



Photo-induced dissolution of zinc in alkaline solutions

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Abstract

The passive behaviour of zinc in an alkaline pH 13.0 solution under dark and illumination conditions has been studied using dc polarization and ac impedance techniques. Illumination with polychromatic light in the wavelength region 200–900 nm caused significant dissolution of anodically formed passive layers on zinc. This was evident from increased anodic currents, a ten-fold decrease in the charge transfer resistance and an increase in the capacitance of the passive layer. The photo-induced dissolution effect was only slightly evident under open-circuit conditions, where a precipitated or adsorbed layer forms on the electrode. These results are explained in terms of the n-type semi-conducting properties of ZnO. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photo-dissolution; Photo-decomposition; ZnO; Passivity; Semiconducting

1. Introduction

Zinc and many zinc alloys exhibit passive behaviour in alkaline solutions due to the formation of a zinc oxide/hydroxide passive film [1,2]. It has been reported, in many cases, that the electrochemical behaviour of these passive layers is similar to that of the non-stoichiometric ZnO [3–6], which is an n-type semiconductor with a band-gap energy of approximately 3.2 eV [7,8]. Although, the photo-electrochemical properties of these oxide layers have been studied in some detail [9,10], little attention has been devoted to the possible modifications of the oxides induced by the illumination procedure.

Juzeliunas et al. [11] reported an increase in the corrosion rate of zinc in a 5% NaCl solution on illumination at 488 nm. This increase in the corrosion rate was associated with a light-induced increase in the rate of the oxygen reduction reaction, but no changes in the anodic polarization behaviour were observed. Spathis

and Poulis [12] observed the photo-corrosion of zinc and zinc oxide coatings in a 3.5% NaCl solution on illumination with white light. On exposing the zinc electrodes to the chloride solution an initial more rapid formation of corrosion products occurred under illumination conditions than in the dark. In addition, the electrodes suffered uniform corrosion under dark conditions, but under illumination conditions pitting corrosion was observed.

In this communication, the electrochemical behaviour of pure zinc in an alkaline pH 13.0 electrolyte, with and without the addition of NaCl, under conditions of illumination and non-illumination is examined.

2. Experimental

Electrodes were prepared from pure zinc (99.999%) rods. The test samples were set with epoxy resin in a Teflon holder and electrical contact was achieved by means of a copper wire threaded into the base of the metal sample. Prior to each test the samples were polished to a smooth surface finish and rinsed with distilled water. In the case of the Mott–Schottky exper-

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iments the electrodes were polished to a mirror finish using alumina powder. The electrochemical cell was made of Teflon with a quartz window in the base to allow irradiation of the test electrodes. High-density graphite rods were used as the auxiliary electrodes and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials quoted are relative to this electrode. The electrolytes were prepared using analytical grade reagents and distilled water. Two electrolytes used were an alkaline pH 13.0 solution ($0.1 \text{ mol dm}^{-3} \text{ NaOH}/0.025 \text{ mol dm}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$) and an alkaline pH 13.0 solution containing chloride ($0.1 \text{ mol dm}^{-3} \text{ NaOH}/0.025 \text{ mol dm}^{-3} \text{ Na}_2\text{B}_4\text{O}_7/0.025 \text{ mol dm}^{-3} \text{ NaCl}$).

The illumination source was a 300 W xenon arc lamp (Oriol model 6258). The light was passed through a water cooler to remove infrared radiation. The beam was then passed through a series of filters, lenses and mirrors and focused on the stage to illuminate the entire surface of the exposed electrode. The intensity of the light entering the cell was measured using a Spectra-Physics CW Laser Power Meter model 407A. The intensity was measured as 250 mW cm^{-2} for unfiltered irradiation (200–900 nm). A maximum temperature rise of 1.9°C was recorded over a 30 min illumination period for this high intensity polychromatic illumination procedure.

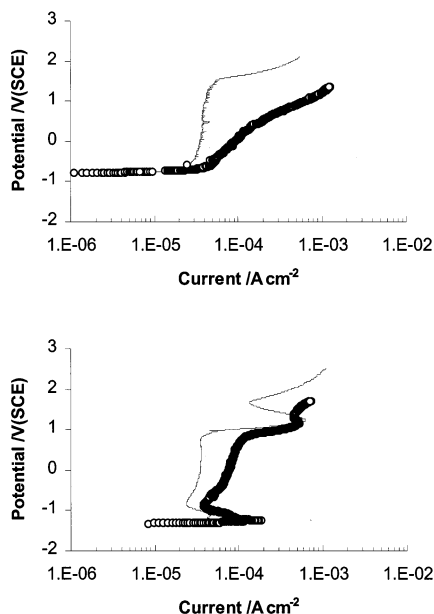


Fig. 1. (a) Anodic polarization plots recorded for Zn in chloride-containing borate solution under — dark and ○ illumination conditions. (b) Anodic polarization plots recorded for Zn in deoxygenated chloride-containing borate solution under — dark and ○ illumination conditions.

