), or the Tafel reaction. Obviously, if the rates of steps (2) and (3) are comparable, these two reactions may take place simultaneously. Normally, the solubility of hydrogen gas in the solution is negligible, so the back reactions of steps (2) and (3) are not considered. If step (1) is the rds, the hydrogen coverage is expected to be low, while a coverage approaching 1 is expected if step (2) is the rds.

The working procedure involves giving values mainly to the rate constants in the impedance expression and to compare the resulting plots with the experimental results until a good fit is obtained [7–9]. This should be done at several potential values in the current rising region and, of course, it should be demonstrated that the fitting parameters are independent of potential. Also, it is important to demonstrate that the fitting parameters are independent of frequency. This means that fittings in the complex-impedance plane are not enough. Fittings of Bode plots (module and phase angle as a function of frequency) should also be done to demonstrate that the fitting parameters do not depend on frequency.

An interesting validation of the fitting of the impedance results and the values of the rate constants obtained has been proposed in this laboratory [12]. By obtaining results at different temperatures, the energy of activation of the reaction can be obtained from the dependence of the rate constant of the rds with

temperature (Arrhenius plots). This magnitude can also be obtained from the dependence of the exchange current density, obtained from Tafel plots, with temperature. This exchange current density is obtained from an experiment that reflects the response of the reaction as a whole, so it does not depend on any mechanistic assumptions. Furthermore, it does not depend on any fitting procedures. Thus, a comparison of the energy of activation obtained from the rate constant of the rds with that from the exchange current density should be an adequate test for the validity of the modeling and fitting procedures to obtain the intrinsic parameters of the HER.

RESULTS AND DISCUSSION

The HER has been studied on electrodeposited and on bulk nickel alloys. Electrodeposited alloys on a cheap substrate, usually carbon steel, constitute a convenient way of producing low cost cathodes. In this case, the formulation of the electroplating bath should be considered carefully because it must have good stability. Otherwise, the repeated preparation of electrodeposition baths makes the process expensive. Usually, plating baths consist of a suitable modification of the traditional Watts bath [13].

Nickel–iron

Nickel–iron alloys have been deposited from an acetate bath, with contents of Fe as high as 65 % [14]. This proved to be a good material. In continuous operation for up to 1200 h in 28% KOH at 135 mA cm^{-2} the overpotential was –0.173 V which is about 270 mV lower than that obtained with carbon steel. Mechanistic studies were done at the time by analysing Tafel plots and the effect of pH [15,16] and led to the tentative proposal that the mechanism of the reaction is Volmer–Heyrovsky, with the Heyrovsky step being the rds. In the operational region of current densities (> 100 mA cm^{-2}), the Tafel slope seem to be independent of temperature. This is in conflict with classical electrochemical kinetics, which predicts an increase in the Tafel slope with temperature. A more normal behaviour was observed at lower current densities (< 100 mA cm^{-2}). Here the Tafel slopes increase with temperature, as expected, and are much lower than those observed on mild steel. Experiments done with pure electrodeposited Fe [15,16], show that on this material overpotentials are still lower than on Ni–Fe. Curiously enough, it is observed that at low cd the Tafel slope decreases for increasing temperatures, so the behavior is opposite to that predicted by classical theory. It is important to point out that on Ni–Fe the performance should be due to a true electrocatalytic effect, because examination of the surface with scanning electron microscopy (SEM) shows that the surface is not particularly porous. The roughness factor was actually estimated to be around 40.

Nickel–Zinc

These alloys were activated after the electrodeposition, by leaching the zinc with 28% KOH at room temperature for more than 10 h [17]. This treatment does not eliminate all the zinc, and a considerable amount remains. Potentiodynamic experiments show that this is a high surface area material, and a comparison of Tafel behaviour with that of pure polished Ni indicates that the roughness factor could be as high as 1100. The overpotentials on Ni–Zn are low ($\approx$ 120 mV at 135 mA cm^{-2}), and this is partly due to the fact that this material presents only one Tafel slope of about 60 mV dec^{-1}. Furthermore, the Tafel slope is very nearly independent of temperature. The material shows good term stability and a model electrolyser was built with 200 cm^2 electrodes and operated for more than 1000 h without losing its characteristics. For these experiments on big electrodes, and working with uncompensated resistances, the overpotential of the cathode on 6.2 M KOH at 70°C remained at 140 mV for more than 1000 h. Under the same conditions and time of operation the overpotential of a carbon steel cathode was 390 mV.

A detailed mechanistic study was carried out on this material with impedance spectroscopy [18]. It is interesting to mention that at 25°C, the response is dominated by the adsorption process and the complex–plane impedance plot presents only one semicircle. This separates into two semicircles at 80°C, as shown in Fig. 1, which also shows the results of the

Figure 2. Bode plots for the HER on Ni–Co–Zn in 0.5 M KOH at different temperatures. (+) Experimental points; (•) simulated values.

fittings with the theoretical model described above. The corresponding Bode plots, including the results of the fittings are shown in Fig. 2. The set of rate constants obtained from the fittings shows that the rate of the Tafel reaction is negligible. So the mechanism of the HER on Ni–Zn is Volmer–Heyrovsky, and the second step is the rds. The composition and the method of preparation of the alloys seems to play an important role in determining the electrocatalytic activity. Ni–Zn alloys were prepared by a different route by Chen and Lasia [19], and studied by impedance measurements. They found results somewhat different from those presented here.

