JOURNAL OF APPLIED ELECTROCHEMISTRY 17 (1987) 1144–1149

Anodic levelling of model profiles with pulsating current

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Received 6 February 1987

The rate of anodic levelling with pulsating current is being investigated with triangular model profiles made of nickel using a flow channel cell. Observed results are compared to theoretical calculations of the rate of anodic levelling of macroprofiles and of microprofiles under d.c. conditions. It follows that the rate of anodic levelling is smaller above the pulse-limiting current density than that below it, and is smaller than that predicted for an ideal macroprofile. With pulsating current the rate of levelling of macroprofiles did not depend on profile orientation with respect to electrolyte flow.

1. Introduction

The use of pulse current for electrochemical shaping and polishing of metals offers an attractive alternative to d.c. because the selection of pulse parameters allows one to influence the current distribution, mass transport conditions and current efficiency at the anode [1–3]. Electropolishing involves anodic levelling and anodic brightening. The latter is usually observed at or above the mass transport-limited current in the presence of a salt film [4]. Datta and Landolt [1] studied the anodic dissolution of nickel in NaCl in a flow channel cell using pulse current and found that the onset of surface brightening correlated with the non-steady-state mass transport conditions leading to salt film precipitation at the anode. No systematic study of the rate of anodic levelling resulting from anodic dissolution with pulse current has been carried out up to now. According to Puippe *et al.* [5] it is to be expected that under mass transport-controlled conditions the rate of anodic levelling with pulse current is low because the pulsating diffusion layer which is usually much smaller than the steady-state Nernst diffusion layer should follow the surface profile closely. The rate of levelling under these conditions, therefore, should correspond to that of macroprofiles in d.c. electrolysis. The rate of anodic levelling of macroprofiles* has recently been studied theoretically and experimentally by the present authors [6]. The aim of the present study is the experimental investigation of the rate of anodic levelling of model profiles with pulse current under well-defined mass transport conditions. Measured rates of levelling are compared to those observed previously with d.c. [7] and to theoretical models. Nickel in NaCl was chosen as a model system because its d.c. levelling behaviour is well known [7].

2. Experimental details

The levelling experiments were carried out in a flow cell apparatus which has been described elsewhere [7]. The electrodes (5 × 3 mm) were positioned flush with the wall of a channel (3 mm wide) at a distance of 0.5 mm. The anode faced downwards and its position could be corrected for dissolution by means of a stepping motor. The model profiles used were mechanically machined from high-purity nickel (Johnson Matthey Specpure, 99.99%) or from commercial grade nickel (nickel 200, 99%). The profiles were of triangular shape. Their height, ε_0, was 39 μm and their wavelength, λ, was 100 μm. They could

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* By definition, a macroprofile has a profile height larger than the diffusion layer thickness, and a microprofile has a profile height smaller than the diffusion layer thickness.

0021-891X/87 $03.00 + .12

Table 1. Experimental conditions of levelling experiments

Number	*Anode material*	*NaCl conc. ($mol\,l^{-1}$)*	*Flow rate ($m\,s^{-1}$)*	t_p *(ms)*	t_{pp} *(ms)*	i_p *($A\,cm^{-2}$)*	i_m *($A\,cm^{-2}$)*
1	Ni 200	0.5	21.3	0.1	10	40	0.40
2	Ni 200 Ni h.p.	5.0	3.0	1.0	100	38.4	0.38
3	Ni 200	5.0	3.0	0.1	10	38.4	0.38
4	Ni 200	5.0	3.0	0.01	1	38.4	0.38
5	Ni 200 Ni h.p.	5.0	8.0	0.1	10	350	3.50

be oriented parallel or perpendicular to the electrolyte flow. Rectangular current pulses were furnished by a pulse generator (Egatec PLS 300, 100 A/100 V), having a risetime in the microsecond range. Current and cell voltage were recorded with a digital oscilloscope (Nicolet Type 206). All experiments were performed at 25°C using a 0.5 M or a 5 M NaCl electrolyte prepared from analytical grade chemicals (Merck) and doubly distilled water. Before an experiment the electrodes were washed with soap solution, ultrasonically cleaned for 5 min, rinsed, then cathodically prepolarized in the working electrolyte for 5 s at 5 mA cm^{-2}. After rinsing and drying they were placed in the flow cell. Dissolution was carried out in steps. After each step the surface profile was recorded with a mechanical surface tester (Talysurf 10) by scanning over eight consecutive asperities at a distance of 1.5, 2.5 and 3.5 mm from the upstream end. The resulting average values of profile height are reported in the results section.