Potentiodynamic electrochemical experiments were carried out using an EG&G potentiostat, model 263. The working electrodes were polarized from the corrosion potential at a scan rate of 0.5 mV s^{-1} in the anodic direction, following either an initial delay period of $1.3 \times 10^3 \text{ s}$ under open-circuit conditions, or cathodic reduction at -1.3 V (SCE) for 6 min. Impedance measurements were recorded using a Solartron 1255 frequency response analyser and an EI 1287 electrochemical interface. The spectra were recorded at the corrosion potential following an initial delay of $1.3 \times 10^3 \text{ s}$ under open-circuit conditions. Alternatively, the impedance data were recorded at 800 mV (SCE) . In both cases an excitation voltage of 10 mV was used. All impedance data were fit to appropriate equivalent circuits using a complex non-linear least-squares fitting routine, using both the real and imaginary components of the data. Mott–Schottky analyses were performed by measuring the capacitance as a function of potential at 1 kHz using an excitation voltage of 10 mV and a sweep rate of 0.01 V s^{-1} .

3. Results

In Fig. 1(a) representative anodic polarization curves recorded for Zn polarized under conditions of illumination and in the dark in the Cl^- -containing borate solution are shown. These measurements were performed by, first allowing the zinc electrode to stabilise in the solution for $1.3 \times 10^3 \text{ s}$ and then, polarising the electrode in the dark or under continuous illumination from the corrosion potential. These data are somewhat different to those reported in other communications [2,6] as a pre-reduction step was not employed. Thus, the high anodic currents normally observed in the potential region of -1.2 V (SCE) are not seen here. The electrode polarized in the dark exhibits a passive region from about -600 mV (SCE) to 1.6 V (SCE) . At potentials more anodic than 1.6 V , oxygen evolution occurs to give rise to the relatively sharp increase in current. The polarization behaviour of the electrode recorded under illumination conditions is very different. The anodic current is approximately an order of magnitude higher than that recorded for the electrode polarized in the dark at 500 mV (SCE) . The anodic current increases gradually to a value of about 1 mA cm^{-2} at 1 V (SCE) , at which point the current is approximately two orders of magnitude higher than that recorded for the electrode polarized in the dark. These data indicate that illumination has a significant effect on the passive behaviour of zinc under these conditions, promoting dissolution. Similar data were recorded in the absence of chloride.

In Fig. 1(b) similar data recorded under illumination and non-illumination conditions, but with a deoxy-

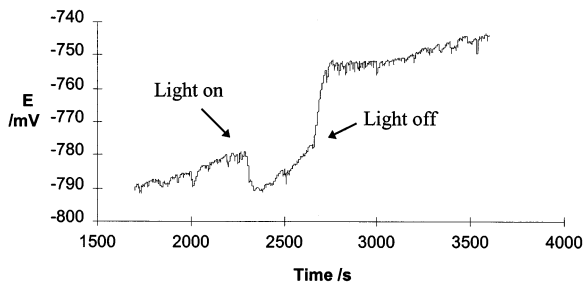


Fig. 2. Open-circuit potential recorded for zinc in chloride-containing borate solution as a function of time. Surface is illuminated for 360 s after 2.3×10^3 s of immersion.

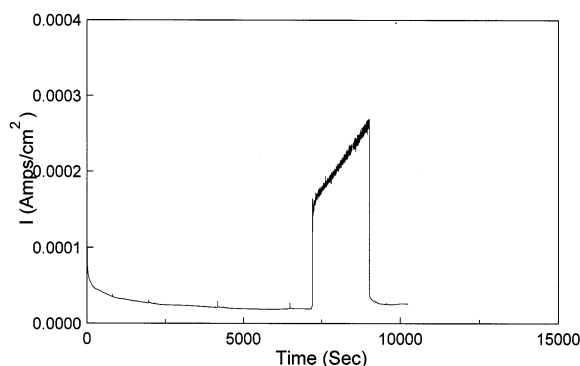


Fig. 3. Potentiostatic current–time plots recorded for Zn in borate electrolyte. Surface illuminated after a period of 2 h. After a further period of 30 min the light is removed.

