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# The effect of the concentration of TBACl on the electrodeposition of zinc from chloride and perchlorate electrolytes

M. SÁNCHEZ CRUZ, F. ALONSO, J. M. PALACIOS

*Instituto de Química Física Rocasolano, CSIC, 28006 Madrid, Spain*

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The effect of the concentration (5 to 220 mg $l^{-1}$) of tetrabutylammonium chloride (TBACl) on zinc deposition overpotential and on the degree of levelling of Zn electrodeposited on a Zn RDE was studied by cyclic voltammetry, galvanostatic measurements and SEM examination. The overpotential for Zn electrodeposition initially increases with increasing TBACl concentration until reaching a limiting value, at which point the surface becomes blocked by adsorbed $TBA^+$. The optimum degree of deposit levelling is obtained for intermediate TBACl concentrations, whose value depends on the concentration (1 or 2.5 M) of NaCl supporting electrolyte. When $NaClO_4$ is substituted for NaCl in the bath, the overpotential for Zn electrodeposition markedly increases and consequently the levelling power of TBACl decreases.

## 1. Introduction

It is well known that tetrabutylammonium salts are specifically adsorbed on the surface of many metal electrodes, thus exerting a large retarding effect on the electrodeposition of $Zn^{2+}$ cations [1–3]. The adsorbed $(TBA^+)_{ads}$ cation desorbs from Zn at fairly negative potentials, the exact value depending essentially on the $TBA^+$ concentration and on the nature of the anion of the supporting electrolyte [4, 5]. According to Chuang-Hsin [6] complete desorption from Zn in 1 M KCl + $10^{-3}$ M $TBA^+$ occurs at a potential of − 1.58 V SHE.

MacKinnon *et al.* [7–9] have recently found that TBACl was the most effective levelling agent for smoothing Zn electrodeposits in chloride media. In long duration experiments (24 h) and at fairly high current densities (323 A $m^{-2}$) the addition of 15 mg $l^{-1}$ TBACl to a solution containing 15 g $l^{-1}$ $Zn^{2+}$ + 0.12 M HCl increases the cathodic overpotential for Zn deposition, decreases the grain size of the deposit, suppresses dendritic growth, and increases the current efficiency (CE) to $\geqslant 95\%$.

It has been found that additives which produce the largest increase in cathodic overpotential generally produce zinc deposits with the finest grain size [8, 9]. Diggle and Damjanovic [10] have found that the suppression of dendritic growth and the compactness of the Zn deposit in alkaline zincate solutions increase with TBABr concentration, in the range $10^{-5}$–$10^{-2}$ M.

The effect of the concentration of TBACl on the kinetics of Zn cathodic electrodeposition and on the degree of its levelling effect on the zinc deposit is reported. The effects of total $Cl^-$ concentration and of substituting $ClO_4^-$ for $Cl^-$ anions have also been determined.

## 2. Experimental details

A Metrohm 618-10 rotating disc electrode, 500–3000 rpm, with a detachable Zn (Puratronic, 99.999 Zn pure) cylinder, 0.109 $cm^2$ exposed area, embedded in Araldite was used as the cathode in this study. The use of a detachable zinc cylinder allowed the electrode to be polished mechanically and to be examined by SEM. A vitreous carbon auxiliary electrode, 3 $cm^2$ (one side) area, was located in a separate compartment to avoid contamination of the catholyte by the anodic products.

The reference electrode was an ultrapure Zn wire, 0.2 cm in diameter situated at 3 cm from the working electrode in order to avoid disturbances of the hydrodynamic flow. In this way the cathodic overpotential for Zn electrodeposition was measured directly and independently of the formation of Zn chlorocomplexes. The rest potential of the Zn electrode in the different solutions was also measured with respect to an SCE electrode.

The solutions were prepared with Milli-RO + Milli-Q (Millipore, Bedford, Mass.) ultrapure water and $ZnCl_2$, NaCl, and $NaClO_4$ analytical reagents (AR) from Merck. The $Zn(ClO_4)_2$ solution was prepared by dissolution of AR ZnO with $HClO_4$. The solution pH was always adjusted to 2.6 with HCl or $HClO_4$. TBACl (Ventron-Alfa) was always added to freshly prepared solutions.

Before each experiment the electrode was successively polished in a Buehler 'Minimet' Polisher/Grinder with No. 600 silicon carbide paper and with increasingly fine alumina powder, down to 0.05 $\mu$m,

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on Microcloth, then rinsed thoroughly with ultrapure water, and finally cleaned in an ultrasonic bath.

A Solartron 1286 Electrochemical Interface, with ohmic drop compensation, a Hewlett-Packard 'Color-Pro' plotter (for log $I$ against $\eta$ curves), and a YEW-3033 X-Y-t recorder (for the $I$ against $\eta$ and $\eta$ against $t$ curves) were used. In the cyclic voltammetry experiments a scan of $1\,\mathrm{mV\,s^{-1}}$ was chosen, and galvanostatic experiments were carried out at $-20\,\mathrm{mA}$ for 30 min.

