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Effect of electrolyte composition on the dynamics of hydrogen gas bubble evolution at copper microelectrodes

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The dynamics of hydrogen gas bubble evolution at copper microelectrodes in H_2SO_4 and HCl solutions of various compositions have been studied by means of galvanostatic polarization experiments and simultaneous video taping. As long as the solution contains acid only, gas evolution is dominated by the growth of a single bubble at the electrode at any one time. The transients in H_2SO_4 solutions exhibit regular sustained relaxation oscillations that can be distinctly related to events occurring at the cathode. The electrode response in HCl solutions is somewhat noisier and shows much larger cathodic polarization and oscillation frequency and amplitude, presumably due to an interaction between Cl^- and the copper surface. Additions of Na_2SO_4 and NaCl to these solutions promote the nucleation and growth of numerous small bubbles at any one time and the diminishing of the oscillations of the electrode potential. The addition of thiourea to 2.0 M H_2SO_4 does not destroy the single bubble growth characteristic of acid-only solutions, but increases the cathodic overpotential at all organic levels with a maximum occurring at about 0.13 mM thiourea. Oscillation frequency and amplitude, and bubble departure diameter all show a similar dependence on thiourea concentration to that of overpotential.

1. Introduction

Regardless of whether it is a main or a side reaction and desired or not, gas evolution can have a significant effect on the polarization at electrodes. Most of the early work in this area was concerned with the physical processes involved in the nucleation, growth and detachment of bubbles [1–7]. A great deal of this work was not directed specifically to electrochemical systems, but to gas evolution in general.

In recent years, there has been increased interest in gas evolution occurring in electrochemical processes and in its relation to the resulting electrode response [8–15]. The system which has received by far the most attention is hydrogen evolution, both as a main reaction or as a side reaction in such processes as metal electrowinning and metal plating [16–21]. Gabrielli *et al.* [18–20] conducted galvanostatic experiments at Fe and Pt electrodes in H_2SO_4 solutions and obtained potential-time transients showing continuous irregular oscillations. From observations of the electrode surface, Gabrielli *et al.* [19, 20] concluded that the steep anodic jumps in the transients corresponded to the detachment of hydrogen gas bubbles from the electrode and that the slower cathodic shifts coincided with bubble growth. Their oscillations were very irregular presumably due to "roughness" of the electrode surface and consequently only average bubble departure diameters and oscillation frequencies and amplitudes could be obtained.

Brandon and Kelsall [21] opted to use microelectrodes in order to obtain a smoother and more reproducible electrode surface and investigated the growth of electrogenerated hydrogen, oxygen and chlorine on platinum and silver. By monitoring bubble size over time with a video camera, they showed that each bubble passed successively through inertia-controlled, diffusion-controlled and faradaic growth regimes over the course of its lifetime. However, Brandon and Kelsall made no effort to relate physical phenomena occurring at the electrodes with the resulting electrode responses.

Although the addition of inorganic salts and organics has been shown to have significant effects on the dynamics of gas evolution and growth, most of this work [22–24] has not dealt directly with gas generation at electrodes and its effect on electrode response. In one study on the corrosion of various steels, Jofa [25] showed that thiourea could either inhibit or promote hydrogen evolution depending on its concentration in strong acid.

The objective of this study is to examine the effects of acid type (H_2SO_4, HCl), inorganic electrolytes Na_2SO_4 and NaCl and of the organic thiourea on hydrogen gas evolution dynamics at a copper electrode. The relation between gas bubble evolution and growth and the resulting electrode response are examined by monitoring events occurring at a microelectrode during galvanostatic polarization using a video camera and comparing these with the potential–time transients. Microelectrodes have been used in this work since these are most effective for producing the controlled and reproducible surfaces that are critical to a systematic and hopefully unambiguous study of gas evolution.

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2. Experimental details

2.1 *Fabrication of copper microelectrode and surface preparation*

Both 40 μm and 225 μm copper wires (99.99% purity, Goodfellow Corporation, Malvern, PA) sealed in borosilicate glass were used as microelectrodes. An excellent seal between the metal and glass was obtained by rotating the assembly in a propane flame and applying a small vacuum to one end. No epoxy or other chemical additives were used for sealing since this could affect the gas evolution process. Special attention was devoted to the preparation of the copper electrode surface in order to ensure good reproducibility. Before each experiment, the electrode was subjected to a series of polishing stages (no. 600 emery, 1.0 μm and 0.05 μm α-alumina) for a precise length of time on a Buehler Monopol-8 polisher (Buehler, Lake Bluff, IL). The final stage involved an anodic polarization at 1000 A m^{-2} in a 2.0 M H_2SO_4 solution for several seconds.

Throughout the polishing steps, the electrode was mounted in a castolite–epoxy mould for ease of handling and most importantly for stability. An important feature of the Buehler polisher is that it can keep the electrode surface perpendicular to the plane of the polishing wheel so that a reproducible flat surface with the same exposed area can be produced from electrode to electrode.

SEM micrographs of the two electrodes at the different stages of preparation were taken to assess their effectiveness. These showed that very satisfactory surfaces smooth down to a scale below about 0.1 μm could be produced.

2.2 *Apparatus*

The experiments were carried out at room temperature in a 10 cm × 2.5 cm × 2.5 cm glass electrochemical cell. Chemicals were all reagent grade and water was triply distilled and pre-electrolysed for 5 h before use to remove metallic impurities. The results reported here apply for the electrode surfaces oriented horizontally in one of two configurations: upward- or downward-facing. When the working electrode or cathode was mounted facing downwards, it was inclined at an angle of 6° from the vertical to facilitate the departure of the bubble from the electrode surface. The reference electrode used throughout was a saturated calomel electrode connected to the solution via a Luggin capillary placed approximately 1 mm from the cathode. The Luggin capillary and the 1 mm Pt wire anode were placed so as not to interfere with gas bubble evolution at the cathode.