generated electrolyte, are shown. Again, significant anodic currents induced by illumination are evident. The anodic current measured at 0.4 V is approximately $30 \mu\text{A cm}^{-2}$ in the dark, but approximately $90 \mu\text{A cm}^{-2}$ under illumination conditions. Here, anodic peaks at approximately -1.2 V are evident, as the electrode was maintained at, and polarized from, a much lower initial potential. Thus, reduction of the air-formed oxide occurred. Indeed, similar data were recorded on first polarising the electrode at -1.3 V (SCE) for 6 min and then polarising in the anodic direction. The decay of these anodic peaks has been attributed to the nucleation of a ZnO barrier layer [13]. Illumination of the electrode did not appear to have any effect on the kinetics of zinc dissolution in this potential region. The onset of transpassive dissolution is seen at 0.94 V for the dark electrode and at 0.92 for the electrode polarized under illumination conditions. A second anodic current peak is observed for both electrodes at about 1.2 V. On increasing the potential further a secondary-passive region is observed. Similar anodic peaks and secondary-passive regions have been observed by Davies and Lotlikar [13] and Aufustynski et al. [14] in de-oxygenated and oxygenated boric acid–sodium hy-

droxide electrolytes, and were attributed to the formation of zinc peroxide, ZnO_2 . This secondary passive region is much more pronounced for the electrode polarized under non-illumination conditions. Again, similar data were recorded in the absence of chloride, indicating that chloride anions are not necessary for the onset of the photo-induced anodic reactions.

In Fig. 2, the open-circuit potential of zinc recorded in the chloride-containing borate solution, in the presence and absence of illumination, is shown as a function of time. The open-circuit potential was recorded for 2.3×10^3 s and the light was applied for a period of 360 s. Within seconds of the light application the open-circuit potential dropped to more cathodic potentials, $\Delta E = 10$ mV. This negative displacement in the open-circuit potential on illumination is consistent with the n-type conductivity of the film formed under these open-circuit conditions. On removal of the light source the open-circuit potential reverted back to more positive values, with the displacement, ΔE , being of the order of 20 mV. This difference in the extent of the photo-potential over the 6 min illumination period points to the fact that this continuous illumination period leads to a modification of the oxide layer.

In Fig. 3, the influence of a light stimulus on the anodic behaviour of zinc is shown. In these tests the electrodes were polarized at 800 mV (SCE) in the borate electrolyte. After a polarization period of 2 h the surface was illuminated. Illumination was continued for a further period of 30 min, at which point the light was removed. Within a few seconds of illumination, a sharp increase in the current is observed, but the extent of this current increase varied somewhat from experiment to experiment. The current continued to increase during the illumination period, signifying intense dissolution. However, once the light stimulus was removed the surface re-passivated within approximately 10 s. However, the passive current did not return to the value prior to illumination. There was a difference of about $5 \mu\text{A cm}^{-2}$ in the current before and following the illumination period. This tends to suggest that the intense dissolution observed during the illumination period leads to some degree of surface roughening and a change in the surface area.

In Fig. 4, the impedance spectra, presented in both Bode and Nyquist plots, recorded for zinc at the open-circuit potential under conditions of illumination and non-illumination in the borate electrolyte are shown. These spectra were recorded after an initial delay period of 1.3×10^3 s in the dark. Similar data recorded after the light is removed is shown in Fig. 5. In this latter case, the impedance was recorded under dark conditions for electrodes previously immersed in the borate electrolyte for 6.2×10^3 s under illumination and non-illumination conditions. It can be seen from these figures that continuous illumination of the electrode

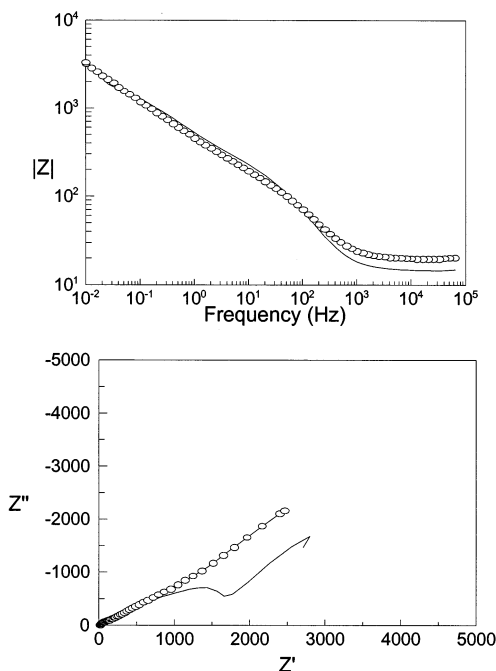


Fig. 4. Impedance data recorded for zinc in borate electrolyte at open-circuit potential under conditions of \circ illumination and $—$ non-illumination. $|Z|$ in units of $\Omega \text{ cm}^2$.