Three different solutions, with the same concentration in total Zn and a variable concentration (from 5 to $220\,\mathrm{mg\,l^{-1}}$) of TBACl were used: (1) 0.5 M $ZnCl_2$ + 1 M NaCl; (2) 0.5 M $ZnCl_2$ + 2.5 M NaCl; (3) 0.5 M $Zn(ClO_4)_2$ + 2.5 M $NaClO_4$.

## 3. Results

### 3.1. *0.5 M $ZnCl_2$ + 1 M NaCl + x TBACl solutions*

*3.1.1. Cyclic voltammetry.* The log $I$ against $\eta$ cathodic curves presented in Fig. 1 (C) were obtained at a scan rate of $1\,\mathrm{mV\,s^{-1}}$ and at a cathode rotation speed of 3000 rpm in solutions with TBACl concentrations in the range $0$–$220\,\mathrm{mg\,l^{-1}}$. These curves show two inflexion points, (b) and (c). Point (b) corresponds to the activation overpotential, $\eta_A$, necessary to initiate zinc deposition. The segment (b)–(c) is that of zinc nucleation and growth. At point (c) the electrode is totally covered by zinc and electrodeposition now occurs under mixed charge transfer-diffusion control.

The absolute value of $\eta_A$ increases with increasing TBACl concentration, as expected. The dotted curves, (2′) and (4′), Fig. 1 (C), correspond to curves (2) and (4), respectively, but they were obtained at a lower rotation speed; that is 500 rpm. The small increase of $\eta_A$ observed upon increasing the rotation speed by a factor of 6 at constant additive concentration does not provide direct evidence for diffusion control of the inhibiting action of TBACl [11], since the electrodeposition of Zn itself in TBACl-free solution is also affected by the rotation speed of the cathode.

Several anodic voltammograms are given in Fig. 1 (A). They show that the anodic dissolution of the electrode is also partially inhibited by TBACl.

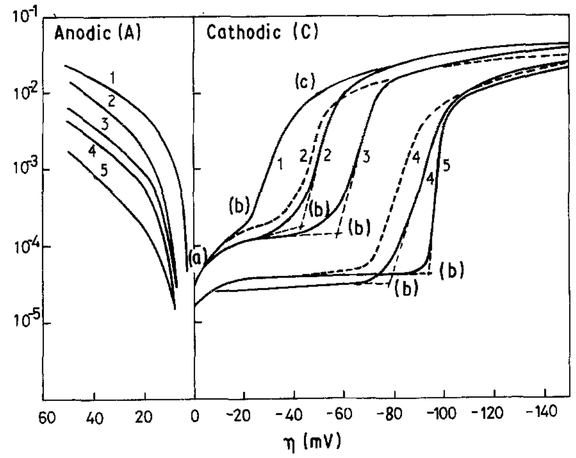

Fig. 1. Cathodic (C) and anodic (A) voltammograms at $1\,\mathrm{mV\,s^{-1}}$ and 3000 rpm of 0.5 M $ZnCl_2$ + 1 M NaCl solutions with the following TBACl concentrations ($\mathrm{mg\,l^{-1}}$): 1(0), 2(5), 3(20), 4(40), 5(100, 160, 220). $E_r = -1025\,\mathrm{mV}$ (SCE).

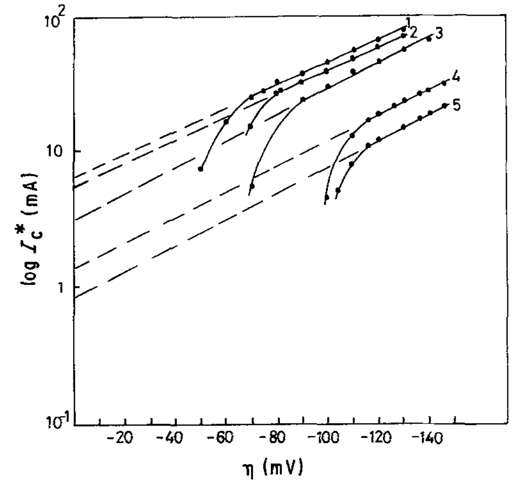

Fig. 2. Cathodic Tafel polarization curves calculated from the voltammograms of Fig. 1 (C).

The cathodic curves of Fig. 1 (C) were corrected for the mass-transport effect of the depositing $Zn^{2+}$ ions by using the conventional method of plotting $1/I$ against $\omega^{-\frac{1}{2}}$ at constant $\eta$, and finding the ordinate at the origin, ($\omega \longrightarrow \infty$), by extrapolation. The corrected cathodic curves, Fig. 2, show a linear segment with a Tafel slope of $-100 \pm 6\,\mathrm{mV\,(decade)^{-1}}$, indicating that the charge-transfer reaction is not controlled by the TBACl concentration.