The cell was operated under galvanostatic conditions using a PAR EG&G model 273 potentiostat/galvanostat. The cathode potential reported on the standard calomel electrode scale was monitored as a function of time and transferred digitally to a Zenith 286 microcomputer through the PAR GPIB interface. At the same time, the cathode surface was monitored with a video camera to capture the evolution of hydrogen gas bubbles and recorded on a JVC BR6400U video cassette recorder for subsequent image processing. The images captured on tape were digitized and the growth dynamics of the hydrogen bubbles could be directly compared with the potential-time behaviour at the cathode. It must be noted that limitations in the speed of the videotaping and the resolution of the video camera (magnification 70 ×) restricted the capture of reliable images to the period when the bubble was already equal to or greater than the diameter of the copper.

2.3 *Reproducibility of electrode responses*

Each test was repeated to ensure that the electrode responses were reproducible. With the special attention focused on electrode preparation, we were able to achieve excellent reproducibility of the electrode responses and gas evolution dynamics throughout the study for any particular set of conditions. Furthermore, the electrode response rapidly reached a steady pattern that could be sustained indefinitely throughout the course of an experiment.

3. Results and discussion

3.1 *Effect of electrode configuration on electrode response*

Comparisons of the potential–time curves obtained for downward- and upward-facing microelectrodes were made in order to determine the effect of configuration on the electrode responses. In all cases, we found that electrode orientation has essentially no effect on the average potential, oscillation frequency and amplitude and the regular or irregular nature of the oscillations. The only difference is observed in the shape of the oscillation waveforms obtained in those cases where the oscillations were found to be regular and periodic. As an example, Fig.1 shows the detail of the steady potential–time curves for downward- and upward-facing electrodes at an applied current of 100 μA in 2.0 M H_2SO_4. The upward-facing electrode exhibits a waveform with more of the asymmetric shape of a relaxation oscillation than does the downward-facing electrode. In particular, the anodic rise corresponding to bubble detachment is much steeper than cathodic passivation due to bubble growth. This is not surprising since an upward-facing electrode presents less of an impediment to bubble departure than does a downward-facing electrode.

It is important to point out that the primary emphasis of this study is more on the general features of the electrode response and gas evolution dynamics rather than on the details of the dynamics. Consequently, the above results show that the observations to be described are general for any of the electrode configurations.

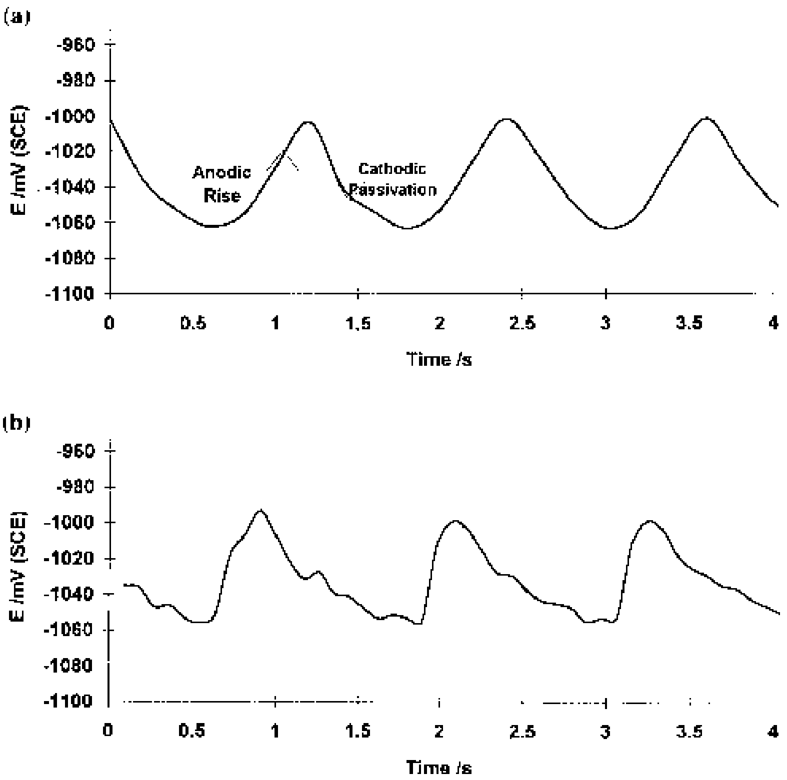

Fig. 1. Voltage fluctuations for hydrogen evolution at 40 μm diameter copper microelectrodes in 2.0 M H_2SO_4 and 100 μA current oriented in a downward (a) or upward (b) direction.

3.2 *Electrode response in 2.0* M *H_2SO_4*

Analysis of the videotapes reveals that as long as the electrolyte contains H_2SO_4 only, gas evolution occurs by the nucleation and growth of a single bubble at any one time. The corresponding electrode responses always display regular and periodic oscillations, such as those shown in Fig. 1. Under these conditions, there is a clear one-to-one correspondence between events at the electrode and the potential–time curves.

Sets of potential–time responses obtained at different applied currents on downward-facing electrodes in quiescent solutions of 2.0 M H_2SO_4 are presented in Figs 2 and 3. Transients for the 40 μm electrode which appear in Fig. 2 cover a range of applied currents from 30 to 200 μA, while those for the 225 μm electrode (Fig. 3) span a range from 500 μA to 5.7 mA. Several trends from the transients in Figs 2 and 3 can be observed. First, the oscillation amplitude and frequency and magnitude of the average potential increase as the current is raised in the lower current range (see Table 1). As the current is increased further, the frequency reaches a maximum and decreases slightly thereafter. Secondly, current also influences the shape of the oscillation waveform. At lower current densities ($<80\,\mu$A), the fraction of time between detachment of one bubble and nucleation of the next one is much smaller than the time it takes the bubble to grow to its departure diameter. This leads to the asymmetric relaxation oscillation pattern in the voltage fluctuations. As the current density is increased to relatively high values ($>100\,\mu$A), the nucleation time does not change significantly (on the time-scale of our measurements) whereas the growth time decreases resulting in similar nucleation and growth times and a more symmetric waveform.