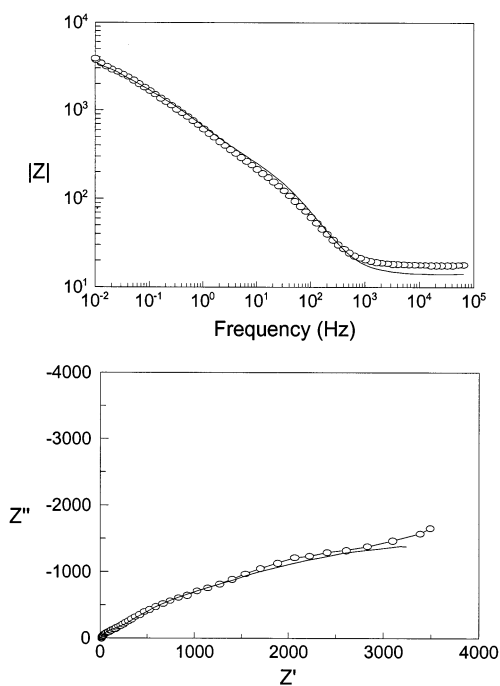


Fig. 5. Impedance data recorded for zinc under dark conditions in borate electrolyte at open-circuit potential, following $—$ 6.2×10^3 s in the dark, and \circ 6.2×10^3 s under illumination conditions. $|Z|$ in units of $\Omega \text{ cm}^2$.

causes slight changes in the measured impedance. However, once the light stimulus is removed there is very little difference in the impedance spectra. It can also be seen that the impedance changes with immersion from a comparison of the data recorded under dark conditions in Figs. 4 and 5. The spectra recorded after a period of 1.3×10^3 s, Fig. 4, are characteristic of a low frequency diffusional process, but with continued immersion and the accompanying hydroxide induced dissolution of Zn, these diffusional processes become less evident, Fig. 5.

These data were fit to the equivalent circuit depicted in Fig. 6(a). Here, R represents resistance elements and Q_1 and Q_2 are constant phase elements. Excellent agreement between the experimental data and the theoretical fitted data was obtained when these frequency-dependent constant-phase elements (CPE) were used as opposed to using pure capacitance and Warburg impedances. The impedance of a constant-phase element, is defined as $Z_{\text{CPE}} = [Q(j\omega)^n]^{-1}$ where $-1 \leq n \leq 1$ [15]. The n value was close to unity in the case of Q_1 indicating that Q_1 is a true capacitance element while the n value obtained for Q_2 , was close to 0.5 indicating that this is a Warburg diffusional term. This low-frequency Warburg response, the Q_2R_2 parallel combination, is probably related to the adsorbed intermediate species generated during dissolution of zinc in the alkaline solution and then subsequently adsorbed or precipitated on the surface leading to passivation. Thus, the dissolution reaction appears to be limited by this adsorbed/precipitated layer. The terms R_1 and R_2 are resistance elements, where the charge transfer resistance, R_{ct} is equal to the sum of R_1 and R_2 . The Q_1R_1 parallel combination, recorded at higher frequencies, reflects the properties of the oxide solution interface, where Q_1 is the double-layer capacitance.

In Fig. 6(b) the resistance, $R_1 + R_2$ is shown as a function of time for zinc electrodes immersed in the borate solution under different conditions of illumination and non-illumination. Four sets of data are presented. Data are shown for the zinc electrode under continuous dark conditions, illuminated for 1.9×10^3 s and illuminated for 6.2×10^3 s. Finally, the electrode was illuminated for 1.9×10^3 s, then maintained under dark conditions for 6.2×10^3 s followed by further illumination for 1.9×10^3 s. Illumination of the electrode surface seems to have little effect on the charge transfer resistance. However, the values tend to be slightly higher on extended immersion for electrodes illuminated for the longer period of 6.2×10^3 s, during the early stages of immersion. This tends to suggest that some modifications occur during the illumination period.

Illumination had little effect on the double-layer capacitance, Q_1 . Typical values for Q_1 were $3.5 \times 10^{-5} \text{ F cm}^{-2}$ during early immersion, and rising to approxi-

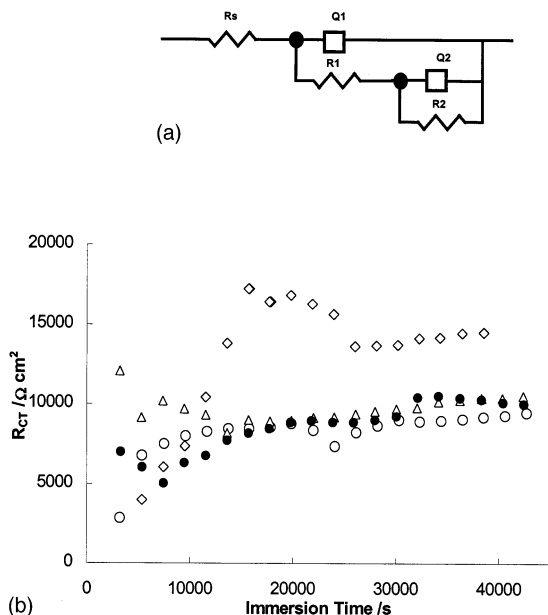


Fig. 6. (a) Equivalent circuit model used to fit impedance data recorded under open-circuit conditions. (b) Charge transfer resistance, R_{ct} , as a function of immersion period for Zn in borate electrolyte under ● dark conditions, ○ illumination for 1.9×10^3 s, ◇ illumination for 6.2×10^3 s and △ illumination for 1.9×10^3 s, then dark conditions for 6.2×10^3 s and further illumination for 1.9×10^3 s.