The values of the exchange current, $I_c^0$, were obtained by extrapolating these curves to $\eta = 0$. The inhibiting effect of TBACl is clearly seen in the decrease of $I_c^0$ (Fig. 3, curve (1)), and in the increase of $\eta_A$ (Fig. 3, curve (2)), that results from an increase in the TBACl concentration. Both $I_c^0$ and $\eta_A$ tend towards a limiting value for [TBACl] $\geqslant 100\,\mathrm{mg\,l^{-1}}$.

If the potential sweep is reversed at the negative limit (Fig. 4), the cathodic current is higher in the positive going sweep ($\eta \rightarrow 0$) than in the initial negative-going sweep, due to the increased roughness of the zinc deposit. In subsequent negative-going sweeps (in $100\,\mathrm{mg\,l^{-1}}$ TBACl) the cathodic current increases, that is, the inhibiting effect of TBACl decreases (Fig. 4, curves (2)). However, it is nearly completely recovered if the potential sweep is stopped ($\eta = 0$) and the electrode held at open circuit for 30 s (Fig. 4, curve (4)). During this period of time the

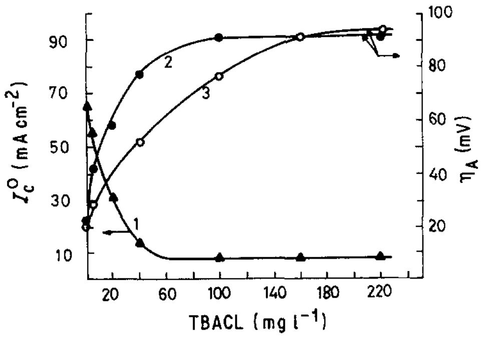

Fig. 3. Effect of TBACl concentration on the exchange current density and $\eta_A$ in 0.5 M $ZnCl_2$ solution with 1 M NaCl (curves 1 and 2) and with 2.5 M NaCl (curve 3) supporting electrolyte.

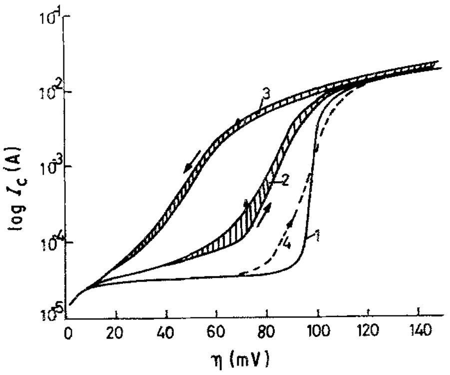

Fig. 4. Voltammograms in 0.5 M $ZnCl_2$ + 1 M NaCl + 100 mg $l^{-1}$ TBACl solution at 3000 rpm and 1 mV $s^{-1}$ (1): 1st scan, (2, 3): 2nd to 4th cyclic consecutive scans, (4): 5th scan after leaving the electrode in open circuit for 30 s.

concentration of TBACl at the interface probably reaches its bulk value again.

*3.1.2. Scanning electron microscopy.* The SEM photomicrograph in Fig. 5 gives unequivocal proof about the mechanism of the levelling action of TBACl. The electrode had been subjected to a cathodic polarization at −0.3 mA for 30 s (40 mg $l^{-1}$ TBACl), conditions that correspond to the beginning of Zn electrodeposition, which, as can be clearly seen, takes place preferentially in the grooves left in the surface by an imperfect mechanical polishing.

Zn electrodeposits obtained under fairly stringent conditions, that is, moderate rotation speed (500 rpm), −20 mA current (corresponding to $I_c/I_d \simeq 0.5$, since $I_d$ was 35–38 mA) and for 30 min, and a series of TBACl concentrations in the range 5–220 mg $l^{-1}$ have been examined by SEM.

The values of $\eta$ at the end of each experiment (30 min) is given under each micrograph in Fig. 6. These values are not corrected for the ohmic drop; the ohmic resistance was 10 Ω for solution 1, and 7 Ω for solutions 2 and 3.

In the absence of TBACl the zinc deposit was rough with large protrusions appearing at the edges (Fig. 6a), while the central area of the disc is covered by randomly oriented hexagonal platelets (Fig. 6a′).

Fig. 5. SEM photomicrograph showing the mechanism of the levelling action of TBACl at the beginning of Zn electrodeposition. $I$ = −0.3 mA, $t$ = 30 s. 0.5 M $ZnCl_2$ + 1 M NaCl + 40 mg $l^{-1}$ TBACl.

Addition of 5 mg $l^{-1}$ TBACl inhibits the growth of protrusions at the edges (Fig. 6b) and promotes a finely grained structure at the centre (Fig. 6b′). The photomicrograph corresponding to 20 mg $l^{-1}$ TBACl (not shown) is similar to that shown in Fig. 6b.

At higher concentrations (Fig. 6c and 6d), the levelling effect of TBACl decreases; both the grain size and the protrusions at the edges increase. For [TBACl] ⩾ 160 mg $l^{-1}$ the central area acquires a ‘rice structure’ (Fig. 6d′).