A related material, Ni–Co–Zn, containing 52% Ni and 12% Co was prepared and studied in the same way [20]. The presence of cobalt in these electrodeposits was found to produce surfaces that show better mechanical stability. On the other hand, the electrocatalytic activity decreases in the presence of Co. The mechanism is the same as that for Ni–Zn but the values of k_2 are one order of magnitude lower. This may be related to a reduced adsorption of hydrogen as shown in Fig. 3, presenting the dependence of the hydrogen coverage with overpotential. Energies of activation were also determined, and Fig. 4 shows a comparison of the plots obtained with the exchange cd and with the values of k_2. The comparison is very good and, as discussed above, validates the procedure used to make the kinetic analysis.
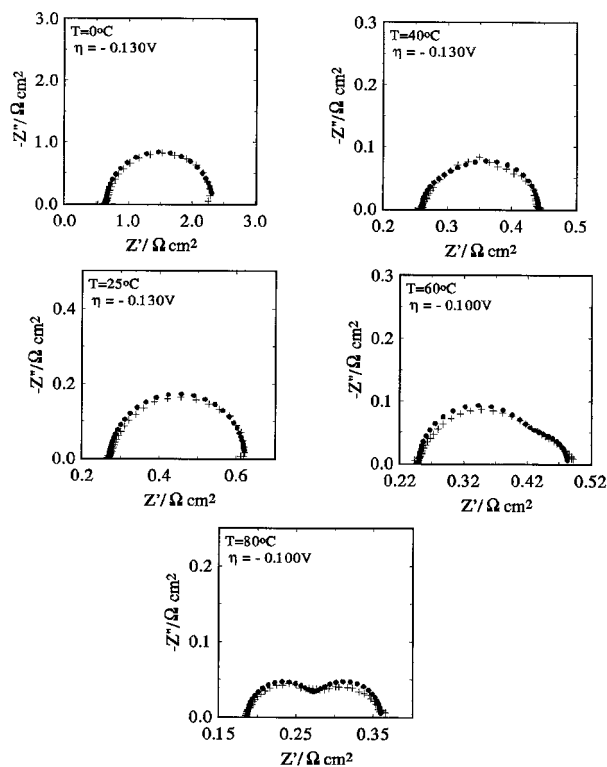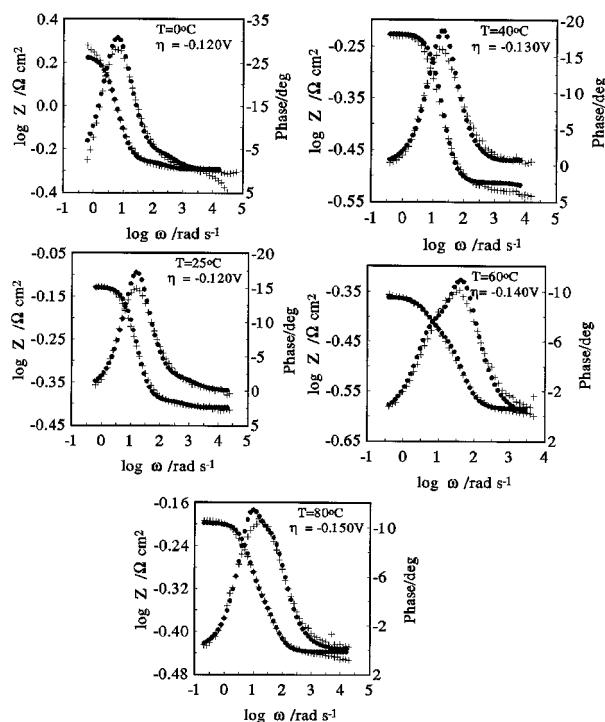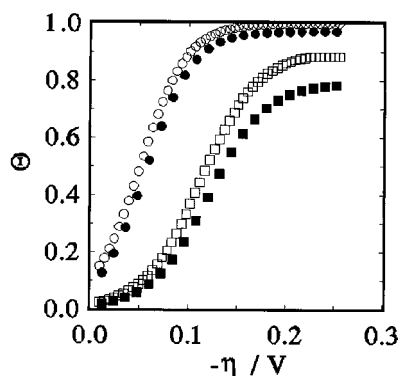

Figure 1. Impedance (Nyquist) plots for the HER on Ni–Zn in 0.5 M KOH at different temperatures. (+) Experimental points; (•) simulated values.

Figure 3. Hydrogen coverage as a function of the overpotential for Ni–Zn (•) 0, (■) 60 and Ni–Co–Z n (○) 0, (□) 60°C
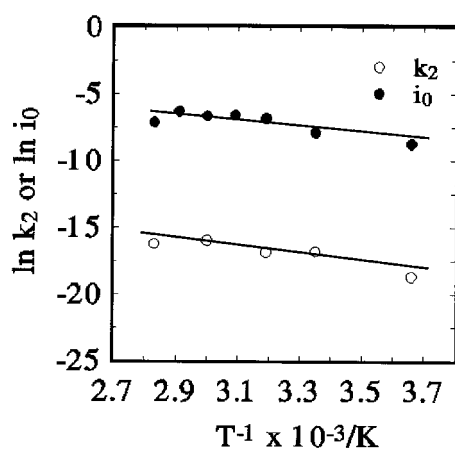

Figure 4. Arrhenius plots from the values of k_2 and i_o for Ni–Co–Zn.