Analysis of the video images for the experiments that yield the transients in Figs 2 and 3 also allows the effect of applied current on bubble departure diameter to be investigated. Previous work by Janssen and Hoogland [17] at current densities between 300 and 2000 A m^{-2} has shown that the hydrogen bubble departure diameter increases linearly with applied current. We have extended the study to higher current densities than has been reported previously. The results in Fig. 4 for both the 40 and 225 μm electrodes show that this linearity continues into this higher current region. Fourier analysis of these transients shows a single dominant frequency for each applied current. Fig. 5 gives a plot of frequency as a function of applied current density for both electrodes. In both cases, a maximum appears at an intermediate current density.

3.3 *Electrode response in 2.0* M *HCl*

Similar sets of experiments were conducted in 2.0 M HCl and in general the electrode responses were found to be noisier than those obtained in H_2SO_4 solutions (Fig. 6). In addition, the electrode is more polarized than in the case of sulfate solution, presumably due to an interaction between Cl^- and the copper surface [26].

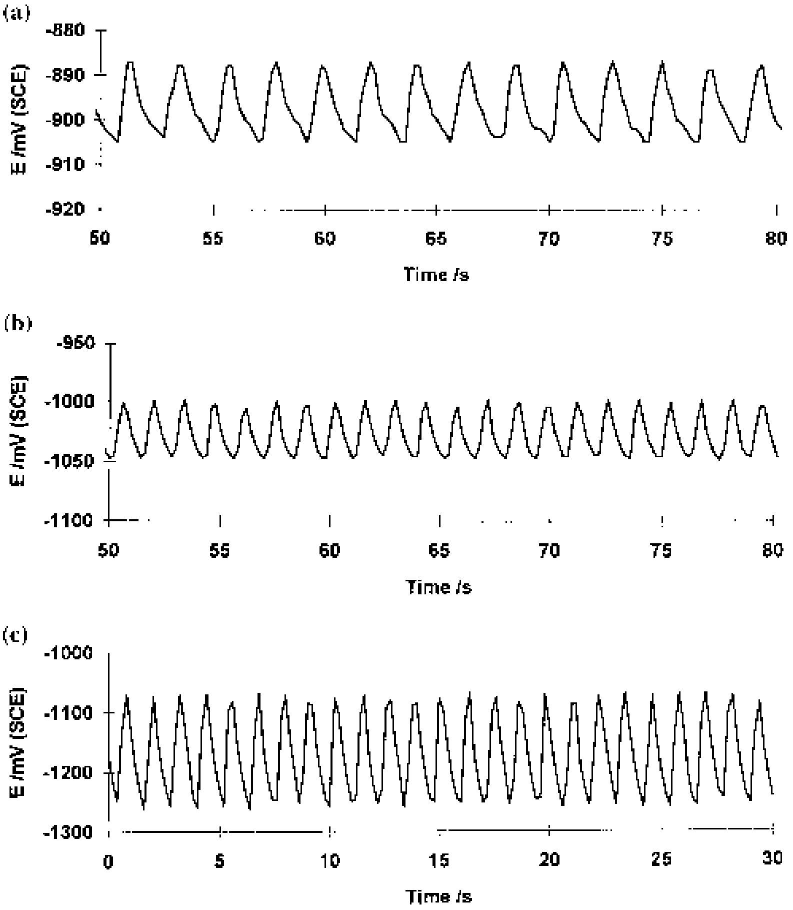

Fig. 2. Potential–time plots for hydrogen evolution at a 40 μm diameter Cu electrode at 2.0 M H_2SO_4 and several applied currents: (a) 30 μA, (b)100 μA and (c) 200 μA.

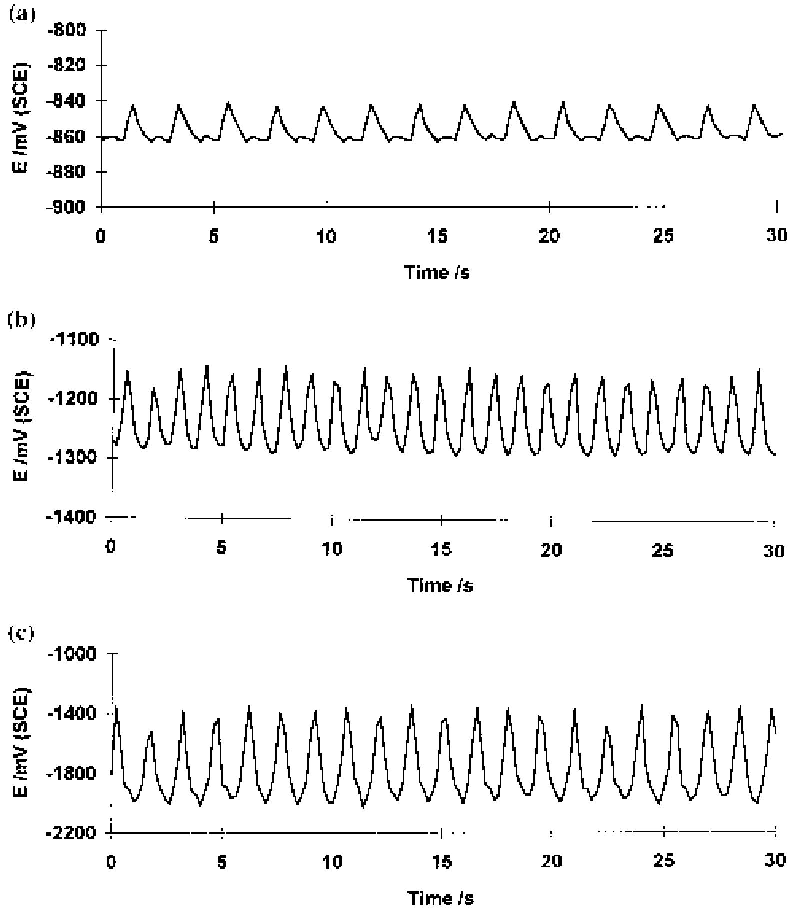

Fig. 3. Potential–time plots for hydrogen evolutions at a 225 μm diameter Cu electrode at 2.0 M H_2SO_4 and several applied currents: (a) 500 μA, (b) 3.0 mA and (c) 5.7 mA.