The experimental conditions employed in the levelling experiments, carried out with pulsating current, are summarized in Table 1. The duty cycle, $\gamma = t_p/(t_p + t_p')$ (where t_p is the pulse on-time and t_p' the pulse off-time), was 0.01 in all experiments. Table 2 lists the mass transport conditions corresponding to the different experiments. The Nernst diffusion layer thickness, δ, and the steady-state limiting current density, i_l, were calculated for flat electrodes using dimensionless mass transport correlations [7]. The non-steady-state mass transport parameters, δ_p (pulsating diffusion layer thickness) and i_{pl} (pulse-limiting current density), were calculated from the Ibl duplex diffusion layer model [8] adapted to anodic dissolution by Datta and Landolt [1]. For small duty cycles ($\gamma \ll 1$) and constant current efficiency, the thickness of the pulsating diffusion layer is [9]:

$$\delta_p \approx \left(\frac{4}{\pi} D t_p\right)^{1/2} \qquad (1)$$

and the limiting pulse current density is:

$$i_{pl} \approx \frac{i_l}{\frac{\delta_p}{\delta}\left(\frac{1 - t_p}{t_{pp}}\right) + \left(\frac{t_p}{t_{pp}}\right)} \qquad (2)$$

Here $t_{pp} = t_p + t_p'$ is the pulse period. The limiting pulse current density, i_{pl}, is the current density at which the saturation concentration of nickel chloride is reached at the anode at the end of a pulse.

Table 2. Mass transport parameters of levelling experiments

Number	*Reynolds number*	δ *(μm)*	i_l *($A\,cm^{-2}$)*	δ_p *(μm)*	i_{pl} *($A\,cm^{-2}$)*	δ_p/δ	i_m/i_l	i_p/i_{pl}
1	17800	1.3	54	0.34	200	0.27	0.01	0.2
2	1900	5.9	8.0	1.1	43	0.18	0.05	0.9
3	1900	5.9	8.0	0.34	120	0.06	0.05	0.32
4	1900	5.9	8.0	0.11	288	0.02	0.05	0.13
5	5050	3.6	13.0	0.34	127	0.1	0.26	2.8

The physical properties used in the calculations were the same as in [7], namely $\nu = 1.03 \times 10^{-2}\,\mathrm{cm^2\,s^{-1}}$ and $\nu = 1.35 \times 10^{-2}\,\mathrm{cm^2\,s^{-1}}$ for the kinematic viscosity of 0.5 M and 5 M NaCl, respectively, and $D = 9 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$ for the effective diffusion coefficient. The saturation concentration of nickel in 5 M NaCl is $C_{\mathrm{sat}} = 2.71 \times 10^{-3}\,\mathrm{mol\,cm^{-3}}$ and is estimated as $C_{\mathrm{sat}} = 4 \times 10^{-3}\,\mathrm{mol\,cm^{-3}}$ in 0.5 M NaCl.

3. Results

All results are presented in dimensionless form. The dimensionless amplitude is $\varepsilon/\varepsilon_0$, where ε is the measured profile height at any time t and ε_0 is the initial profile height. The dimensionless charge density, Q^*, is the measured charge density q (referred to the projected area) divided by the charge density, q_0, which corresponds to dissolution of a thickness ε_0 on a flat surface.

The results of experiment 1 are presented in Fig. 1. The applied pulse current density in this experiment (Table 2) was much smaller than the pulse-limiting current density ($i_{\mathrm{p}}/i_{\mathrm{pl}} = 0.25$), and the average current density, i_{m}, was much smaller than the d.c. limiting current density ($i_{\mathrm{m}}/i_{\mathrm{l}} = 0.01$). Mass transport effects, therefore, are negligible.