Nickel–iron–zinc

Because of the good properties of Ni–Fe and Ni–Zn, discussed above, the effect of introducing Fe into a Ni–Zn alloy was investigated [21]. An experimental problem, not fully investigated, appeared here. Only alloys with very small amounts of Fe could be prepared. Attempts to increase the amount of Fe in the alloy by increasing the Fe content in the bath led to non–adherent deposits. The composition of the alloy, after leaching with KOH, was 55% Ni, 44% Zn and 1% Fe [21]. A low content of an element may be subjected to a large error, so the amount of Fe was determined in this case by atomic absorption spectroscopy, after dissolution of the deposit, and confirmed by EDX analysis. As will be seen in the results, this small amount of Fe is enough to affect the behavior of the material, which is a very important operational consideration. An electrolyser operates with a solution prepared with commercial KOH, which must contain non–negligible amounts of Fe, which eventually deposits on the cathode. This is an uncontrolled deposition and is not expected to produce a stable deposit, but it may explain the fact that commercial cathodes seem to improve their performance with the time of operation. SEM

micrographs obtained for this deposit show that it has a rather compact structure before the leaching. After this treatment, the surface appears full of cracks and pores [20], which explains the large electrochemical surface area determined for these materials.

Tafel slopes obtained for Ni–Fe–Zn show that at all temperatures there is only one slope, and it increases with temperature, as shown in Fig. 5. So, as in the case of Ni–Zn, one slope with a small value (52–67 mV dec^{-1}) is obtained, but in the case of NiFeZn it increases more with temperature. In this sense, the behavior is more similar to that observed for Ni–Fe at low cd. It was also found that the overpotential at a cd of 135 mA cm^{-2} and 80°C was only 104 mV, slightly lower than of either Ni–Fe or Ni–Zn cathodes. Obviously, this material deserves a more careful evaluation together with a mechanistic study.
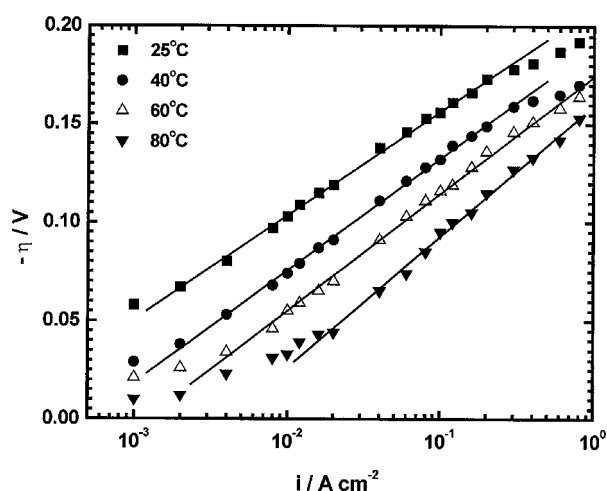

Figure 5. Tafel plots in 1 M NaOH for different temperatures for NiFeZn.

Nickel–Nickel sulphide

Different from the Ni alloys mentioned above, surfaces containing sulphur have been found to exhibit low overpotentials and reasonably good stability [22]. Electrodeposits containing NiS have been prepared from baths containing thiocyanate, and the roughness factor of these materials was found to be usually low (≈ 130) [22]. The overpotential is about 200 mV lower than that of carbon steel, and the stability was demonstrated for about 200 h. After this operation period the sulphur content stabilises to a relatively low value of about 3%. This material presents an intriguing Tafel behavior. In 28 % KOH and up to 40°C there is only one Tafel slope of about 85 mV dec^{-1}. Above this temperature, two Tafel slopes are present: one at high cd, which is almost independent of temperature and one at low cd, that decreases with temperature, which is opposite to the

predictions of classical theory. This material with such anomalous behavior could only be studied by impedance measurements [22]. The impedance response shows only one semicircle in the complex impedance plane, indicating that the impedance of the adsorption process is probably high. This study shows that the reaction follows a Volmer–Heyrovsky mechanism, with the second reaction being the rds. The rate of the electrochemical desorption step is more than one order of magnitude lower than for Ni–Zn [18]. This is probably due to the fact that hydrogen coverages are low, and high ovepotentials are necessary to observe high coverages.

Nickel–Iron sulphide

A different approach was followed in making an electrodeposit in two stages; First, Ni was electrodeposited on carbon steel, and then, Ni together with FeS particles were deposited onto this surface [23]. SEM micrographs show that the surface of this material is very different from that of NiS. The surface presents cauliflower type structures and an abundance of cracks, so the material must present a high effective area. The characteristics of Ni/NiFeS were found to be critically dependent on the amount of FeS particles present in the deposition bath, so this parameter was optimized

experimentally. Current–potential curves at different temperatures show that the overpotential at 135 mA cm^{-2} is about 250 mV lower than that of carbon steel, making of this electrodeposit an attractive alternative. The Tafel behavior in the low cd region is similar to that of NiS, i.e., the slope decreases with increasing temperatures. But the high cd Tafel slopes also decrease with increasing temperature. Thus, the Tafel behavior of Ni/NiFeS is probably one of the more anomalous observed so far. Because of this, the possibility of a classical kinetic analysis is not possible, and the reaction had to be studied with impedance spectroscopy as described above.