Table 1. Average potential, amplitude and frequency of oscillations obtained on a 40 μm diameter Cu electrode in 2.0 M H_2SO_4 as a function of applied current

I /μA	Amplitude /mV	E_{ave} /mV	Frequency /Hz
30	17	− 887	0.47
50	29	− 952	0.63
80	43	−1010	0.76
100	53	−1027	0.82

Gas evolution is still dominated by the growth of a single bubble, as is observed when sulfuric acid is the electrolyte. However, examination of the video images shows that there is some difference in the way a bubble grows in the two cases. In chloride solutions, a larger central bubble is surrounded by a few small ones which continually collapse into it and are replaced by newer ones. On the other hand, virtually no small bubbles appear around the large bubble during polarization in H_2SO_4 solutions. Evidently, coalescence on the resolution scale of the equipment is not significant to growth in sulfuric acid.

The amplitudes of the potential oscillations are also significantly larger in magnitude in an HCl solution and show a stronger dependency on current density, as shown in Fig. 7. The blocking of active nucleation sites probably increases the ohmic and activation overpotentials. The effect of the current density on oscillation frequency is also found to be affected by the nature of the electrolyte. The frequencies are higher, but do not vary with current density over the range studied, unlike the case of H_2SO_4 (as shown in Fig. 5)

3.4 *Effect of Na_2SO_4 on hydrogen bubble evolution in 2.0 M H_2SO_4*

We carried out a series of galvanostatic polarization experiments on both upward- and downward-facing electrodes in which currents varying from 30 to 100 μA were applied to copper electrodes immersed in solutions containing 2.0 M H_2SO_4 and different amounts of Na_2SO_4. For both electrode configurations, the results of these experiments show that when no amount or small levels of Na_2SO_4 are added to

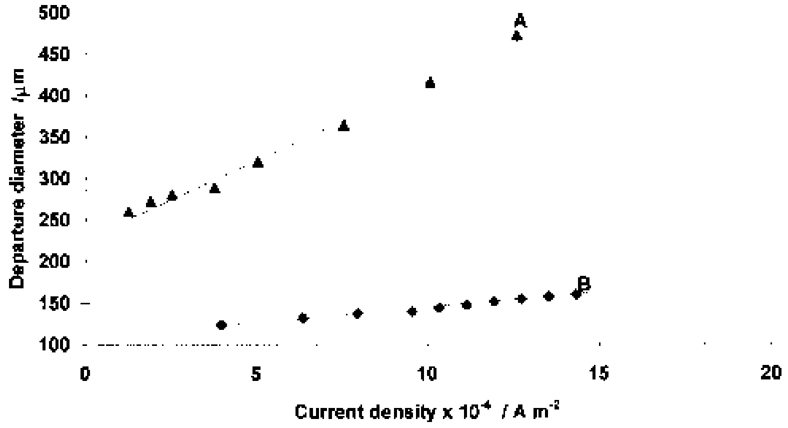

Fig. 4. Hydrogen bubble departure diameters as a function of current density at a (a) 225 μm and a (b) 40 μm diameter Cu electrode in 2.0 M H_2SO_4.

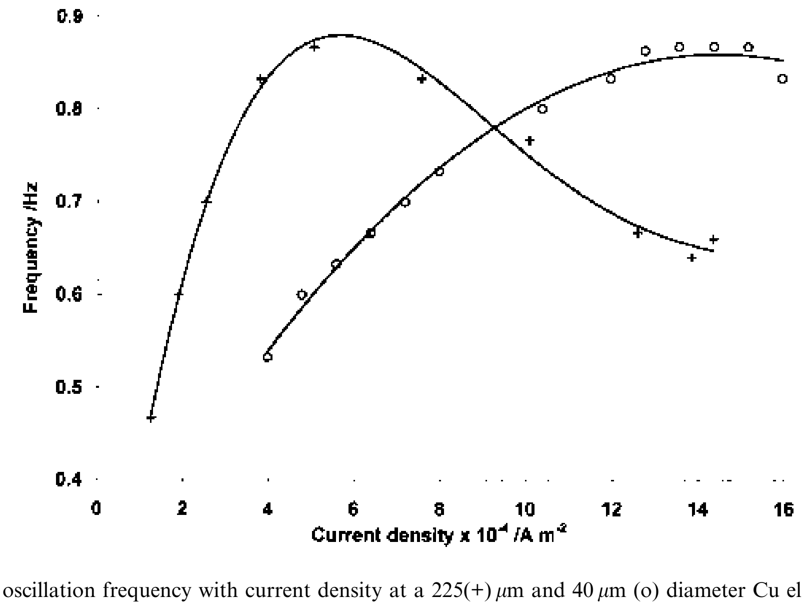

Fig. 5. Variation in the oscillation frequency with current density at a 225(+) μm and 40 μm (o) diameter Cu electrode in 2.0 M H_2SO_4.