Under these experimental conditions the maximum levelling effect is achieved with low TBACl concentrations, 5–20 mg $l^{-1}$. It seems clear that there is no direct relationship between the increase in overpotential with TBACl concentration (Fig. 1 (C)) and the degree of levelling of the zinc deposit.

### 3.2. *0.5 M $ZnCl_2$ + 2.5 M NaCl + X TBACl solution*

*3.2.1. Cyclic voltammetry.* In the absence of TBACl an increase in NaCl concentration from 1 (Fig. 1, curve 1)

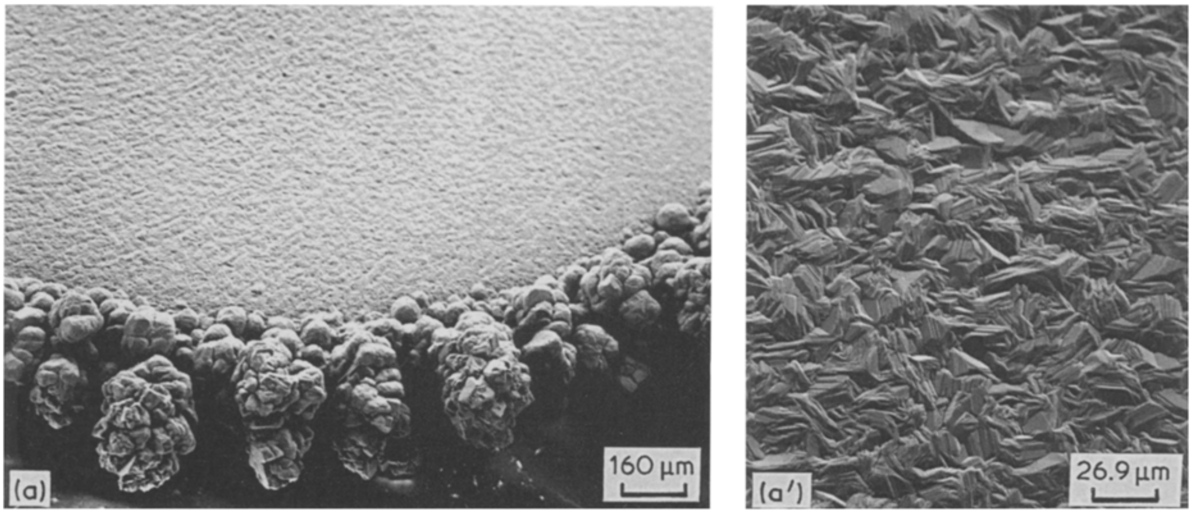

Fig. 6. SEM photomicrographs of Zn deposits after cathodic polarization ($I$ = −20 mA, $t$ = 30 min, $\omega$ = 500 rpm) illustrating the levelling action of TBACl. Electrolyte: 0.5 M $ZnCl_2$ + 1 M NaCl with the following TBACl concentrations: (a) 0 mg $l^{-1}$ ($\eta$ = −22 mV); (b) 5 mg $l^{-1}$ ($\eta$ = −32 mV); (c) 40 mg $l^{-1}$ ($\eta$ = −80 mV), (d) 160 mg $l^{-1}$ ($\eta$ = −91 mV). a′, b′, c′, d′: central area of the disc.