At low temperatures, impedance measurements show only one semicircle in the complex impedance plane, but at higher temperatures a second semicircle starts to be defined quite clearly. This is because at low temperatures, the impedance of the adsorption process is high and dominates the impedance of the interface. As the temperature increases, the impedance of the adsorption step decreases and the high frequency semicircle, due to the charge transfer reaction can be detected. The same effect is observed when the overpotential increases at constant temperature, indicating that the adsorption step is more sensitive to potential changes. This can be seen in Figures 6–8, which show the impedance responses as Nyquist and
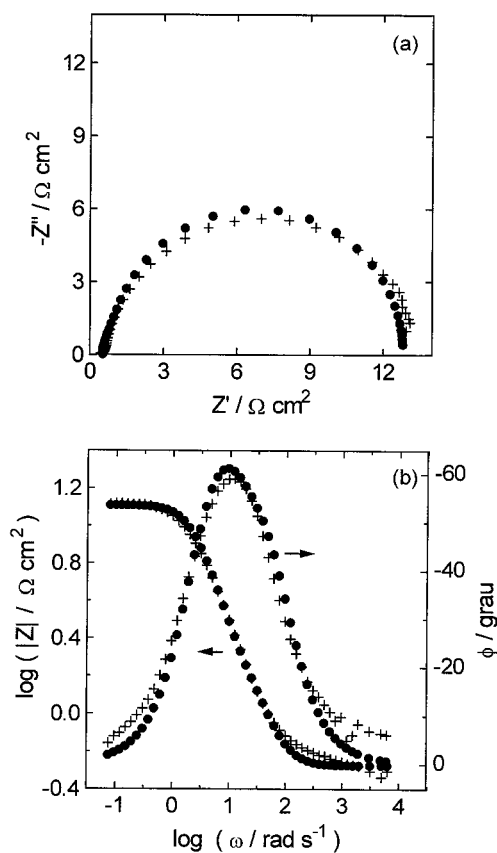

Figure 6. Impedance plots, Nyquist (a) and Bode (b), for the HER on Ni/NiFeS in 1M NaOH at 273 K, for η = –0.114 V: (+) Experimental points; (•) Simulated values.
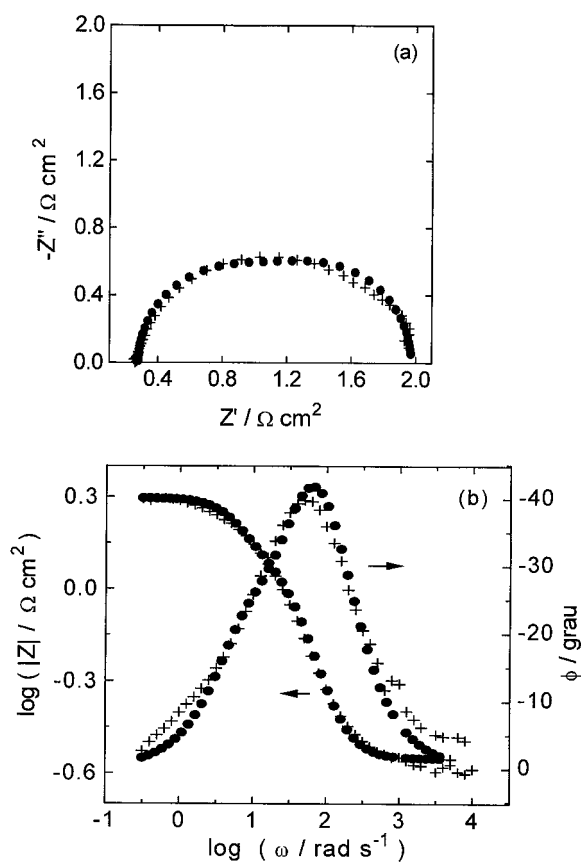
Figure 7. Impedance plots, Nyquist (a) and Bode (b), for the HER on Ni/NiFeS in 1M NaOH at 313 K, for η = – 0.114 V: (+) Experimental points; (•) Simulated values.
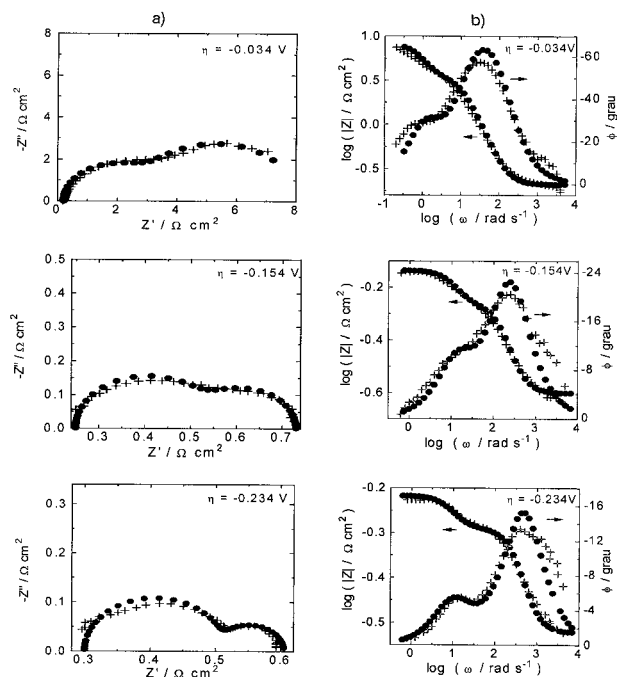
Figure 8. Impedance plots, Nyquist (a) and Bode (b), for the HER on Ni/NiFeS in 1M NaOH at 353 K, for differents overpotentials as indicated in the figure: (+) Experimental points; (•) Simulated values.
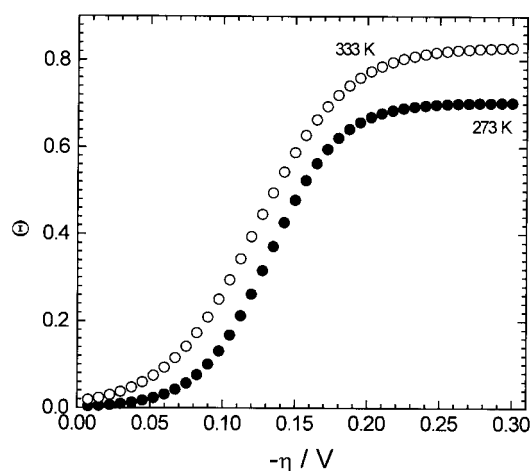

