SHORT COMMUNICATION

Characterization of surface roughness by EHD impedance

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1. Introduction

The EHD impedance response of a smooth electrode with a periodically distributed reactivity has been predicted [1, 2]. A quantitative analysis of the diagram can be performed which allows the average dimensions of the active sites to be measured from consideration of the two time constants appearing in the response. These predictions were compared with an experimental investigation using a photolithographic model of partially blocked electrodes and good agreement between theory and experiment was obtained [3].

A first analogy between partial blocking of a surface and surface roughness was done for the investigation of tellurium electrocrystallization by the EHD impedance technique [4]. Due to the complexity of the electrodeposition process only a qualitative conclusion could be obtained. In the present work a rough surface was obtained by electrodeposition of copper under well defined conditions then the surface was coated with a thick nickel layer so that the reactivity was uniform at any point. This technique of covering the rough surface with a thin inert metal layer was previously used by Vandeputte *et al.* [5, 6]. A redox reaction with a very fast couple ($Fe(CN)_6^{3-}$/$Fe(CN)_6^{4-}$) was performed and all modifications of the EHD impedance diagrams relative to the ideal one obtained on a smooth electrode are ascribable to the roughness. Analysis of the diagrams provides the order of magnitude of the average size and depth of the surface roughness.

2. Experimental details

Electrochemical conditions for obtaining a nodular copper deposit in acidic copper sulfate solution on a copper electrode are well known [7, 9]. The electrolyte was an aqueous solution of H_2SO_4 (1.77 M) with $CuSO_4$ (0.6 M); convection was imposed by means of a rotating disc electrode (1000 rpm), the temperature was 20 °C and the electrode was polarized at −241 mV for 12 min. The corresponding deposit is shown in Fig. 1.

This deposit was washed in distilled water, then immersed in a Watts bath and coated for two minutes to obtain a 1 μm thick uniform nickel layer. On this nickel surface, the limiting current for the ferricyanide reduction in NaOH (2 M) solution was recorded versus the rotation speed of the disc and the corresponding EHD impedance was measured for different rotation speeds.

3. Results

3.1. *Steady-state*

The steady-state current measured on the rough electrode is very close to the current measured on a smooth electrode. In Koutecky–Levich coordinates, a small deviation with respect to the Levich law appears. In fact, this kind of deviation can have different origins: mixed kinetic control, distributed reactivity (partial blocking), diffusion through a porous inactive layer. Steady-state measurements do not provide sufficient evidence to explain this deviation [2], and from these measurements only, it is impossible to obtain information on the surface roughness.

3.2. *EHD impedance*

The EHD impedance diagrams were measured at the limiting current ($V = -142$ mV vs SCE), the frequency range was 0.005–40 Hz and the measurements are performed at three mean velocities: 250, 500 and 1000 rpm. The linearity conditions were verified using a 10% speed modulation of the mean velocity.

The corresponding diagrams are presented in Fig. 3 in Bode coordinates. For theoretical reasons, the diagrams are plotted versus the dimensionless frequency p ($p = \omega/\Omega$).

3.2.1. Low frequency ($p < 0.1$). In this range, diagrams obtained at different rotation speeds collapse on the curve obtained for a smooth electrode. The Schmidt number of the solution can be determined by a fitting procedure [10], and a value of 4300 is obtained from these measurements. In this frequency range, the behaviour of the rough electrode is similar to that of a smooth electrode, this result is in agreement with the steady-state measurements.