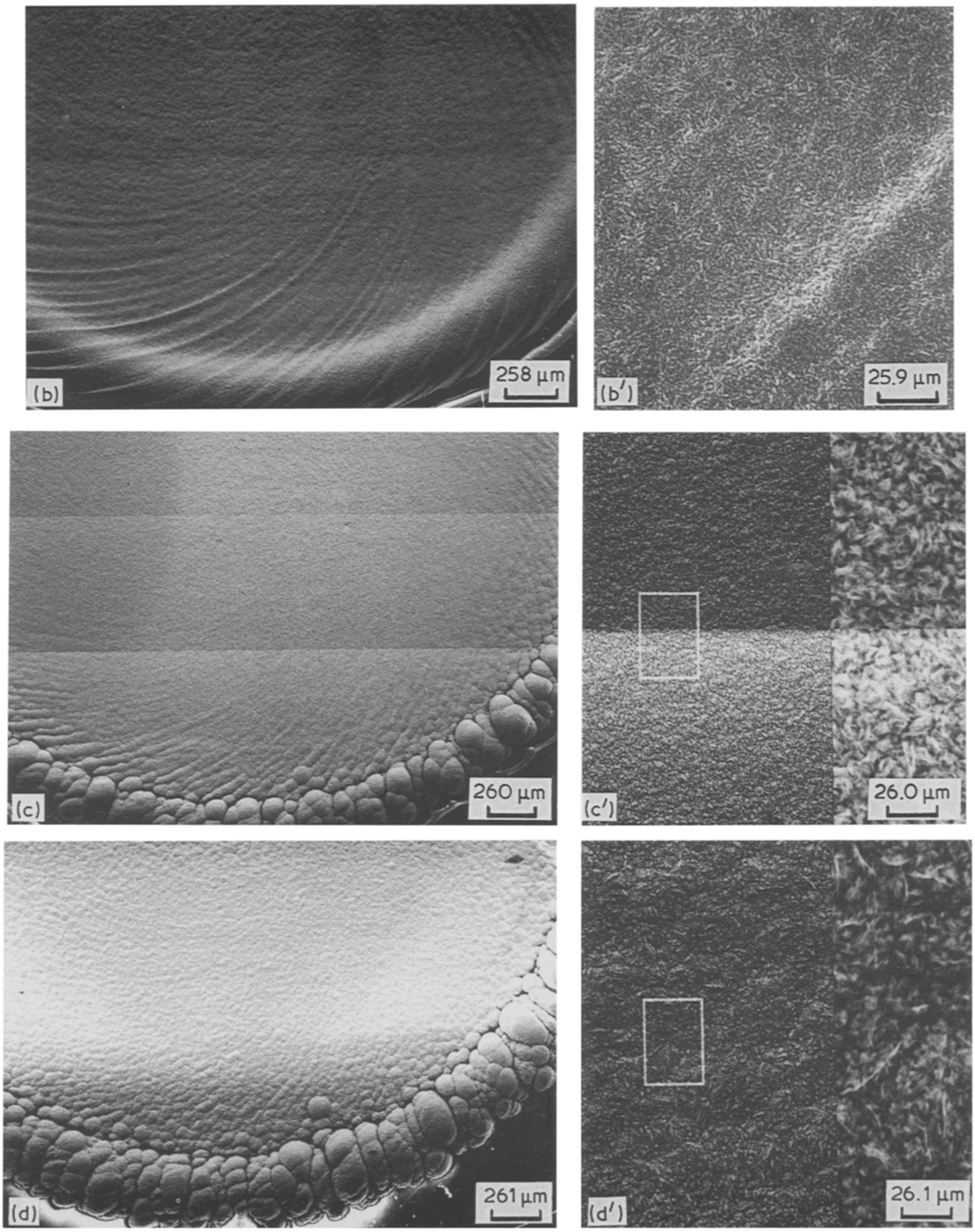

Fig. 6. Continued.

to 2.5 M (Fig. 7, curve 1) markedly increases the rate of the electrochemical reaction: point (c), which corresponds to the beginning of control by $Zn^{2+}$ diffusion, is reached at a lower overpotential in the latter case. At this higher NaCl concentration Zn electrodeposition is less affected by changes in TBACl concentration, and the limiting value of $\eta_A$ is reached at higher TBACl concentrations (Fig. 3, curve 3).

*3.2.2. Scanning electron microscopy.* The experimental conditions were the same as with 1 M NaCl supporting electrolyte (§3.1.2). The increase of NaCl concentration did not affect the diffusion-limited current, which was also 35–38 mA at 500 rpm.

In the absence of TBACl (Fig. 8a) the central area of the deposit consists of large, randomly oriented hexagonal platelets. The addition of 5 mg $l^{-1}$ TBACl

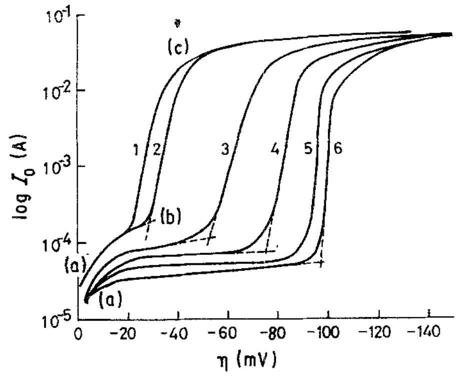

Fig. 7. Cathodic voltammograms at $1\,mV\,s^{-1}$ and 3000 rpm for 0.5 M $ZnCl_2$ + 2.5 M NaCl solutions with the following TBACl concentrations ($mg\,l^{-1}$): 1(0), 2(5), 3(40), 5(160), 6(220). $E_r = -1034\,mV$ (SCE).

does not appreciably change this structure (photomicrograph not shown).

The maximum levelling effect was achieved with 40–100 $mg\,l^{-1}$ TBACl (Fig. 8b and 8c). At concentrations above 160 $mg\,l^{-1}$ (Fig. 8d and d′) a substantial increase of the protuberances at the disc edges was observed, together with a marked ‘rice structure’ in the central area. This behaviour is likely due to the greater surface roughness of the deposits produced by the higher electrodeposition rate, which in turn requires a higher concentration of the levelling agent at the surface.

### 3.3. *0.5 M $Zn(ClO_4)_2$ + 2.5 M $NaClO_4$ + X TBACl solution*

In the absence of TBACl and $Cl^-$ anions $\eta_A$ has a value of $-130\,mV$ (Fig. 9, curve 1), very high compared with those measured with $Cl^-$. The value of $\eta_A$ is further increased by addition of TBACl (Fig. 9, curves 2 and 3). With 40 $mg\,l^{-1}$ TBACl an inflexion appears at the more negative potentials, probably corresponding to the beginning of $H_2$ evolution. Also with 40 $mg\,l^{-1}$ TBACl the use of a mixed solution, 0.5 M $ZnCl_2$ + 2.5 M $NaClO_4$, largely decreases $\eta_A$ (curve 4 as compared with curve 3, both in Fig. 9), which can be attributed to the activating effect of $Cl^-$ anions.