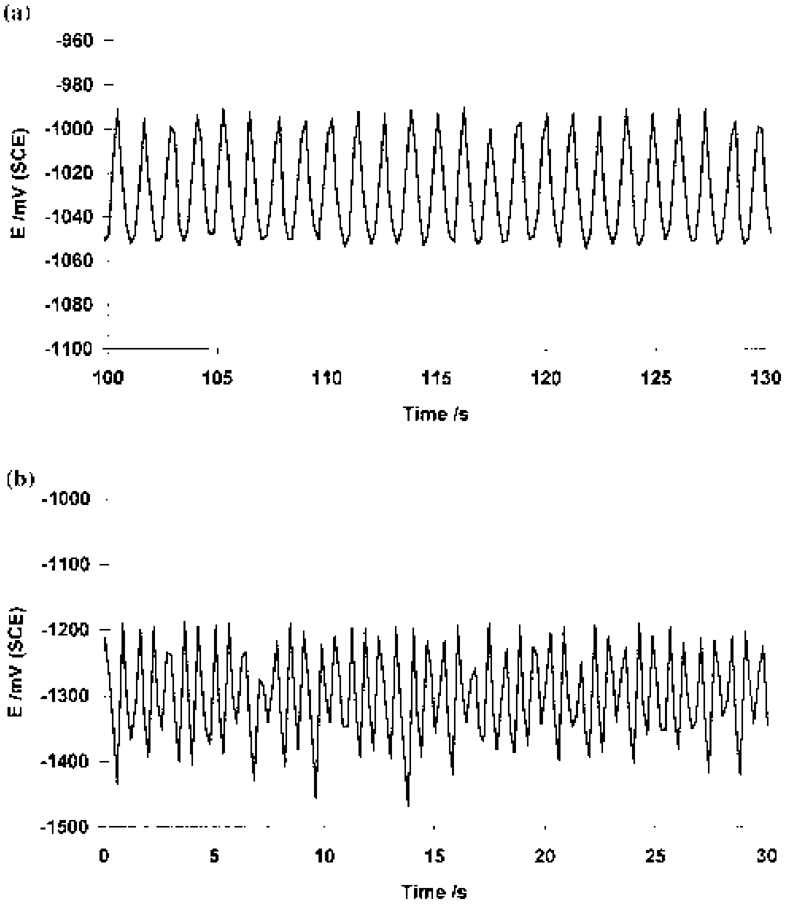

Fig. 6. A comparison of electrode responses at a 40 μm diameter Cu electrode in electrolytes (a) 2.0 M H_2SO_4 and (b) 2.0 M HCl at 100 μA.

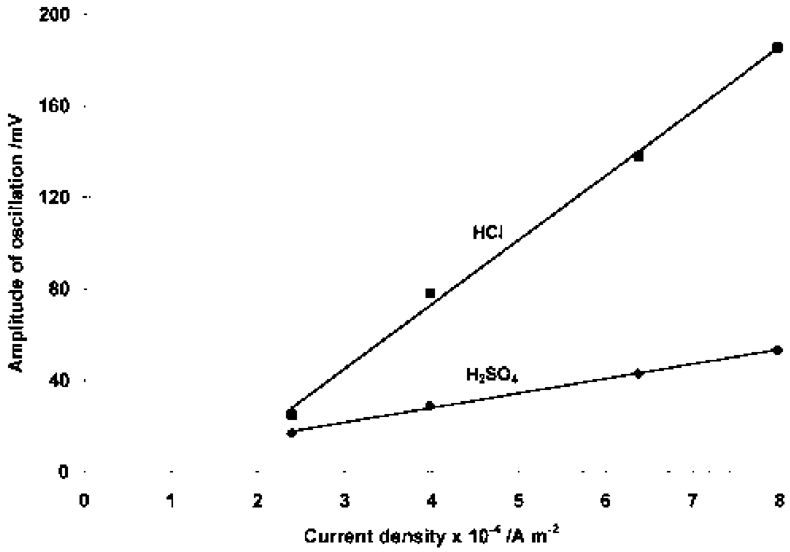

Fig. 7. Comparison of the variation in the oscillation amplitude (cathodic) with the current density at a 40 μm diameter Cu electrode in 2.0 M HCl and 2.0 M H_2SO_4.

H_2SO_4 solutions, gas evolution occurs by the nucleation and growth of a single large bubble at any one time. At the resolution level of the video camera, very little growth occurs via coalescence. As more salt is added, the mode of gas evolution changes to one where it involves the formation and growth of a swarm of several smaller bubbles (heretofore called multibubble growth) rather than a single large one.

Examination of the responses (Fig. 8) for an upward-facing electrode corresponding to this change in Na_2SO_4 concentration confirms that there is a strong relation between the mode of bubble growth and the waveform appearing in the transients. When gas evolution involves only a single bubble at any one instant, nucleation, growth and detachment occur as distinct steps. Consequently, a well-defined, regular

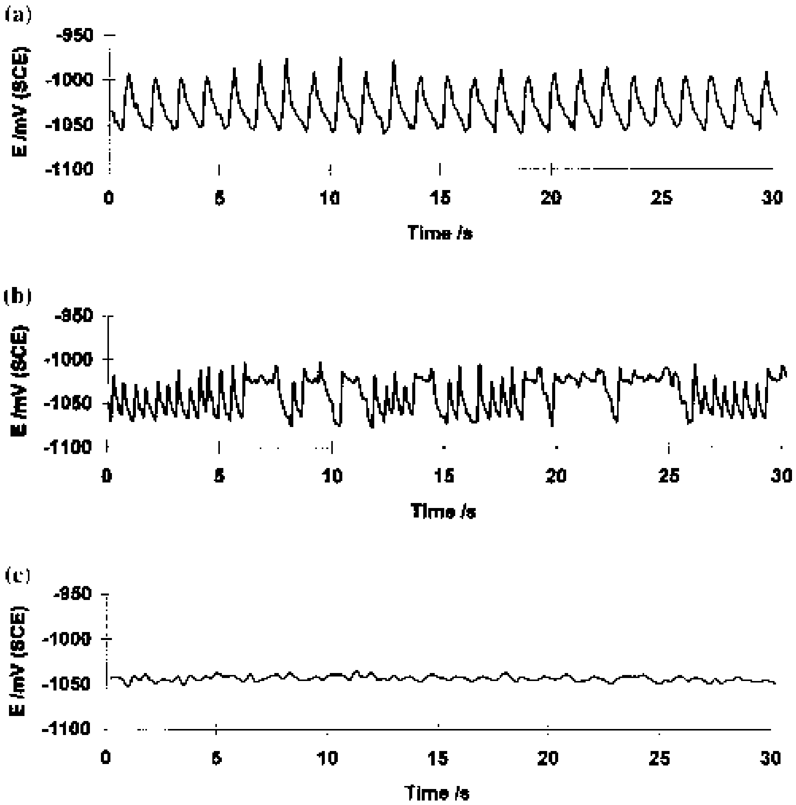

Fig. 8. Electrode responses for hydrogen evolution at 100 μA in 2.0 M H_2SO_4 solutions containing (a) 0.0, (b) 0.25 and (c) 0.50 M Na_2SO_4 at an upward-facing electrode.

and sustained oscillating pattern in the electrode response will result (Fig. 8(a)). On the other hand, whenever many bubbles are nucleating, growing and detaching at any point in time, the synchronicity of events is lost. This leads to a noisy irregular signal or, at the extreme, a flat response with no distinct features when the events occur randomly and completely cancel each other out (Fig. 8(c)).