The Wagner number characterizing current distribution in the absence of concentration gradients is $Wa = \beta\kappa/i_{\mathrm{p}}L$, where β is the Tafel slope (natural logarithmic scale), κ the electrolyte conductivity, i_{p} the pulse current density and L a characteristic length. Using $\beta = 0.085/2.3 = 0.037\,\mathrm{V}$ for nickel, $\kappa = 0.0468\,\Omega^{-1}\mathrm{cm}^{-1}$ for 0.5 M NaCl [7] and setting L equal to ε_0, one obtains $Wa = 0.01$. Such a low value of Wa means that current distribution is of the primary type. Indeed, in Fig. 1 the experimentally measured data points closely follow the theoretical curve for primary current distribution calculated by FEM [10].

The profile orientation with respect to flow does not influence the rate of levelling, confirming that steady-state mass transport is not a limiting factor [7].

Experiments 2 to 4 were performed in 5 M NaCl under the same conditions with respect to electrolyte flow, pulse current density and duty cycle. They differed in the absolute values t_{p}, t'_{p} and, consequently, in the ratio $i_{\mathrm{p}}/i_{\mathrm{pl}}$. In experiment 2, $i_{\mathrm{p}}/i_{\mathrm{pl}} \approx 0.9$ and saturation concentration is almost reached at the surface of the electrode at the end of the current pulse. In experiment 4, the ratio $i_{\mathrm{p}}/i_{\mathrm{pl}} \approx 0.13$ and non-steady-state mass transport effects should be largely absent. Experiment 3 lies inbetween. Results obtained for the three experiments using two nickel qualities and profiles oriented parallel and perpendicular to the electrolyte flow are shown in Fig. 2. The data points of the three experiments lie close to each other, indicating that the choice of pulse parameters had little effect on the rate of anodic levelling within the range studied. Profile orientation and nickel purity had no influence either. However, compared

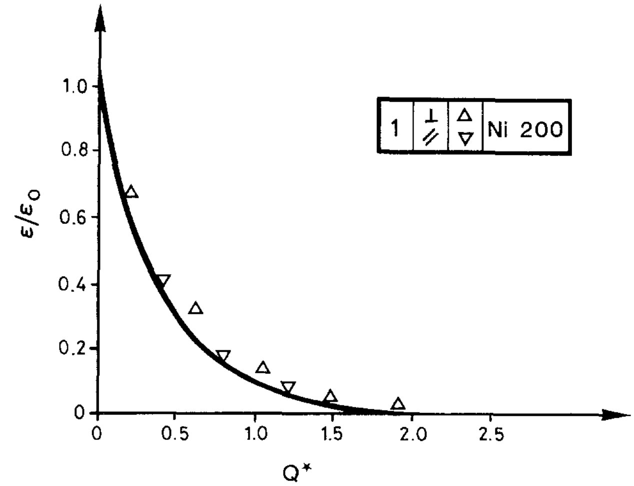

Fig. 1. Decrease of dimensionless profile height as a function of dimensionless charge density for experiment 1. Solid line, calculated for primary current distribution ($\varepsilon_0/\delta = 0$).

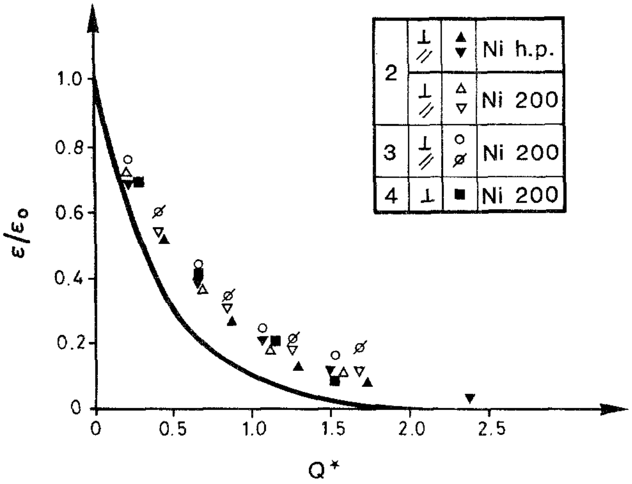

Fig. 2. Decrease of dimensionless profile height as a function of dimensionless charge density for experiments 2 to 4. Solid line, calculated for primary current distribution ($\varepsilon_0/\delta = 0$).

to the data of Fig. 1 the rate of levelling was slightly lower in these experiments. Possible reasons for this behaviour will be discussed below.