Photomicrographs of the electrodeposit without (Fig. 10a) and with 40 $mg\,l^{-1}$ TBACl (Fig. 10b) clearly show that the levelling effect is less than that observed

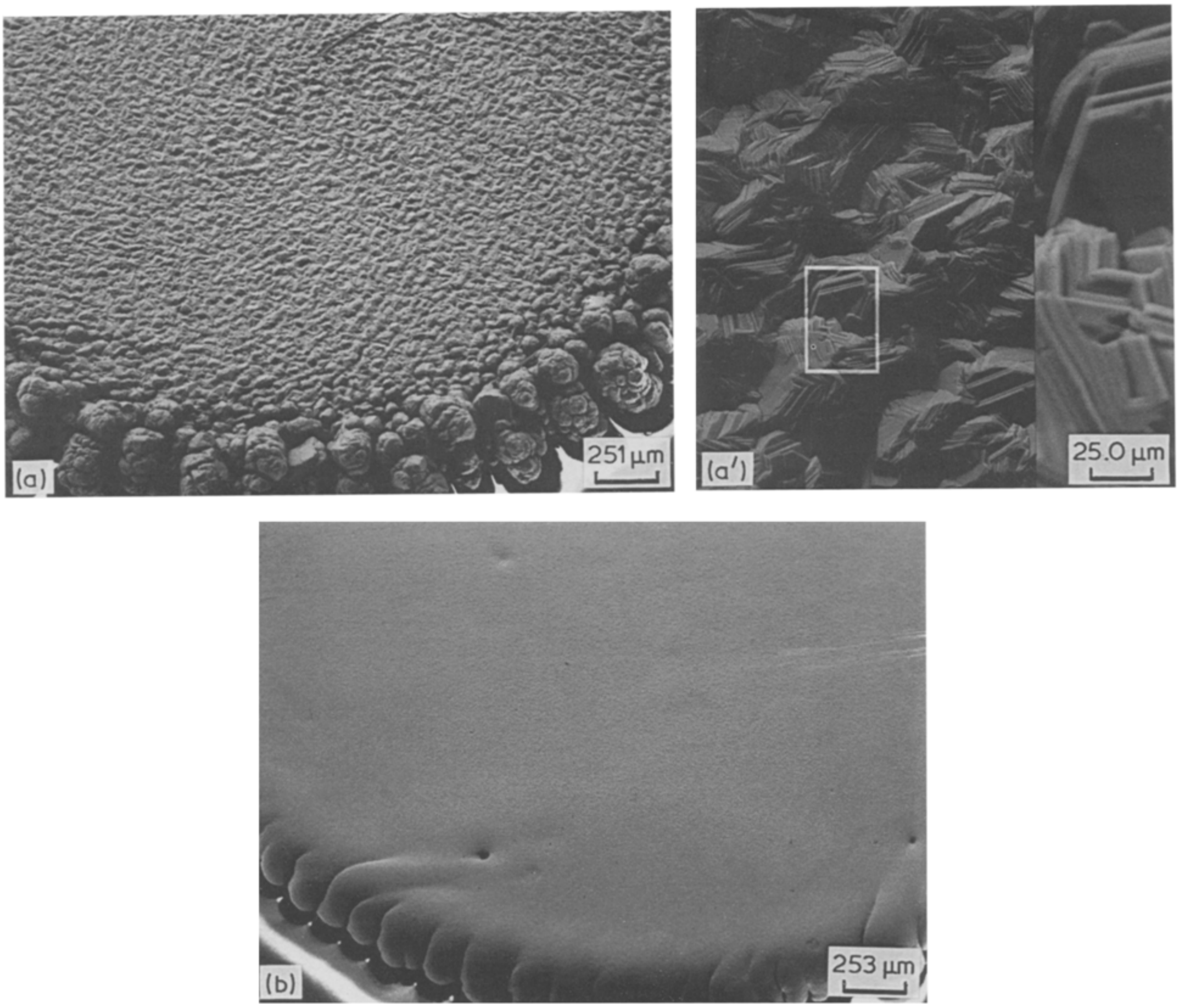

Fig. 8. SEM photomicrogaphs of Zn deposits obtained in 0.5 M $ZnCl_2$ + 2.5 M NaCl solutions with the following TBACl concentrations: (a) 0 $mg\,l^{-1}$ ($\eta = -22\,mV$); (b) 40 $mg\,l^{-1}$ ($\eta = -42\,mV$); (c) 100 $mg\,l^{-1}$ ($\eta = -80\,mV$); (d) 160 $mg\,l^{-1}$ ($\eta = -90\,mV$). Experimental conditions as in Fig. 6.

