JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 187–189

Electrochemical and reflectance study of the conversion of zinc oxide by hexacyanoferrate (II) in offset lithography

Part II: Zinc electrochemistry in sodium dihydrogen phosphate together with other minor components

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Received 24 July 1992; revised 28 September 1992

The effect is examined of the presence of 0.045 M sodium dihydrogen phosphate together with EDTA, or malic acid or 1-ethoxy sulphosuccinic acid or isopropanol on the electrochemistry of zinc metal, studied by cyclic voltammetry from −1.4 to −1.0 V (occasionally, −0.7 V). While sometimes marginal, a clear effect is seen in each case, and new passivating products are transiently introduced by EDTA and $H_2PO_4^-$, which together show a slight synergism of passivation. All additives either weaken the initial ZnO passivation on the anodic-forward sweep or, by doping, allow less negative reductions of Zn^{2+}(aq) or Zn^{II} solids in the reverse, cathodic, sweep.

1. Introduction

Microcrystalline photoconductive zinc oxide, affixed by resin binders to stout backing paper in one form of lithography (Part I [1]) must, in image-free areas, be 'converted' by reaction with hexacyanoferrate (II) into a bulky hydrophilic, hence ink repellent, material. This expands to bridge over exposed binder, which otherwise could also pick up the printing ink to be acquired by the polymer previously imprinted in the form of the image by conventional electrophotography. To examine the mechanism of the conversion reaction, zinc oxide has been electrogenerated on a metallic zinc electrode [1] and its fate in the presence of the individual components of lithographic conversion solution studied. In Part I such processes but devoid of the key hexacyanoferrate (II) component were examined and the background to zinc oxide electrochemistry at the relevant pH (4.6) summarized; the seven forms of $ZnO/Zn(OH)_2$ were [1] referred to inclusively as 'Zn^{II} oxide'. In cyclic voltammograms starting from −1.4 V to on occasion −0.7 V and back, the cathodic i.e. 'reverse' limb was the more relevant [1], providing information regarding the milieu effect on Zn^{II} oxide stability against reduction. Those results with further studies are summarized in Table 1, for 3 cathodizing pretreatments. Two major cathodic features, sometimes with minor accompaniments, at about −1.15 and −1.3 V, were assigned [1] to reductions of Zn^{2+} aquo-species and Zn^{II} oxide, respectively. Diffuse reflectance from the electrode surface provided objective monitoring of visible changes occurring during the cycles [1].

In Part III the interaction of Zn^{II} oxide with hexacyanoferrate (II) and its companion constituents is examined; meanwhile the interactions with Zn^{II} oxide of the major secondary component NaH_2PO_4 in solution, in conjunction with other minor constituents, are reported here, in order to avoid cross-parametric confusion.

2. Experimental details.

The procedures of Part I were employed, but of the three pre-cathodization treatments [1] at −1.4 V summarized in Table 1 above, only (i) (1 h, oxygen free), and (iii) (20 min, oxygen from air) were needed here. Furthermore, diffuse reflectance studies were held over to Part III.

3. Results and discussion

The solid products from increasingly anodic potentials are Zn^{II} oxide, as such, or doped with some of the extra solution components ([1] and Table 1), or possibly compounded with these. The solute products are Zn^{2+} aquo species which include $Zn(ClO_4)_m^{(2-n)+}$ and kindred phosphato species (thus with pH 4.6, $H_2PO_4^-$ 0.045 M, and Zn^{2+} typically submillimolar, [Zn^{2+} HPO_4^{2-}] from pK_{a2} 6.7 and complex formation constant 251 M^{-1} [2] is $\leqslant 2 \times 10^{-5}$ M) but will exclude $ZnOH^+$ ($\sim 10^{-10}$ M from pK_a for Zn^{2+}, 8.96 [3]). Possible cathodic reactions comprise deposition of Zn^{2+} species, reduction of Zn^{II} oxide or other Zn^{II} solids, reduction of H^+, and/or of oxygen in aerated solution.