The addition of supporting electrolyte may have several effects which contribute to multibubble growth. The first one is the salting-out effect which leads to a reduction in gas solubility in water as a salt is added. This will increasingly make it easier for gas bubbles to nucleate than for dissolved molecular hydrogen to diffuse to the surfaces of existing bubbles. Such a promotion of nucleation over growth will lead to multibubble formation at the expense of single bubble formation. Although many small bubbles might form, it still may be possible for a single large bubble to ultimately dominate if the small bubbles can quickly coalesce. The coalescence of small bubbles into larger bubbles requires that the structured water layer between bubbles be broken down to a critical thickness before coalescence can occur [22–24]. Moreover, the time for this process must be less than the contact time between adjacent bubbles. The addition of supporting electrolyte works against coalescence as well since ions are structure-formers that coordinate water into a more ordered and stable structure and oppose the collapse of adjoining bubbles.

Also included in Fig. 8 is the electrode response obtained when the Na_2SO_4 is at an intermediate level of 0.25 M. In this case, we obtain a very interesting result where both single and multibubble growth occur on the electrode at different times during a given polarization experiment. This is marked by an electrode response which displays the regular sustained oscillations of single bubble growth interspersed with the relatively flat signal characteristic of the multibubble regime. Visually this appears as random periods of regular single bubble growth and irregular multibubble growth on the same electrode surface.

This behaviour also enables an important observation concerning the effect of gas evolution on the electrode response to be made. In all instances during the polarization at the intermediate concentration where gas evolution changes from single- to multibubble mode, the potential abruptly shifts in the anodic direction to the value at the positive-most end of the oscillation cycle and remains essentially constant at this level until single-bubble growth resumes. Since this shift can only be attributed to the mode of gas evolution, this observation provides direct evidence that multibubble growth is less polarizing than single-bubble growth.

3.5 *Effect of NaCl on hydrogen bubble evolution in 2.0 M HCl*

The effect of the addition of NaCl to HCl solutions shows some of the same trends observed in the sulphate media, but also some important differences. As shown in Fig. 9, the addition of NaCl tends to promote multibubble growth and dampens out the

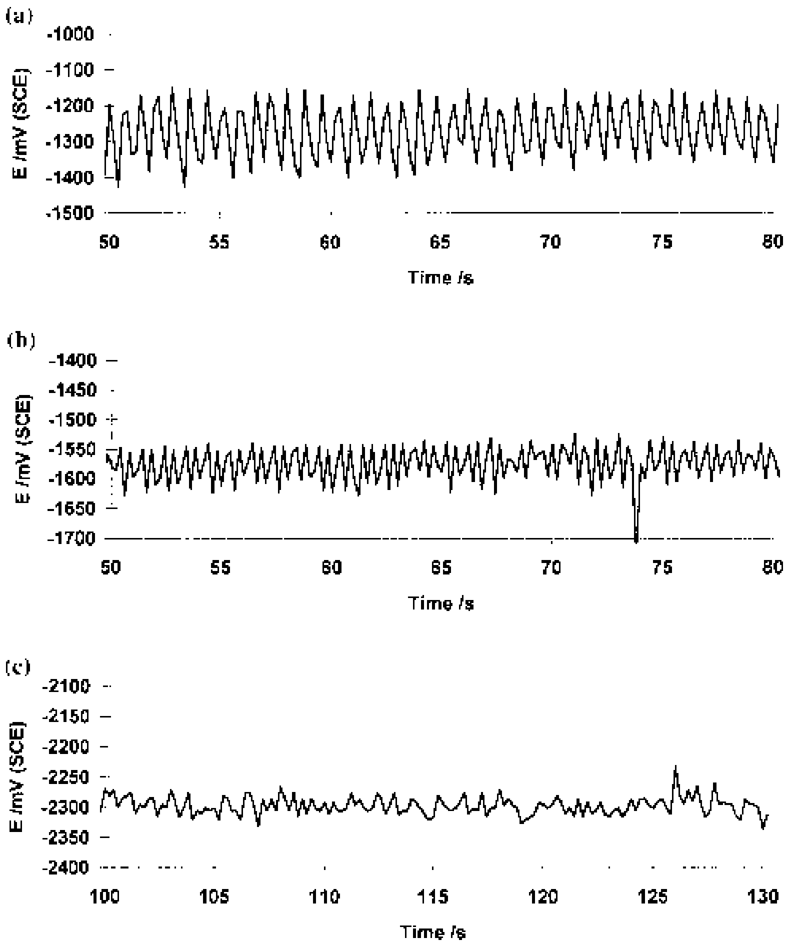

Fig. 9. The effect of NaCl concentration on the electrode responses for hydrogen evolution in 2.0 M HCl at 100 μA: [NaCl]: (a) 0.0, (b) 0.25 and (c) 2.0 M.

oscillations in the electrode response, although, as discussed previously, the signals are always relatively noisy in chloride solutions. Comparisons of Figs 8 and 9 also shows that the oscillation amplitudes and frequencies are always much higher in the chloride system.

Bubble formation appears from the video images to be different from that in sulfate media. Coalescence of small bubbles into larger ones always plays an important role, even at low NaCl concentrations when a single large bubble ultimately dominates. There is consequently no clear distinction between single-bubble and multibubble modes, as there is in the other system. The corresponding electrode response does not display the separate segments characteristic of single-bubble and multibubble growth that the sulfate system exhibits. At low NaCl concentrations, growth begins with a single small bubble (~40–50 μm) establishing itself as a central collector that consumes smaller bubbles surrounding it to ultimately become a large one. Once the NaCl is increased to 0.25 M, there are no periods of distinct multibubble growth or single-bubble growth but rather an intermediate mode when a single large bubble and a few small ones grow simultaneously. With a further increase in NaCl concentration, the system gradually moves into multibubble mode as the single large bubble is replaced by a few of medium size. The resulting distribution of a few medium-sized bubbles surrounding many smaller ones is maintained even when the NaCl concentration reaches 2.0 M. Such a distribution differs from the one associated with multi-bubble growth in sulfate media, which consists of swarms of much smaller and more uniformly sized bubbles.