Figure 9. Hydrogen coverage as a function of the overpotential for Ni/NiFeS at two temperatures.

Bode plots together with the fitting of the impedance derived from the mechanism of the reaction. Figure 9 shows the hydrogen coverage at two temperatures, being clear that as the temperature increases, lower overpotentials are required to obtain the same coverage. This indicates a strong adsorption of the intermediate. Table 1 shows the rate constants obtained from the fittings as a function of temperature. This table shows clearly that the contribution of the Tafel reaction is negligible and that the Heyrovsky step is the rds. The rate of this reaction step is comparable to that on NiZn [18] and larger than on NiS [18]. The results of the impedance analysis were validated by comparing the

Table 1. Tafel parameters for the HER on Ni/NiFeS electrodes, in 6 M KOH at different temperatures.

T	b, mV dec^{-1}		i_o / A cm^{-2}		η_{135}
K	Low c.d.	High c.d.	Low c.d.	High c.d.	V
273	70	112	3.0×10^{-4}	9.0×10^{-4}	0.250
298	62	105	7.5×10^{-4}	2.0×10^{-3}	0.219
313	54	87	1.2×10^{-4}	2.2×10^{-3}	0.170
333	48	79	1.8×10^{-4}	2.0×10^{-3}	0.148
353	45	65	2.7×10^{-4}	2.1×10^{-3}	0.128

c.d.: current density. η_{135}: overpotential at a current density of 135 mA cm^{-2}. i_o: exchange current density.
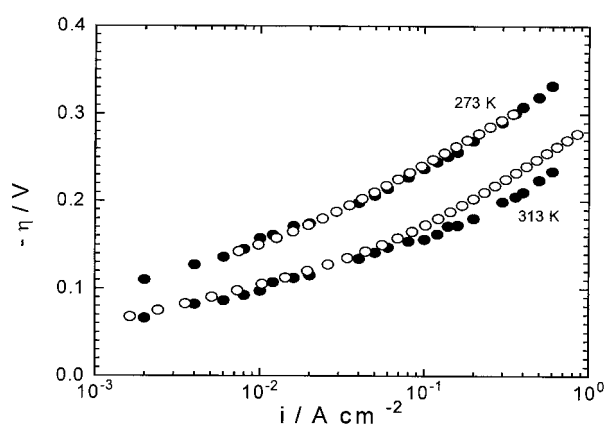

Figure 10. Tafel plots for the her on Ni/NiFeS at two temperatures: (•) experimental points; (o) simulated values.

experimental Tafel plots with those derived from the impedance measurements, as shown in Fig. 10. It was also done by comparing the energy of activation obtained from the rate constant of the rds with that from the exchange current density. Both comparisons are very satisfactory, showing the consistency of the mechanistic analysis.

Nickel–Nickel molybdenite

As in the previous case, this material was obtained by making first a nickel electrodeposit and on top of this a second electrodeposit of nickel with MoS$_2$ particles [24]. A SEM investigation of the surface indicates that the incorporation of molybdenite particles does not alter the morphology of the surface, but increases considerably the active surface area. The nickel molybdenite cathode was evaluated for long term operation in 28% KOH at 135 mA cm^{-2}. The potential increased somewhat during the first 50 hours, but then it remained stable for 172 h [24]. The operational potential was more than 200 mV lower than for a carbon steel cathode showing the good activity of the electrodeposit. In the initial work with this material [24] no detailed
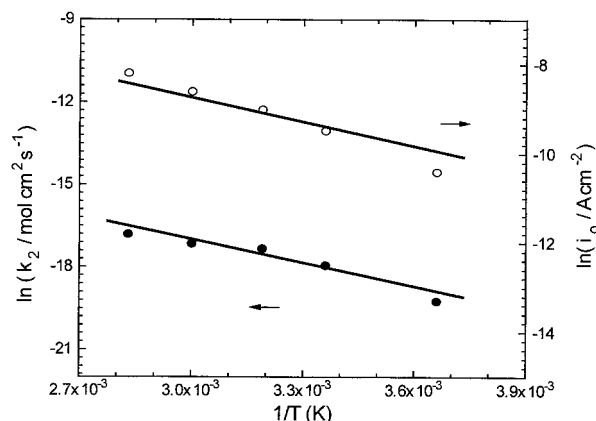
Figure 11. Arrhenius plots from the values of k_2 and i_o for Ni/NiFeS.