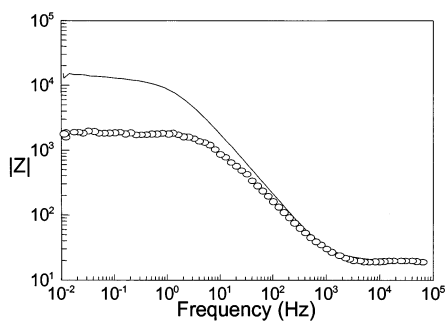


Fig. 7. Impedance data recorded for zinc in borate electrolyte polarized at 800 mV (SCE), after an initial polarization period of 2 h in the dark, under conditions of continuous illumination and — non-illumination. $|Z|$ in units of $\Omega \text{ cm}^2$.

mately $4.5 \times 10^{-5} \text{ F cm}^{-2}$ during extended immersion periods (greater than 12 h). The double-layer capacitance tended to increase in a similar fashion with extended immersion periods, regardless of whether or not the electrode was illuminated. Likewise illumination appeared to have little effect on the Warburg diffusion term. Q_2 decreased from about $8.5 \times 10^{-4} \Omega^{-1} \text{ s}^{0.5} \text{ cm}^{-2}$ to about $5 \times 10^{-4} \Omega^{-1} \text{ s}^{0.5} \text{ cm}^{-2}$ on continued immersion, but illumination of the electrode did not alter the value of Q_2 at any time.

Using the Warburg impedance Q_2 , the diffusion coefficient, D , was calculated using Eq. (1) [15].

$$\frac{1}{\sqrt{2}Q_2} = \frac{RT}{\sqrt{2Dn^2F^2c}} \quad (1)$$

Assuming that the concentration of electroactive species depends purely on the pH of the solution, which gives a value of $10^{-1} \text{ mol dm}^{-3}$ for the hydroxide ion concentration, the D values calculated were of the order of $1.5 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$ for both illuminated and non-illuminated electrodes. This low value for the diffusion coefficient indicates that this diffusion process takes place in the solid phase and that illumination does not alter this solid-phase diffusion process.

In Fig. 7 impedance data recorded for zinc in the borate solution, during polarization at 800 mV (SCE) under conditions of illumination and non-illumination are shown. The electrodes were first polarized at 800 mV (SCE) for 2 h in the dark to ensure the formation of a stable passive layer. It can be seen in this case that illumination of the surface has a significant effect on the impedance data, decreasing the impedance by an order of magnitude. A similar set of data recorded after the light is switched off is shown in Fig. 8. Here, the impedance was measured at 800 mV (SCE) for electrodes polarized under dark conditions for 13.5×10^3 s, and polarized for an initial period of 7.2×10^3 s in the dark and then followed by a period of 6.3×10^3 s in the light. It is evident from this figure that the photo-induced dissolution effect is almost removed once the electrode is exposed to dark conditions.

These data were fit to the equivalent circuits depicted in Figs. 9(a) and (b). In the case of the data recorded in the dark, Fig. 9(a), a diffusion term was required, Q_2 (with $n = 0.5$). There was no evidence of any diffusion process for the specimens polarized under continuous illumination conditions. In this case, a simple parallel

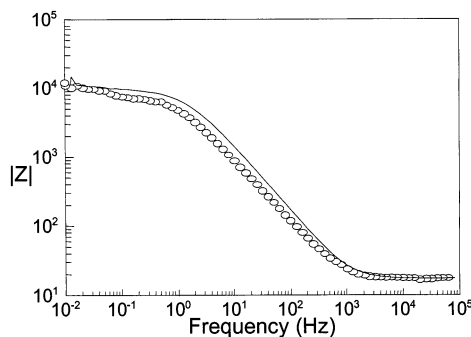


Fig. 8. Impedance data recorded under dark conditions for zinc in borate electrolyte polarized at 800 mV (SCE), — after an initial polarization period of 13.5×10^3 s in the dark ○ after an initial polarization period of 7.2×10^3 s in the dark, followed by 6.2×10^3 s under illumination conditions. $|Z|$ in units of $\Omega \text{ cm}^2$.