When the diffusion layer thickness is larger than the roughness height, no modification of the limiting current can be detected at steady state. In nonsteady-state conditions, the perturbation distance of the concentration boundary layer is approximately $\sqrt{(D/\omega)}$ and hence, in the low frequency range, this distance is larger than the roughness height and no effect appears. The roughness effect appears when its height is of the same order of magnitude as the perturbation distance. Effectively, in Fig. 2, the frequency at the

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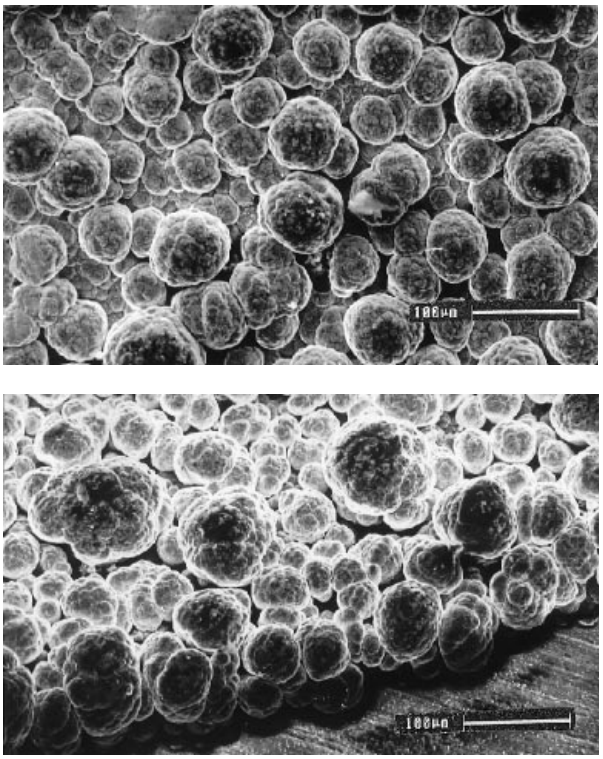

Fig. 1. SEM micrographs of copper deposit (a) perpendicular to the surface and (b) at an angle of 42°.

separation between the curve obtained for a smooth electrode and for a rough electrode, is almost independent of the rotation speed and equal to 1 Hz; then the corresponding perturbation distance is 10 μm. This value is in agreement with the roughness height evaluated from Fig. 1(b).

3.2.2. High frequency ($p > 2$). In this range, again all diagrams collapse to one, whereas in the middle frequency range, they become separated for each rotation speed. As previously mentioned in [4], this behaviour is very similar to that for partial blocking of the interface [1]. In this analogy, the current distribution around each protrusion is similar to that around an active site in a smooth surface. Therefore, as for a partially blocked smooth surface, the HF behaviour of the rough surface yields a single response versus p and the characteristic size, d, of the protrusion in the electrode plane can be deduced from the frequency difference between the two characteristic frequencies of the HF and LF regimes.

According to [1]

$$d = 2.1^{\frac{3}{2}} R \left(\frac{p^*_{HF}}{p^*_{LF}} \right)^{-\frac{3}{2}} \quad (1)$$

The order of magnitude of p^*_{HF}/p^*_{LF} deduced from Fig. 3 is about 50 and therefore an average dimension of the protrusion in the electrode plane can be estimated by use of Equation 1 to 30 μm. This result is in good agreement with the direct observation (Fig. 1) and confirms the fact that, for a rough electrode, only the peaks of the roughness are active, in agreement with the result of Chassaing *et al.* [11] obtained by a visualization technique.

4. Conclusion

The EHD impedance is a useful technique to determine the average size (in a plane parallel to the wall) and the average height (in the direction perpendicular to the wall) of roughness on a uniformly reactive electrode.