Another important difference between sulfate and chloride systems is in the way in which an increase in salt concentration affects the extent of polarization of the copper electrodes. A rise in the Na_2SO_4 level increases the average electrode potential only very slightly at a current of 100 μA (Fig.8), whereas similar changes in the NaCl concentration substantially increase the polarization (Fig. 9). Although not included in this paper, the results obtained at other currents show this same trend. In the absence of gas evolution and any specific interactions between the electrolyte species and the electrode, one would expect a small increase in the cathodic polarization with a rise in supporting electrolyte concentration. Recent calculations have shown this to be due to the competition between Na^+ and H^+ as charge carriers in the boundary layer adjacent to the electrode [27]. The electric field draws Na^+ toward the cathode, replacing H^+ ions that would otherwise be present. Therefore when more Na^+ is added to the solution, the system responds by increasing the cathodic polarization in order to maintain a constant current (i.e., constant rate of H^+ consumption). Although the magnitude of this effect has some dependence upon the nature of the electrolyte, it is nowhere of the magnitude to explain the observed differences between the sulfate and chloride systems.

The difference between the two electrolytes is undoubtedly related to the fact that Cl^- can interact strongly with the copper metal electrode and likely forms surface compounds [26], whereas SO_4^{2-} does not. The formation of these surface compounds blocks possible sites for hydrogen evolution. This causes the cathodic polarization to rise in order to maintain the rate of hydrogen evolution at the level required for a given applied current. Obviously, as more NaCl is added to the electrolyte, the more readily will copper chloride surface complexes form and the higher the polarization for hydrogen evolution will become.

3.6 *Effect of thiourea on hydrogen bubble evolution in 2.0 M H_2SO_4*

A series of polarization experiments were conducted to study the effect of thiourea on hydrogen gas evolution in 2.0 M H_2SO_4 over a range of concentrations. The resulting transients obtained at a current of 100 μA for thiourea levels from 0 to 1.31 mM are presented in Fig. 10. As evident, the addition of the organic does not destroy the regular sustained potential oscillations and the single-bubble mode of gas evolution characteristic of H_2SO_4-only solutions. However, it does have a significant effect on some of the features of the electrode responses.

The average potential obtained over the course of each transient gives a measure of the polarization required to sustain the applied current. Fig. 11 shows how this average potential varies with the thiourea concentration at applied currents of 50 and 100 μA. The curves for both currents are very similar, showing a rise in cathodic overpotential up to a concentration of about 0.13 mM thiourea. Beyond this level, the overpotential decreases until it levels off to a constant value above about 1.3 mM organic. Since this constant value still exceeds the potential obtained in the absence of the organic, it is evident that thiourea always increases the electrode polarization regardless of the amount added.

The dependence of the electrode potential with organic concentration shown in Fig. 11 is very similar to results reported previously by Jofa [25] and Agrawal and Namboodhiri [28] for the same process

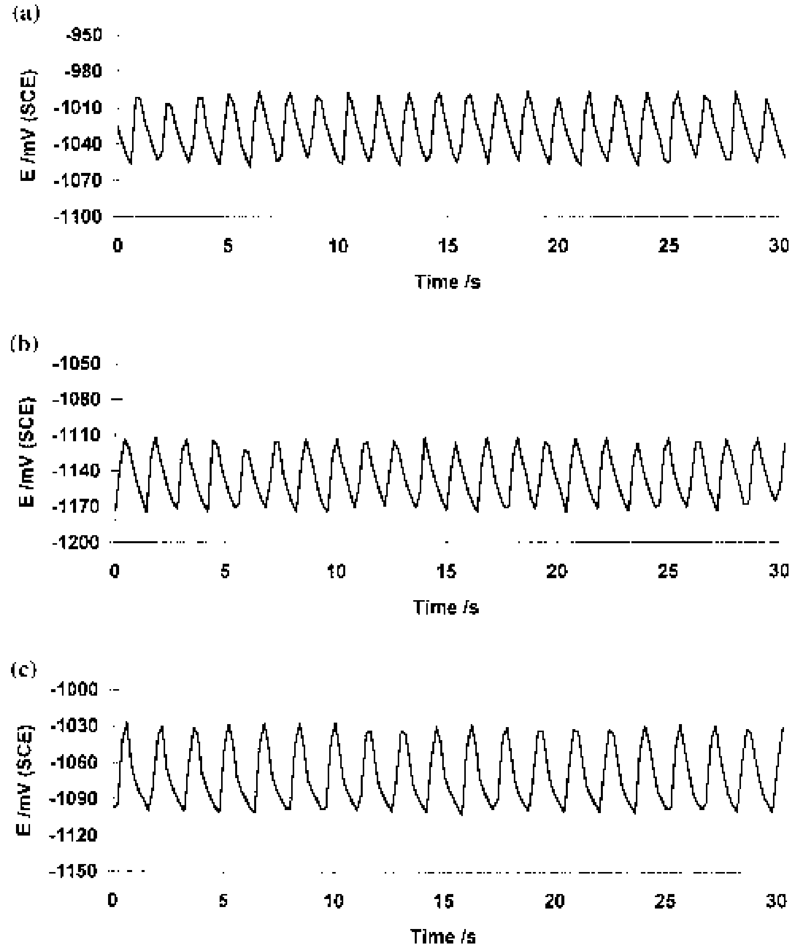

Fig. 10. Electrode responses for hydrogen evolution at 100 μA in solutions containing 2.0 M H_2SO_4 and different amounts of thiourea: (a) 0.0, (b) 0.13 and (c)1.31 mM.