The experiments presented in Fig. 3 were performed at an applied pulse current density exceeding the pulse-limiting current density, $i_p/i_{pl} = 2.8$. Compared to the data of Fig. 2, the rate of levelling is clearly smaller. The rate of anodic levelling is independent of profile orientation with respect to flow direction because non-steady-state rather than steady-state mass transport was limiting.

4. Discussion

Theoretical aspects of anodic levelling of microprofiles and macroprofiles with d.c. have been discussed previously and a finite element code was developed for the calculation of the rate of anodic levelling under different conditions. For the exact calculation of the rate of anodic levelling with pulse current one has to take into account non-steady-state mass transport and double-layer charging and discharging effects. Such a calculation has not been attempted so far. On the other hand, in the limiting case when mass transport effects are negligible ($i_m/i_l \ll 1$, $i_p/i_{pl} \ll 1$) and the times t_p and t'_p are large compared to the time needed for double layer charging, the rate of anodic levelling with pulse current is governed by the primary or secondary current distribution, just as in the case of d.c., and can be calculated accordingly. The

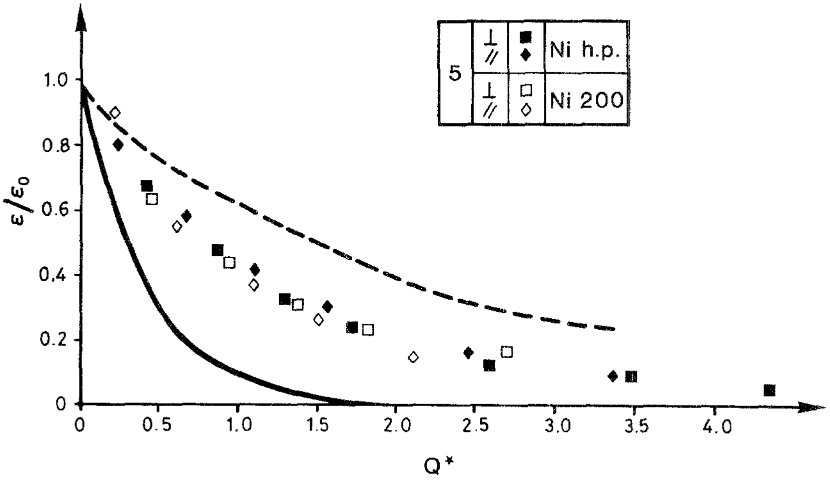

Fig. 3. Decrease of dimensionless profile height as a function of dimensionless charge density for experiment 5. Solid line, calculated for primary current distribution ($\varepsilon_0/\delta = 0$); broken line, calculated for a macroprofile with $\varepsilon_0/\delta = 10$.

maximum rate of levelling thus corresponds to the primary current distribution and is the same with d.c. and pulse current. This rate calculated with the FEM for the cell geometry of the present experiments is shown in Figs 1–3. The experimental data of Fig. 1 obtained in 0.5 M NaCl at low Wagner number in the absence of significant mass transport effects lie close to the limiting rate, thus confirming the described theoretical concepts.

The rate of levelling corresponding to the experimental points in Fig. 2 obtained in 5 M NaCl is close to, but clearly lower than, the limiting rate. Different factors contribute to this behaviour. In experiments 2 and 3 mass transport limitations are not negligible and this is expected to decrease the rate of levelling (see below). In experiment 4, mass transport plays no role but the pulse time is extremely short and double-layer charging and discharging may not be negligible. Since double-layer discharge occurs through faradaic reactions it tends to equalize the current distribution in pulse electrolysis [11]. This slows down the rate of anodic levelling. In addition, compared to the experiments in Fig. 1 the Wagner number is higher here because of the higher electrolyte conductivity.

The experiments in Fig. 3 exhibit the slowest rate of anodic levelling because the applied pulse current density far exceeded the pulse limiting current density. A salt film forms on the anode when the pulse-limiting current density is exceeded during nickel dissolution in NaCl [1]. The presence of a salt film leads to a marked increase in the anode potential and to surface brightening. Experiments performed by the present authors on flat electrodes confirmed this behaviour.