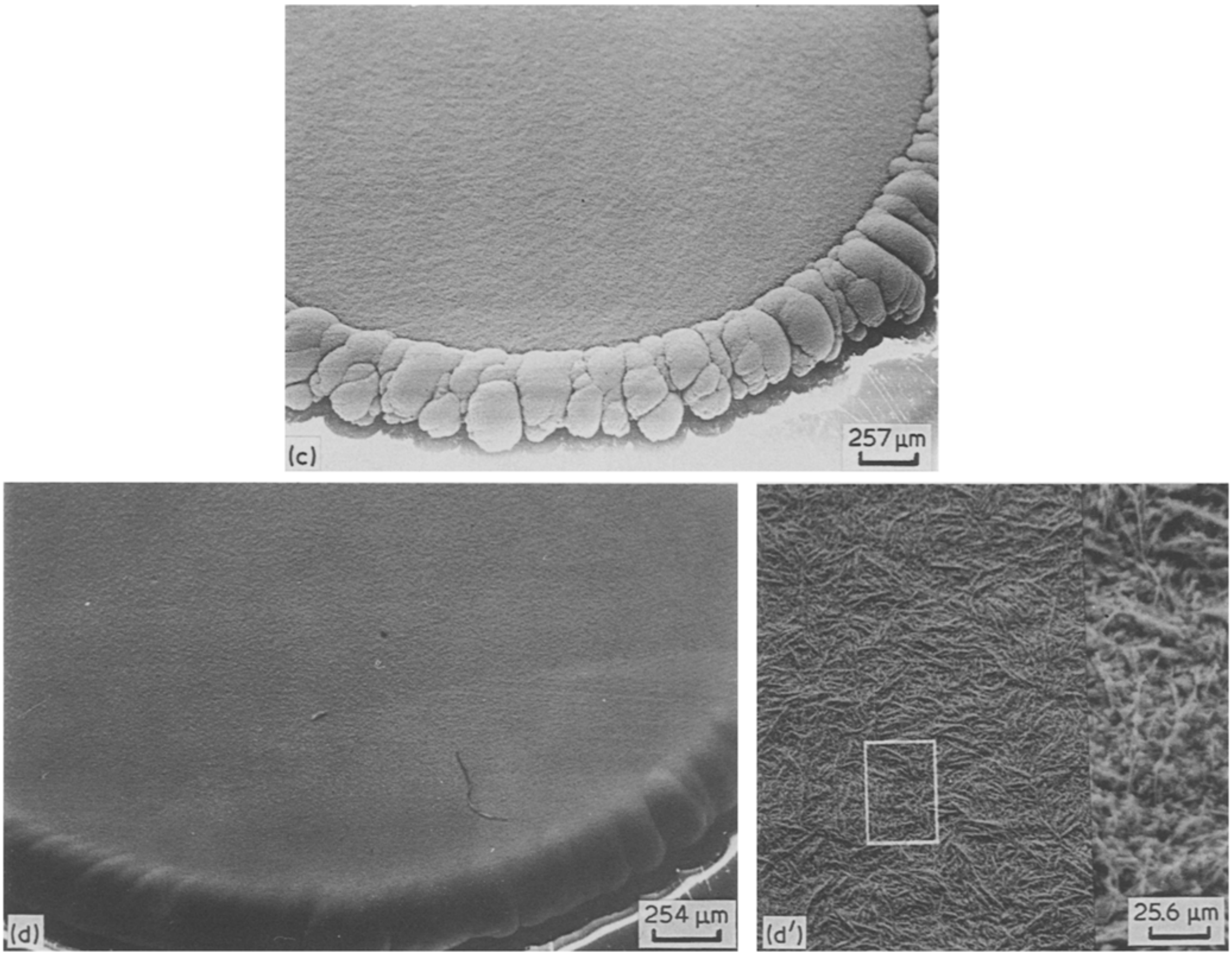

Fig. 8. Continued.

for the chloride bath (Fig. 8b). Besides, pores and spirals following the flow direction, and therefore probably produced by $H_2$ bubbles, are clearly seen.

## 4. Discussion

Addition of TBACl lowers the rate of Zn electrodeposition by increasing the electrode polarization, as already reported by other researchers [7–9]. However, the increase in overpotential with increasing TBACl concentration reaches a limit (Fig. 3), probably corresponding to a TBACl adsorption rate higher than the Zn electrodeposition rate (and therefore than the rate of TBACl consumption). Thus, the limiting value of $\eta_A$ corresponds to a surface concentration of $TBA^+$ approaching saturation ($\theta \rightarrow 1$), which eliminates the heterogeneity of the adsorbed layer of the levelling agent.