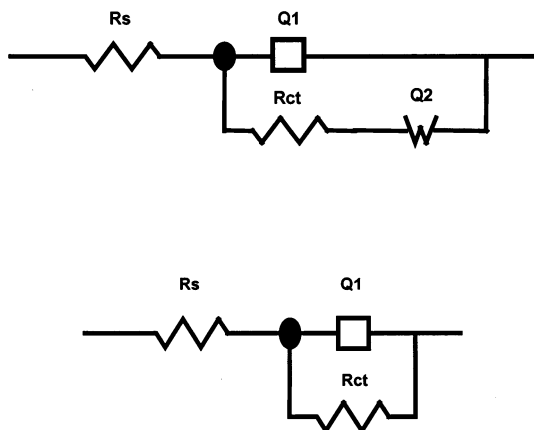


Fig. 9. Equivalent circuit models used to fit impedance data recorded at 800 mV (SCE) under (top) dark and (bottom) illumination conditions.

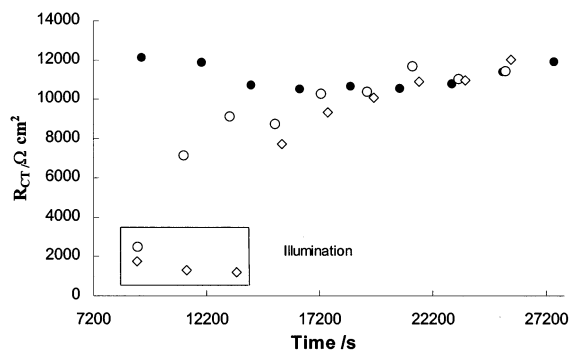


Fig. 10. Charge-transfer resistance, R_{ct} , as a function of time for Zn in borate electrolyte polarized at 800 mV (SCE) under ● dark conditions, ○ illumination for 1.9×10^3 s after an initial period of 7.2×10^3 s under dark conditions, ◇ illumination for 6.2×10^3 s after an initial period of 7.2×10^3 s under dark conditions.

RC circuit was used to fit the data. This indicates that under illumination conditions a faradaic reaction takes place with an impedance for charge transfer of R_{ct} .

In Fig. 10 the charge transfer resistance is shown as a function of time for specimens under continuous dark conditions, under illumination for 1.9×10^3 s and illumination for 6.2×10^3 s following the pre-passivation periods in the dark. The data points recorded under illumination conditions are highlighted in the diagram. It is evident from these data that continuous illumination reduces the charge transfer resistance by an order of magnitude. But when the light stimulus is removed, the charge transfer resistance is restored to a value comparable to that measured under continuous dark conditions. The capacitance, Q_1 , was of the order of $13 \mu\text{F cm}^{-2}$ for the electrodes polarized under continuous dark conditions, $18 \mu\text{F cm}^{-2}$ on and following a

1.9×10^3 s illumination period and about $24 \mu\text{F cm}^{-2}$ on and following a 6.2×10^3 s illumination period. Again, these results show that illumination leads to an increase in the activity of the passivated electrode.

In Fig. 11, representative Mott–Schottky plots recorded under dark conditions, for specimens previously exposed to continuous dark conditions and an intermittent illumination period are shown. In these measurements, a passive film was first formed at 800 mV (SCE) in the borate solution. In the case of the dark experiments, the passive film was formed under dark conditions for 2 h and then the impedance voltage data were recorded. In the case of the illumination experiments, the electrode was first passivated for 30 min under dark conditions, then illuminated for a 30 min period and finally polarized for a further 1 h period in the dark. In the measurements, the potential was swept from the formation potential (800 mV (SCE)) at a sweep rate of 0.01 V s^{-1} in the negative direction. Identical data were obtained on reversing the sweep back to the original formation voltage and with different scan rates. This shows that the film thickness and the donor densities remain constant throughout the experiment.

The capacitance, at this high frequency, was calculated using the expression,

$$Z(j\omega) = R_s + \frac{1}{j\omega C} \quad (2)$$

where the capacitance, C , consists of contributions from the space-charge capacitance and the Helmholtz capacitance. Thus, the space-charge capacitance can be calculated by correcting the measured capacitance data for Helmholtz contributions. All capacitance values were corrected using a value of $20 \mu\text{F cm}^{-2}$ for the

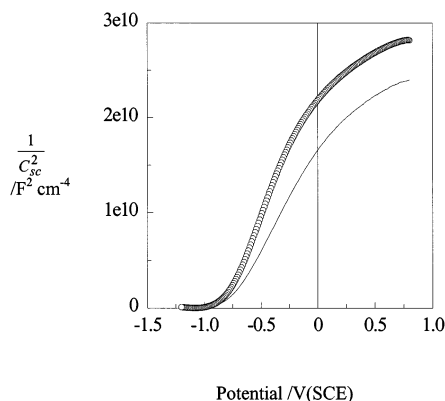


Fig. 11. Mott–Schottky plots recorded under dark conditions for Zn in borate solution following a 7.2×10^3 s polarization period at 800 mV (SCE) under ● dark conditions and ○ dark conditions for the first 1.8×10^3 s, then illumination for 1.8×10^3 s followed by dark conditions for 3.6×10^3 s.