mechanistic evaluation was done. From Tafel slopes recorded at different temperatures, a low energy of activation was obtained ($10.6 \, kJ \, mol^{-1}$). Also, from Tafel slopes it was concluded that the kinetics of the reaction is independent of pH. This led to the suggestion that the mechanism of the reaction is probably a slow first discharge step followed by a fast electrochemical desorption step. Obviously, this mechanistic approach is very crude, so a detailed mechanistic study was carried out later, using impedance techniques [25].
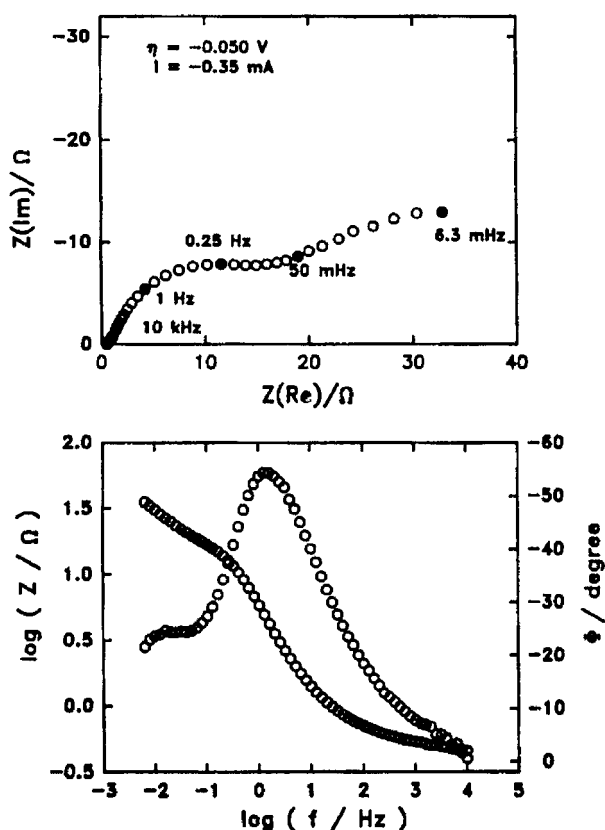

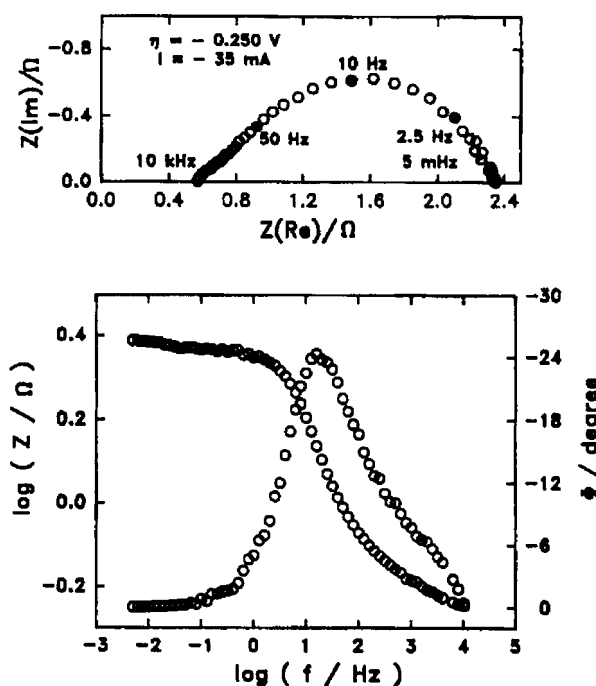Figure 12. Nyquist and Bode diagrams corresponding to the HER on a Ni/NiMoS2 electrode, measured at $\eta = -0.05$ V.

Figure 13. Impedance diagrams of the HER on a Ni/NiMoS2 electrode at $\eta = -0.25$ V.

Figures 12,13 and 14 show that at low overpotentials the impedance loops in the complex impedance plane are ill defined. But this situation improves for increasing overpotentials. A detailed examination of the high frequency region for a plot obtained near the reversible
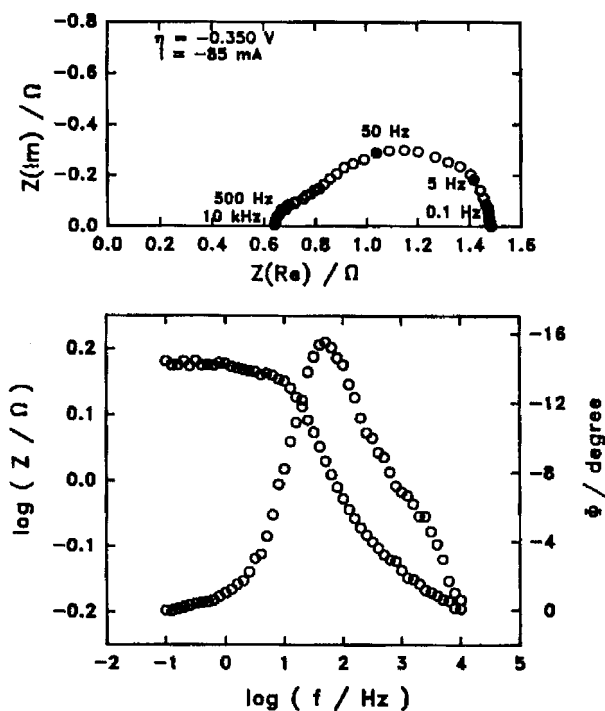