It is known from previous work that in concentrated NaCl, nickel dissolves at 100% current efficiency at pulse current densities below and above i_{pl} [1]. This raises the interesting question of how nickel ions are transported away from the anode. In Fig. 4 linearized concentration profiles of nickel ions near the anode are shown schematically, assuming $\delta_p \ll \delta$ and $\gamma \ll 1$. Since constant current pulses are applied, the concentration gradient of nickel ions at the surface must be constant in the absence of a second reaction. When $i_p < i_{pl}$, the concentration of nickel ions at the surface increases during t_p. At $i_p = i_{pl}$, the saturation concentration is reached at the end of the pulse; this corresponds to $t_p = \tau$ where the transition time, τ, is the time necessary to reach saturation concentration at the anode surface. If $i_p > i_{pl}$, i.e. $t_p > \tau$, the concentration gradient at the anode can be accounted for by either increasing supersaturation or by precipitation and growth of a salt film (Fig. 4). Previous data [1] suggest that significant supersaturation does not occur under present experimental conditions. It is proposed, therefore, that growth of a salt film takes place during the pulse on-time and dissolution of the salt film during the pulse off-time. The rate of levelling under these conditions depends on several factors, including the time-dependent potential and concentration distribution at the beginning of the pulse when $t < \tau$, the potential gradient across the growing salt film and the dissolution rate of the film. Theoretical modelling of these processes is not possible at present. Qualitatively, however, the described behaviour can explain the lower rate of levelling observed in Fig. 3.

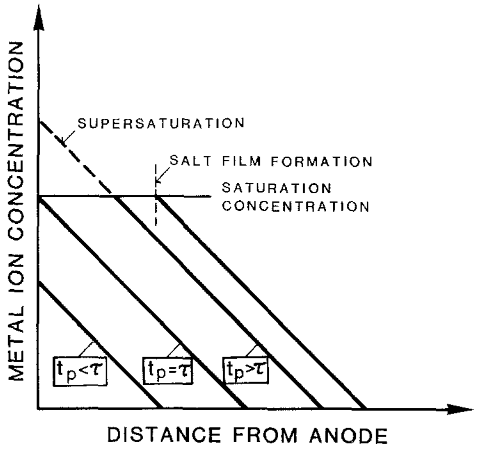

Fig. 4. Linearized concentration profiles of nickel ions in the pulsating diffusion layer (schematic) below ($t < \tau$), at ($t = \tau$) and above ($t > \tau$) the pulse limiting current density.

It has been suggested by Ibl [8] that with pulse current, a pulsating diffusion layer of constant thickness closely follows the surface profile. Puippe *et al.* [5] applied this concept to pulse polishing. To test this idea in a more quantitative way the rate of anodic levelling at constant current was calculated for a macroprofile using the FEM. Results are shown in Fig. 3 for a ratio $\varepsilon_0/\delta = 10$ where δ is the thickness of the Nernst diffusion layer. The value of $\varepsilon_0/\delta = 10$ was chosen because the FEM program used was unstable at values of $\varepsilon_0/\delta > 10$. Comparison of the calculated rate of levelling with the experimental points shows that the theoretical model of a uniform diffusion layer of thickness δ_p leads to levelling rates which are too small. Indeed, a value of $\varepsilon_0/\delta = 100$, which more closely corresponds to the experimental conditions of Fig. 3, would yield an even lower value of the theoretical rate of levelling. Therefore, it is concluded that the simple model of a macroprofile with $\delta \approx \delta_p$ does not give a good description of anodic levelling behaviour in pulse polishing.

5. Conclusions

1. With pulsating current, rates of anodic levelling close to the maximum theoretical rate corresponding to primary current distribution can be realized by a suitable choice of pulse parameters.

2. The rate of anodic levelling well above the pulse limiting current density for salt film formation is smaller than that observed below the pulse-limiting current density, but is higher than that predicted for a macroprofile with a diffusion layer of uniform thickness equal to the pulsating diffusion layer thickness.

3. Over a wide range of conditions, the rate of anodic levelling with pulsating current was found to be independent of the profile orientation with respect to flow, and to be relatively insensitive to the choice of pulse parameters. The use of pulse current, therefore, is an interesting alternative to d.c. for certain surface finishing applications.

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