Helmholtz capacitance to give the space-charge capacitance C_{sc} . The potential dependence of $1/C_{sc}^2$ follows the Mott–Schottky equation [16,17],

$$\frac{1}{C_{sc}^2} = \frac{2}{q\epsilon\epsilon_0 N_D} \left(E - E_{fb} - \frac{kT}{q} \right) \quad (3)$$

where N_D is the donor density, E_{fb} is the flatband potential, ϵ is the dielectric constant of the semiconductor film (i.e. 8.5 for ZnO [18,19]), ϵ_0 is the permittivity of free space and q is the electronic charge. The Mott–Schottky plots shown in Fig. 11, exhibit well-defined linear portions over a relatively wide potential region, and are characteristic of those for an n-type semiconductor, in agreement with other publications [2,6,20]. The donor densities, calculated from the slopes of the linear regions of the plot were found to be about $5.2 \times 10^{20} \text{ cm}^{-3}$ for the electrodes under continuous dark conditions and $7.3 \times 10^{20} \text{ cm}^{-3}$ for the electrodes exposed to prior illumination. This difference lies well outside the experimental error which was $\pm 0.2 \times 10^{20} \text{ cm}^{-3}$. The flat-band potentials were calculated as -0.76 V (SCE) for the dark electrodes and -0.80 V (SCE) for the illuminated electrodes, a difference of about 40 mV, which is close to the experimental error of $\pm 30 \text{ mV}$. The donor densities calculated here are slightly higher than those calculated previously [2,6], which range between 1×10^{20} and $3 \times 10^{20} \text{ cm}^{-3}$, but this is due to the more alkaline solutions used in this study. But, the flat-band potentials are in good agreement with those reported by Bohe et al. [6].

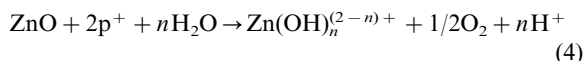
4. Discussion

The experimental results presented here are consistent with the facts that anodically formed passive layers on Zn consist predominantly of ZnO and that the anodic ZnO film may be considered as a highly-doped amorphous n-type semiconductor. There is much evidence to suggest that the passive films formed in alkaline solutions under anodic polarization contain high concentrations of ZnO. For example, the presence of ZnO in passive layers formed in alkaline media has been confirmed by in situ laser Raman spectroscopy studies [21] and by electron diffraction experiments [22]. It is also well known that ZnO is a highly-doped n-type defect semiconductor [2–6] ($\text{Zn}_{1+\delta}\text{O}$ where $\delta > 0$) with the principal defect being the zinc interstitial.

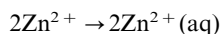
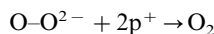
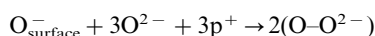
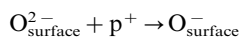
On illumination of the anodically biased ZnO semiconductor with sufficiently energetic photons, electrons are promoted from the valence to the conduction band generating electron-hole pairs. Due to band bending, the electron-hole pair separates. The holes are transported to the film–solution interface where they undergo an electrochemical reaction (or recombine via surface recombination centres) and the electrons mi-

grate into the bulk. The extent of the photo-induced reaction will depend on the concentration of surface holes, which increases with increasing surface potential barrier. The anodic polarization plots shown in Fig. 1 are consistent with increasing photo-induced reactions with increasing anodic potential. It can also be seen from Fig. 1 that a steady-state, or saturation, photo-current is not observed. This indicates that the anodic reactions have not exhausted all the photo-generated holes available at the surface.

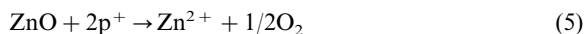
These observed photo-induced anodic reactions, may be attributed to the photo-corrosion of the ZnO layer, and can be represented by,



where n depends on the pH of the solution. In the case of the alkaline pH 13.0 solution used in this study, the corrosion products are most likely Zn(OH)_4^{2-} and Zn(OH)_3^- species [23], in which case n is equal to 3 or 4. According to Gerischer [24], the sequence of steps involved in the photo-decomposition of ZnO crystals consists of two slow steps where two holes are trapped on the surface, followed by the fast formation of an oxygen molecule and the fast expulsion of Zn^{2+} from the surface, i.e.



The overall reaction may be represented as,



The anodic decomposition potential for this reaction is 0.65 V (SCE). This potential is lower than the redox potential for the oxidation of water by holes and thus the decomposition of the ZnO is the thermodynamically more favourable reaction. It has been reported that water oxidation occurs as a parallel reaction to the photo-decomposition of ZnO, but only at very high current densities [25]. The redox potential for the oxidation of Cl^- by surface holes is also more positive than the anodic decomposition potential of ZnO. Thus, the increased anodic currents observed in this study may be attributed, almost solely, to the photo-induced decomposition of the passive layer. This photo-induced decomposition does not depend on the presence of Cl^- in solution, at least at the concentrations used in this study, as essentially identical data were recorded in the absence and presence of chloride anions.