Addition of 0.045 M NaH_2PO_4 [1] leads to the usual −1.02 V anodic-current onset (Table 1) but from

Table 1. Effects of constituents on two cathodic ('reverse') CV peaks on Zn/Zn^{II} oxide, showing peak-current (i_p) dependence on total (forward + reverse) anodic charge Q_A. 24° C, aqueous $LiClO_4$, pH 4.6. Pre-cathodisation at −1.4 V for (i) 1 h, no O_2 (ii) 20 min, no O_2 (iii) 20 min, O_2 from air. (Anodic current onset potential is cited for forward limb following (i))

Constituents *[Anodic current onset]*	*Reverse i_p (and effect of Q_A on it)*		*Interpretation*
	Aquo Zn^{2+} peak at −1.15 V	*Zn^{II} oxide film peak at −1.3 V*	
1. No additive [−1.02 ± 0.02 V]	small i_p (some increase)	monolayer (increase)	Zn^{II} oxide film and Zn^{2+} aq. form (forward); are reduced (reverse).
2. NaH_2PO_4 [−1.02 ± 0.02 V]	(large increase)	(? Hidden by H_2 evolution)	Weakens (thins) film and enhances Zn^{2+} aq. formation.
3. Na_2EDTA [−1.03 ± 0.03 V]	(i), (ii) plateau (iii) peak to −1.05 V (increase)	(i), (ii) small i_p plateau (iii) broad peak at −1.26 V	Weak Zn^{II} oxide is replaced by new passive film, on which reverse peaks shift positive: 'mediation' through new film?
4. Malic acid [−0.99 ± 0.01 V]	(increase)	Plateau (~ independent of Q_A)	No Zn^{II} oxide? Yet anodic onset *more* positive (as A102) and reverse features as for just 5–10 mM Zn^{2+}.
5. A102 [−0.99 ± 0.01 V]	(i) (ii) i_p ~ 0 (unless large Q_A) (iii) i_p small	(i)(ii) i_p ~ 0 (iii) i_p small (small)	(i) more pos. anodic onset, (iii) less pos. anodic onset, thus itself passivating, but weakens Zn^{II} oxide.
6. Isopropanol [−0.97 V]	~ as (1) (not tested)	Peak to −1.27 V (not tested)	Though weaker than with 4 and 5, adsorption effects passivation, but (*cf.* 3) mediation indicated in reverse

−1.16 V a merging of reverse features into a single plateau with hydrogen evolution; large Q_A restore peaks at −1.16 to −1.18 V for Zn^{2+}-species reduction, the clear 10–30 mV cathodic shift (cf. −1.15 V, Table 1) being of kinetic rather than complexing origin (*vide supra* the low [$ZnHPO_4$]). The appearance of *anodic*-current peaks at −1.10 V in the *forward* limb with oxygen present (see [1], Fig. 4(d) and (e)) was insufficiently highlighted in [1] since it significantly indicates a new passivation against Zn^{2+} evolution; such anodic peaks result in a progressively growing extra cathodic shoulder at ~ −1.23 V during reversal, this reduction indicating that the new passivating material survives the copious (forward) Zn^{2+} evolution at the anodic limit. (Rehearsing this already available evidence [1] here is necessary in accounting for new observations as follows.)

3.1. *Addition of disodium EDTA to NaH_2PO_4 solution*

Following pretreatment (i), the presence of NaH_2PO_4 alters the CV with EDTA [1] qualitatively very little, with the same anodic-onset potential, current crossover following reversal, and only a moderate smoothing-out of reverse features at ~ −1.15 and −1.3 V owing to some hydrogen evolution. With oxygen present, a different outcome ensues: without NaH_2PO_4, EDTA, Fig. 1(a) shows a new forward anodic passivation peak similar to that generated by NaH_2PO_4 alone; with NaH_2PO_4 also present, Fig. 1(c), besides this forward anodic passivation peak, there is a shoulder to the main Zn^{2+} evolution current, and consistently two extra cathodic (reverse) features are seen. Larger Q_A, Fig. 1(b), results in such enhance-