Table 2. Amplitude and frequency of overpotential oscillations for hydrogen evolution at a 40 μm Cu electrode and 100 μA as a function of thiourea concentration in 2.0 M H_2SO_4

Thiourea concentration /mM	0	0.065	0.13	0.20	0.26	0.52	0.78	1.05	1.30
Frequency /Hz	0.80	0.90	0.76	0.74	0.74	0.74	0.74	0.74	0.74
ΔV /mV	53	40	57	63	65	65	65	65	65

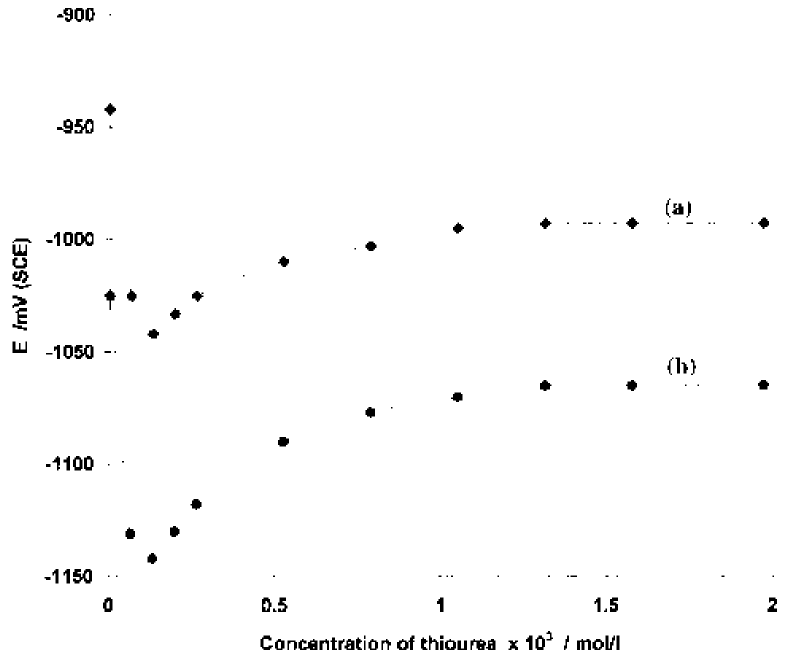

Fig. 11. Effect of thiourea concentration on the overpotential at a 40 μm diameter Cu electrode in 2.0 M H_2SO_4 at (a) 50 and (b) 100 μA.

on an iron electrode. Moreover, they found that maximum polarization occurred at essentially the same thiourea level as the value of 0.13 mM reported here. Evidently, the action of thiourea does not depend on the nature of the metal substrate, at least as far as copper and iron are concerned. Accordingly, the explanation for the effect of thiourea concentration offered previously for iron may apply for the case of copper as well.

At low organic levels, a rise in its concentration increases its adsorption onto the metal and so blocks more of the surface. Chemisorption of thiourea at metal surfaces takes place through its sulfur atom with electron transfer by the loosely bound electrons in the S=C π bond. The amine groups of the adsorbed thiourea are oriented towards the solution and can be protonated by H^+ ions that are in the vicinity of the electrode. This further reduces the amount of hydrogen evolution that occurs.

A maximum in the polarization occurs because once enough thiourea is present, thiourea itself can be electrochemically reduced by the reaction [25]:

$$(NH_2)_2CS + 8H^+ + 6e^- \rightarrow H_2S + CH_3NH_3^+ + NH_4^+ \quad (1)$$

This reaction removes adsorbed species from the electrode surface and restores some of the nucleation sites. In addition, the production of H_2S at the surface is believed to further facilitate hydrogen-ion discharge [29, 30].

Since gas evolution is still dominated by the nucleation and growth of a single bubble in the presence of thiourea, it is possible to evaluate the oscillation frequency and amplitude and bubble departure diameter, as was done in Section 3.2. The results of the analysis of the transients for a current of 100 μA in Table 2 show that the oscillation frequency reaches a maximum of 0.9 Hz and the amplitude reaches a minimum of 40 mV at a thiourea concentration close to where the polarization well appears in Fig. 11. Although not shown here, the bubble departure diameter varies with thiourea concentration in a manner similar to these other electrode response measures.

A surface tension effect which could alter the lifetime of a bubble is not likely an important factor for this dependence on thiourea concentration since it has been found that this organic has no detectable effect on the surface tension in similar electrolytes [31]. Furthermore, there was no evidence from the video images of departing bubbles leaving behind a layer of gas which would be indicative of a decreased surface tension between the electrode and bubble.

A possible explanation is related to the previously discussed reactions involving thiourea and their effect on the electrostatic interaction between the bubble and electrode. At a low concentration of thiourea, the electrode surface is covered with thiourea in its protonated form. Thus, the cathode which is highly negatively charged in thiourea-free electrolyte, becomes less so as more thiourea is added. It is also known that hydrogen bubbles are positively charged in 2.0 M H_2SO_4 solution [21]. Therefore, with an increase in thiourea, a positive bubble senses a less negative electrode surface and consequently the departure diameter shrinks. At high thiourea concentrations, on the other hand, HS^- produced as a result of Reaction 1 adsorbs on the electrode, making it more negative in comparison to the case of a thiourea-free system. This enhances the electrostatic attraction between bubble and electrode so that departing bubbles in a concentrated solution of thiourea would be larger than in the thiourea-free electrolyte. More work is needed to verify this possible explanation.

4. Conclusion

Electrolyte composition has been shown to have a significant effect on the dynamics of hydrogen gas evolution at copper microelectrodes and the corresponding potential-time curves. In acid-only solutions, nucleation of gas bubbles remains difficult enough that one bubble dominates the events occurring at the microelectrode at any one time. This is closely reflected in the response of the microelectrode, which exhibits regular and sustained oscillations in the electrode potential. The addition of inorganic salts such as Na_2SO_4 and NaCl facilitates nucleation and inhibits coalescence so that at any point in time numerous small bubbles are nucleating, growing and detaching. With a sufficiently high salt ion concentration, the loss in synchronicity of events at the cathode leads to the total disappearance of potential oscillations. This mode of bubble evolution has also been found to be less polarizing than the type where nucleation is inhibited. The addition of an organic such as thiourea to a 2.0 M H_2SO_4 solution has been found not to change the mode of bubble evolution, but instead to change it quantitatively by increasing the cathodic polarization and altering the oscillation frequency and amplitude of the electrode response.

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