This photo-induced corrosion of ZnO is consistent with the large increase in the anodic currents, measured on illumination of the anodically formed oxide layers

on zinc, Figs. 3 and 7, and the ten-fold decrease in the measured charge-transfer resistance, Fig. 7. Using the capacitance values of $13 \mu\text{F cm}^{-2}$ for the electrodes polarized under continuous dark conditions, $18 \mu\text{F cm}^{-2}$ following a 1.9×10^3 s illumination period and about $24 \mu\text{F cm}^{-2}$ following a 6.3×10^3 s illumination period, it can be seen that prior illumination leads to progressively higher capacitance values. Using the well-known parallel plate expression for the capacitance, C , to estimate the thickness of the passive layer,

$$L = \frac{\epsilon\epsilon_0 A}{C} \quad (6)$$

where ϵ is the dielectric constant for ZnO, ϵ_0 is the permittivity of free space and A is the surface area, the approximate thickness of the ZnO barrier layer is calculated as 0.58 nm in the dark, 0.42 nm following 1.9×10^3 s of illumination and 0.32 nm following 6.5×10^3 s of illumination. Thus, it can be seen that the thickness of the ZnO barrier layer, which is relatively thin under these conditions, is decreased even further on illumination.

It is seen from a comparison of the impedance data recorded at the open-circuit potential and at 800 mV (SCE), Figs. 4 and 7, that significant photo-induced dissolution only occurs when an anodically-formed oxide layer is present. These effects are not seen, to the same extent, under open-circuit conditions. This is partly due to the lower concentration of photo-generated holes available at the surface under open-circuit conditions. However, Justice and Hurd [26] observed that the open-circuit (-650 mV (SCE)) dissolution rates of an $8.5 \Omega \text{ cm}$ ZnO crystal in 1.0 mol dm^{-3} KOH solution were higher by a factor of 2 under irradiation conditions. Thus, the lack of any substantial photo-decomposition reaction under open-circuit conditions in this study may be due to the formation of an adsorbed or precipitated layer, which is much less photo-active. The presence of this layer, probably $\text{Zn}(\text{OH})_2$ or $\text{ZnO}_{1-x}(\text{OH})_{2x}$ [27] which forms by precipitation from a supersaturated solution of zincate near the surface, is clearly evident in the impedance data presented in Figs. 4 and 5. It appears that this precipitate layer is relatively inert to any photo-induced decomposition. However, the photo-potential observed under open-circuit conditions, Fig. 2, indicates that some degree of photo-activity is possible under open-circuit conditions.

It is also seen, from Figs. 3 and 7, that significant dissolution only occurs while the specimens are illuminated and that once the light source is removed that the specimens re-passivate. However, there is some evidence to suggest that the passive layers are modified by the illumination procedure. This is evident from the fact that prior illumination leads to a decrease in the donor densities by approximately a factor of 1.4, Fig. 11.

Since these experiments were recorded by polarising the electrode a further 1 h after the photo-induced dissolution period, to ensure similar oxide film thickness, it seems that the dissolution/repassivation events induced by illumination lead to a decrease in the defect structure.

Illumination of the surface has an additional effect in the secondary passivation region. At potentials more positive than 1.2 V (SCE), Fig. 1(b), a sharp rise in current is observed. This corresponds to the transpassive dissolution of the barrier ZnO layer. This is followed by the onset of secondary passivation, which corresponds to repassivation through the formation of higher oxidation states of zinc, for example, ZnO_2 . In the absence of illumination the current decays to approximately $100 \mu\text{A}$, but only to $400 \mu\text{A}$ on illumination. As the ZnO barrier is removed prior to the onset of this repassivation event, the generation of surface holes and the accompanying oxidation of H_2O by these holes, cannot be responsible for the higher anodic currents observed in this region. Thus, the higher anodic currents, which are evident on illumination, appear to be associated with a slower nucleation of the peroxide-containing film. These events are not seen if the electrode is polarized from a higher potential (-800 mV (SCE)), Fig. 1(a). In this case, the original air-formed film is not reduced, but becomes attacked in the OH^- solution and eventually gives rise to the barrier ZnO film. This film remains stable in the potential region of 1.2 V, but undergoes more significant photo-decomposition.

5. Conclusions

Significant dissolution of anodically formed passive layers on zinc was observed on illumination with polychromatic light. This was attributed to the photo-decomposition of ZnO, which occurs through reaction with surface holes generated during the illumination period. The photo-induced dissolution effect was only slightly evident under open-circuit conditions, where a precipitated or adsorbed layer forms on the electrode.

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