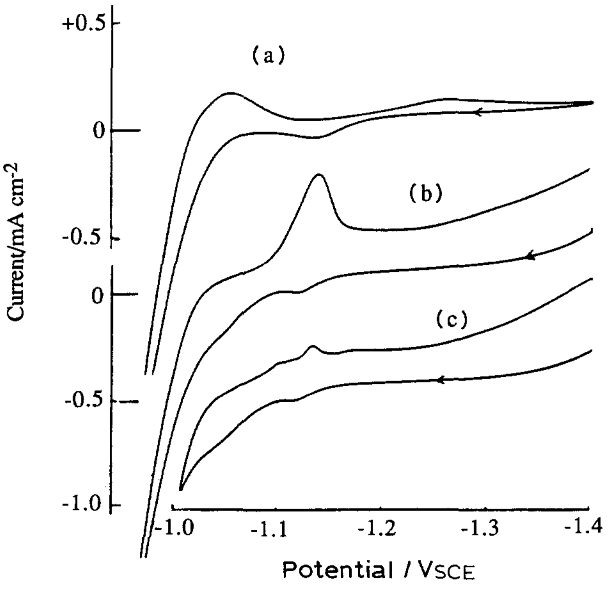

Fig. 1. CVs after pretreatment (iii) with 8.9 × 10^{-4} M EDTA, pH 4.6, and (a) no NaH_2PO_4; reversed at −0.9 V. (b) 0.045 M NaH_2PO_4; reversed at −0.95 V. (c) 0.045 M NaH_2PO_4; reversed at −1.01 V. (Note minor satellites to −1.13 V main peak, at −1.05 V and −1.17 V, respectively).

ment of the presumed Zn^{2+}- reduction peak (shifted to −1.13 V) as to totally obscure these satellites (or alternatively, all trace of the passivating matter just deposited is removed by the copious forward evolution of Zn^{2+} that follows). Forward anodic peak potentials of the NaH_2PO_4/EDTA mixture compared with those (italicized) for the components separately, −1.12 V (*−1.14 V, Na_2EDTA*) and −1.05 V (*−1.10 V, NaH_2PO_4*) [1] imply some synergism by the mixture in delaying anodic onsets but also in weakening the just-invoked passivating materials. In the reverse, the *EDTA-only* cathodic peak corresponding to −1.10 V in the mixture (Fig. 1c) is *missing* or *obscured*, but the mixture −1.17 V satellite peak (Fig. 1(c)) is matched by the shoulder at −1.24 V (*NaH_2PO_4 alone*) [1]. The 20–70 mV positive shift in the reverse limb for mixtures implies mixed-ligand (phosphato-EDTA) mediation to these reductive processes.

3.2. *Addition of malic acid to NaH_2PO_4 solution*

Anodic-current onset at −1.00 V and behaviour much as in NaH_2PO_4-free solution are observed, and in repeated scans marked negative shifts of the anodic-onset potentials are observed, showing weakening or doping of the passivating Zn^{II} oxide film, as before (Table 1).

3.3 *Addition of disodium 1-ethoxysulphosuccinate (A102) to NaH_2PO_4 solution; and of isopropanol (IPA)*

A102 in NaH_2PO_4 depresses the already muted features observed without NaH_2PO_4 [1], thus the strong adsorption already inferred is enhanced by phosphate. Small IPA effects, Table 1, discerned since [1], are likewise depressed.

4. Conclusions

While the addition of NaH_2PO_4, deemed to be a key constituent, has remarkably subdued effects on the zinc electrochemistry, it prompted reexamination of several features already established; furthermore, some new passivation regions clearly occur after anodic conditions are met, and undoubted synergisms arise both in promoting (with EDTA) and depressing (with A102 and IPA) NaH_2PO_4-free features. The evidence of clearcut phosphate-dependent features determined the decision, in Part III, to study the effect of hexacyanoferrate (II) both with and without NaH_2PO_4 present.

Acknowledgements

A CASE studentship to A.M.S. from SERC and Gestetner Manufacturing Ltd is gratefully acknowledged.

Corrigendum

Minor transcription errors in Part I, [1] of minimal interpretative consequence, occurred as follows.

p. 774 2nd column, 9 lines down: ref. is [17] (not [7]).
p. 777 2nd column, 14 lines down: Fig. 4(a), not 5(a).
p. 777 Fig. 4(b), add to legend: second CV, after first reversed at −0.95 V.
p. 779 Table 3, final column, 3 lines up: for 'Absent' read 'Plateau'.

References

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