Figure 14. Impedance diagrams of the HER on a Ni/NiMoS2 electrode at $\eta = -0.35$ V.
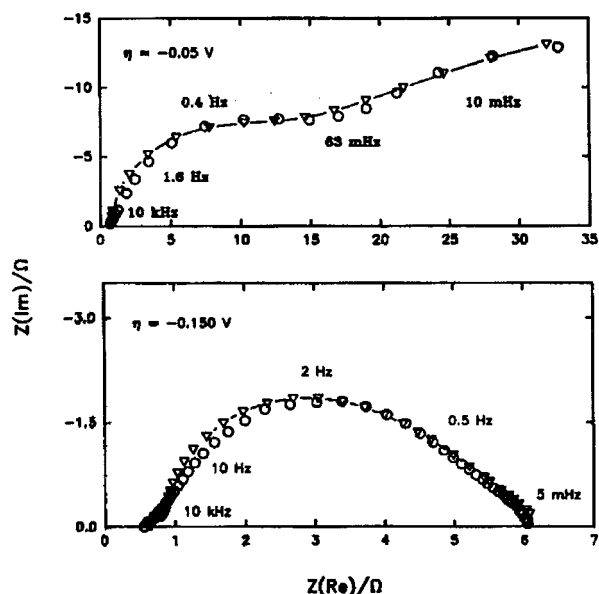
Figure 15. Comparison between experimental results (O) and theoretical impedance data (▽) simulated in terms of equation (20), corresponding to the HER on a Ni/NiMoS2 electrode at η = −0.05 V (a) and η = −0.150 V (b).
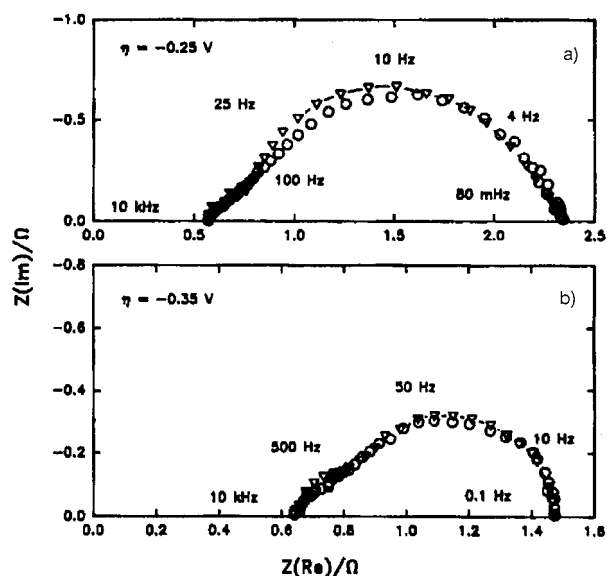

Figure 16. Experimental (O) and simulated (▽) impedance data corresponding to the HER on a Ni/NiMoS2 electrode at η = −0.05 V (a) and η = −0.35 V (b).

potential shows that the phase angle is near 45°, indicating a rough and porous surface, in agreement with the SEM study of a previous work [24]. At high overpotentials, the phase angle is almost 90°. This probably means that the bubbles generated by the reaction block the pores and the inhomogeneities of the surface and the response is that of a flat surface. A good fitting of the experimental results was obtained at high overpotentials with the 3–step HER mechanism. On the other hand, the fitting at low overpotentials was very

Table 2. Parameters used for the simulation of experimental impedance data: $b_1 = b_2 = 19.5\ V^{-1}$, $b_{-1} = 19.5\ V^{-1}$.

	η (V)			
	− 0.050	− 0.150	− 0.250	− 0.350
Ar (cm^{-2})	100	20	16.7	14.2
K_1^r / Ar (mol s^{-1} cm^{-2})	$5 \cdot 10^{-9}$	$3.5 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$	$1.5 \cdot 10^{-9}$
K_{-1}^r / Ar (mol s^{-1} cm^{-2})	$1 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$1.25 \cdot 10^{-5}$	$4.9 \cdot 10^{-5}$
K_2^r/ Ar (mol s^{-1} cm^{-2})	$1.35 \cdot 10^{-10}$	$1.4 \cdot 10^{-10}$	$17 \cdot 10^{-11}$	$3 \cdot 10^{-11}$
K_3 / Ar (mol s^{-1} cm^{-2})	$< 10^{-11}$	$< 10^{-11}$	$< 10^{-11}$	$< 10^{-11}$
K_4 / Ar (mol s^{-1} cm^{-2})	$7\ 10^{-9}$	$4.5\ 10^{-9}$	$8.6\ 10^{-9}$	$2.1\ 10^{-8}$
K_{-4} / Ar (cm s)	$2.9 \cdot 10^{-6}$	$1.5 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	$9.8 \cdot 10^{-6}$
D (cm^2 s^{-1})	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$
Γ / Ar (mol cm^{-2})	$1 \cdot 10^{-9}$	$7.5 \cdot 10^{-10}$	$6 \cdot 10^{-10}$	$2 \cdot 10^{-9}$
C_d / Ar (F cm^{-2})	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$8 \cdot 10^{-5}$
θ^0	0.035	0.54	0.69	0.94
I^0 (mA)	− 0.35	− 8	− 35	− 85

poor. This was attributed to the diffusion of hydrogen into the electrode, so a fourth step had to be added to the mechanistic scheme

$$MH_{ads} \overset{k_4}{\underset{k_{-4}}{\rightleftharpoons}} M + H_{abs} \tag{4}$$