Due to the maximum frequency available for

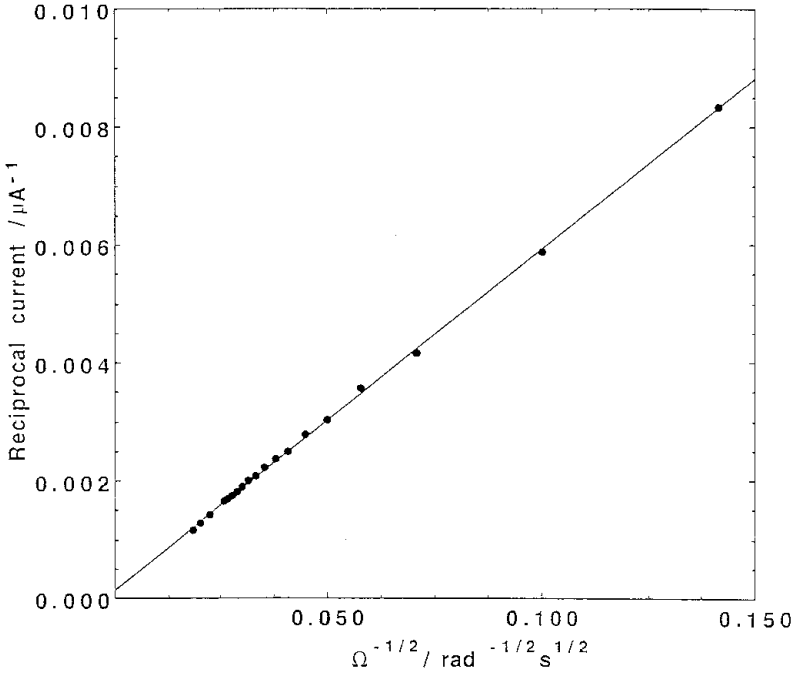

Fig. 2. Koutecky–Levich plot of the limiting current.

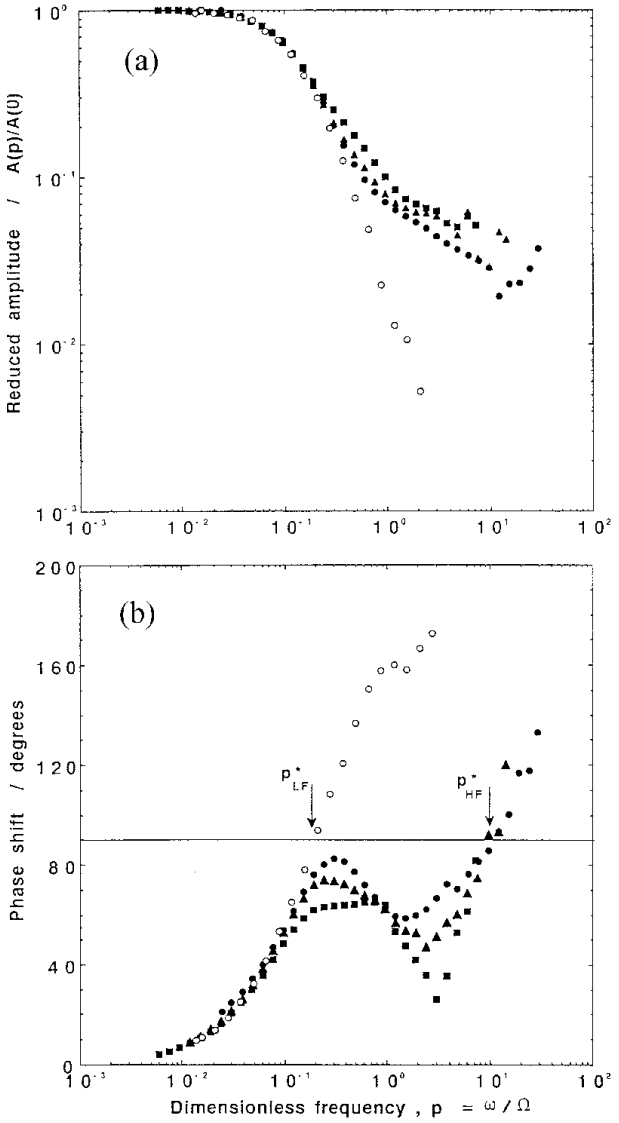

Fig. 3. EHD impedance diagrams obtained at different rotation speeds: (●) 250 rpm, (▲) 500 rpm and (■) 1000 rpm on the rough electrode of Fig. 1. (○) 900 rpm on a smooth nickel electrode in the same electrolyte.

mechanical modulation and the signal to noise ratio, the lower limit of detection for the roughness dimension is of the order of few micrometres.

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