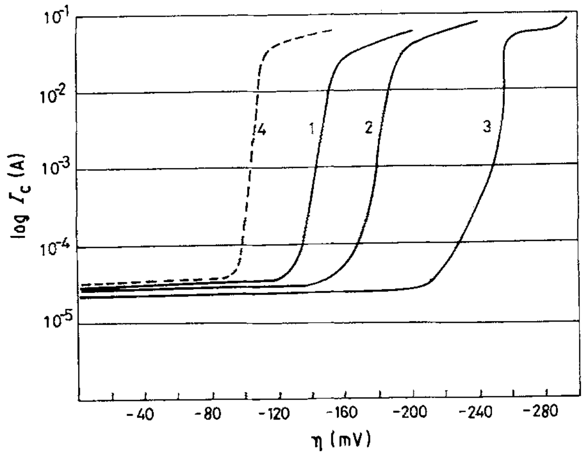

Fig. 9. Cathodic voltammograms at $1\,mV\,s^{-1}$ and 3000 rpm for 0.5 M $Zn(ClO_4)_2$ + 2.5 M $NaClO_4$ with the following TBACl concentrations ($mg\,l^{-1}$): 1(0), 2(5), 3(40). $E_r = -995$ mV (SCE). Curve 4: 0.5 M $ZnCl_2$ + 2.5 M $NaClO_4$ + $40\,mg\,l^{-1}$ TBACl.

When the NaCl concentration is increased to 2.5 M, the rate of Zn electrodeposition increases (Fig. 7) and, consequently, the limiting value of $\eta_A$ is reached at higher TBACl concentrations (curve 3 in Fig. 3). It is obvious that the greater surface roughness involves higher TBACl consumption by incorporation into the deposit

The increase of the rate of Zn electrodeposition effected by an increase of the NaCl concentration in the absence of TBACl has been attributed to a higher concentration of Zn chloro-complexes [12]. Other possible causes are an increase in the nucleation rate on newly deposited Zn, or an increase in the activity coefficient of the electroactive species brought about by the increase of ionic strength.

Andreeva [13] found an effect similar to that in Fig. 3 for the cathodic reduction of $H^+$ on Hg in the

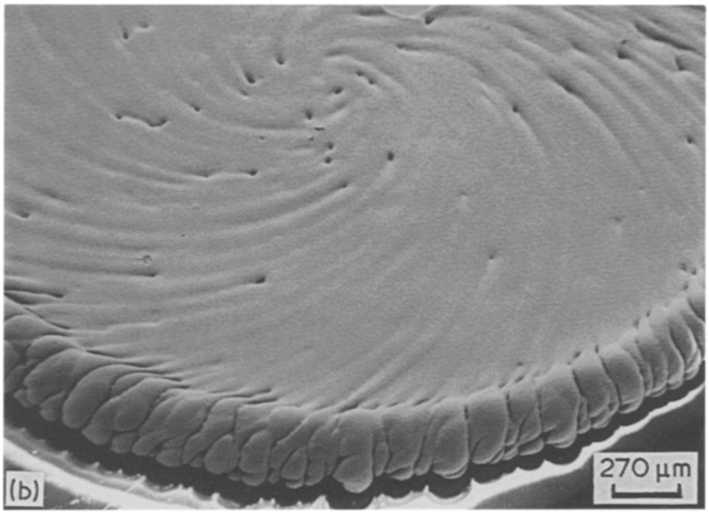

Fig. 10. SEM photomicrogaphs of Zn electrodeposits obtained in a 0.5 M $Zn(ClO_4)_2$ + 2.5 M $NaClO_4$ solution. (a) without TBACl ($\eta$ = −120 mV), (b) with 40 mg $l^{-1}$ TBACl ($\eta$ = −192 mV). Experimental conditions as in Figs 6 and 8.

presence of $[(C_4H_9)_4N]_2SO_4$. The decrease in the $H^+$ reduction rate was attributed to a combination of several factors, including: a shift of the OHP potential towards more positive values, change in the potential distribution in the compact layer (as in the adsorption of large neutral organic molecules) and surface blockage by the inhibitor.

The independence of the Tafel slope for Zn electrodeposition in 1 M NaCl on TBACl concentration shows that the reaction mechanism is unaffected by TBACl. This fact, together with the inhibition of the anodic process as well (Fig. 1(A)) suggests that the inhibiting action of TBACl is simply due to surface blockage. The same conclusion had been reached by Loshkarew [14], who used $[(C_2H_5)_4N]_2SO_4$ instead of TBACl.

When $ClO_4^-$ is substituted for $Cl^-$ anion the cathodic overpotential increases, and is also further increased by the addition of TBACl, the potential dangerously approaching the region of hydrogen evolution. This clearly shows the importance of the anionic nature of the electrolyte on the effect of TBACl.

The SEM photomicrographs of the Zn deposits obtained at constant current show that the optimum levelling effect is achieved with low TBACl concentrations, which ensure its adsorption on the protrusions only. This fact is in agreement with the adsorption-diffusion theory of preferential adsorption of levelling agent upon the micropeaks of the cathodic profile [11], which favours deposition on surface recesses, as shown in the photomicrograph in Fig. 5.

The relationship between levelling degree, concentration of TBACl, and increase of overpotential is rather complex. However, the results clearly show that the overpotential increase produced by TBACl is not correlated directly with the degree of levelling that is attained. The degree of levelling depends on the interaction of several parameters, the most important being the rate of Zn electrodeposition, which controls the balance between adsorption and consumption of TBACl.

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