A complete expression for the impedance was obtained considering eq. (4) [25] and with this it was possible to fit the experimental results at all overpotentials. Figures 15 and 16 show examples of the fitting at several overpotentials. From the fittings, the parameters presented in Table 2 were obtained. From the values of the rate constants in Table 2 it was concluded that the HER on Ni/NiMoS2 proceeds through a Volmer–Heyrovsky mechanism and the Heyrovsky step is rds. This shows the importance of doing a careful kinetic analysis of the reaction with adequate techniques, because the conclusions about the nature of the rds derived from current–potential plots were not correct [24]. It is interesting to note that step (4) is not potential dependent, so as the overpotential increases the rate of the electrochemical recombination increases and the influence of step (4) on the overall reaction decreases. This explains why the fittings at high

overpotentials are reasonably good without consideration of step (4).

CONCLUSIONS

The results of the kinetic and mechanistic studies of the HER presented here show that the mechanism of this reaction depends strongly on the state of the electrode surface and its morphology. An understanding of the HER involves a knowledge of the rate constants of the different steps, which allows an unambiguous identification of the rds. The dependence of the hydrogen coverage with overpotential and temperature and the possibility of absorption of adatoms into the electrode, are factors that must be known to evaluate the performance of a given material. All this information can be obtained by examining the electrode reaction with a powerful experimental technique like impedance spectroscopy.

Nickel alloys with appropriate metals and nickel composites can be produced by electrodeposition on carbon steel substrates, yielding active, low cost cathodes for hydrogen evolution. The overpotentials of these materials are 200–250 mV lower than that of carbon steel under the same conditions, which represents a considerable economy in the production of electrolytic hydrogen.

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REFERENCES

[1]   J. Tafel, Z. Phys. Chem., **50** (1905) 641

[2]   J. Perez, E. R. Gonzalez and H. M. Villullas, J. Phys. Chem B., **102** (1998) 10931

[3]   J. O'M. Bockris and T. N. Veziroglu, Solar Hydrogen Energy, Macdonald, London,1991.

[4]   M. M. Jakšic, J. Mol. Cat., **38** (1986) 161

[5]   B. E. Conway and M. Solomon, Electrochim. Acta, **9** (1964) 1599.

[6]   L. P. Bicelli, La Chim. L'Ind., **55** (1973) 792.

[7]   D. A. Harrington and B. E. Conway, Electrochim. Acta, **32** (1987) 1703

[8]   L. Bai, D. A. Harrington and B. E. Conway, Electrochim. Acta, **32** (1987) 1713

[9]   L. Bai and B. E. Conway, J. Electrochem. Soc., **138** (1991) 2897

[10] R. D. Armstrong, R. E. Firman and H. R. Thirsk, Faraday Disc., Chemical Society, London, **56** (1973) 244

[11] R. D. Armstrong and M. Henderson, J. Electroanal. Chem., **39** (1972) 81.

[12] M. J. Giz, M. Ferreira, G. Tremiliosi–Filho and E. R. Gonzalez, J. Appl. Electrochem., **23** (1993) 641

[13] B. V. Tilak, A. C. Ramamurthy and B. E. Conway, Proc. Indian Acad. Sci., **97** (1986) 359

[14] J. Carvalho, G. Tremiliosi–Filho, L. A. Avaca and E. R. Gonzalez, Hydrogen energy Progress, V. **2** (1984) 923

[15] J. Carvalho, G. Tremiliosi–Filho, L. A. Avaca and E. R. Gonzalez, in Electrode Materials and Processes for Energy Conversion and Storage, The Electrochemical Society, Proc. Volume 87–12 (1987) 356

[16] J. Carvalho, G. Tremiliosi–Filho, L. A. Avaca and E. R. Gonzalez, Int. J. Hydrogen Energy, **14** (1989) 161

[17] J. M. Giz, S. A. S. Machado, L. A. Avaca and E. R. Gonzalez, J. Appl. Electrochem., **22** (1992) 973

[18] M. J. de Giz, M. Ferreira, G. Tremiliosi–Filho and E. R. Gonzalez, J. Appl. Electrochem., **23** (1993) 641

[19] L. Chen and A. Lasia, J. Electrochem. Soc., **138** (1991) 3321

[20] M. J. Giz, G. Tremiliosi–Filho and E. R. Gonzalez, Electrochim. Acta, **39** (1994) 1775

[21] M. J. Giz, S. C. Bento and E. R. Gonzalez, Int. J. Hydrogen Energy, in press.

[22] M. J. Giz, J. C. P. Silva, M.. Ferreira, S. A. S. Machado, E. A. Ticianelli, L. A. Avaca and E. R. Gonzalez, Int. J. Hydrogen energy, **17** (1992) 725

[23] N. A. Assunçao, M. J. de Giz, G. Tremiliosi–Filho and E. R. Gonzalez, J. Electrochem. Soc., **144** (1997) 2794

[24] L. B. Albertini, A. C. Angelo and E. R. Gonzalez, J. Appl. Electrochem., **22** (1992) 888

[25] E. B. Castro, M. J. de Giz, E., R. Gonzalez and J. R. Vilche, Electrochim. Acta, **42** (1997) 951

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