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Anodic oxidation and self-polarization of zinc metal

Part 1 *Structural changes*

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X-ray diffraction techniques have been applied to study the structural changes and processes which take place when zinc metal is subjected to oxidation and self-polarization at the metal–electrolyte interface. The effect of electrolyte concentration and anodizing voltage on the structure and composition of the ZnO layer formed was investigated.

1. Introduction

The Bragg scattering of X-rays by semiconductor crystals subjected to diffusion of impurity atoms [1–3] and mechanical or chemical surface treatments have revealed characteristic features in the behaviour of the diffraction curves.

Zinc metal represents a familiar electrode material for a number of energy conversion devices, for example as anode material for dry batteries of the "Leclanché"-type with NH_4Cl solution, and as photosensitive electrodes for photoelectrochemical cells. Baugh [4] has conducted studies of the corrosion and polarization characteristics of zinc in NH_4Cl, $NaClO_4$ and Na_2SO_4 media. He investigated the formation of surface oxide/hydroxide films in weakly acidic media by differential capacitance measurements over a wide frequency range. These anodic films act as potential barriers and their composition and structure are the main factors which determine the electrical and photoelectric properties of the photoelectrochemical cell. X-ray diffraction measurements [5, 6] have indicated that white anodic films formed consisted essentially of zinc oxide, which possesses semiconducting properties.

Gatos and Lavine [7, 8] have applied the "dangling bond" model to the electronic structure of ZnO. In this model the oxygen atoms at the $(0 0 0 \bar{1})$ surface would have two electrons in a "dangling bond", or lone pair orbital, whereas the zinc atoms would have no dangling bonds. On this basis [8] they concluded that any surface distortion is likely to be greater for oxygen atoms than for zinc atoms. Duke and Lubinsky [9], using an elastic low-energy electron diffraction technique for ZnO, have shown that on the metal polar surface of II–VI semiconductors, the uppermost lattice spacing is contracted relative to its bulk value because the metal atoms, stripped of their "extra" valence electrons which are present in the solid, tend to relax toward the layer below them to form planar sp^2 bonds rather than tetrahedral sp^3 bonds. Moreover, many experimental results concerning zinc oxide are interpreted assuming the existence of surface states [10–14].

The aim of the present work is to investigate, using X-ray diffraction techniques, the structural changes and processes which take place in zinc metal when subjected to anodic oxidation and self-polarization at a metal–electrolyte solution interface.

2. Experimental procedure

A conventional photoelectrochemical cell was used the anode of which was made from a circular zinc sheet of thickness 0.37 mm thickness and cross sectional area 1 cm^2. The zinc surface was previously polished, etched in 0.5 N HCl for 30 sec and then carefully washed with distilled water. A rectangular platinum cathode was used, and both electrodes

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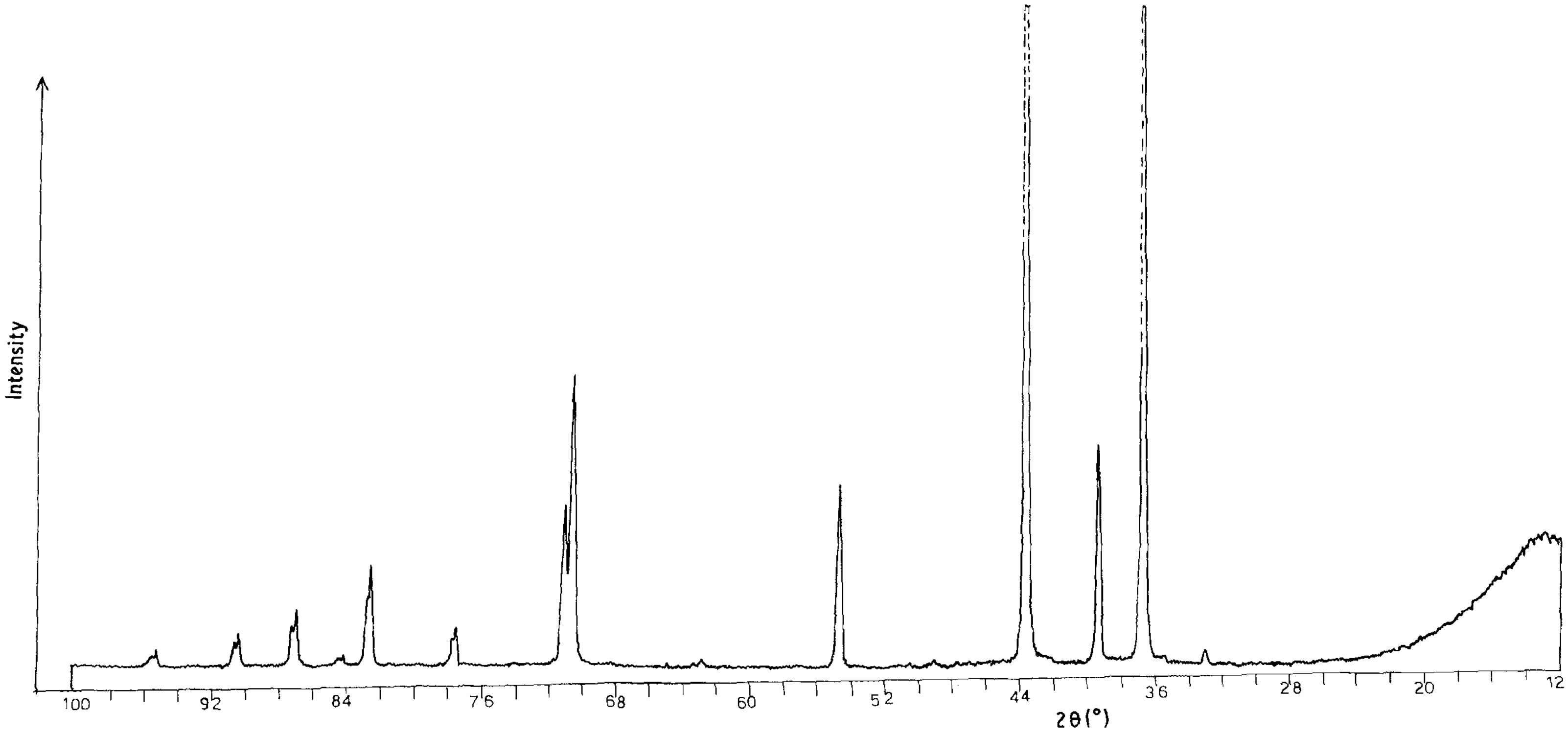

Figure 1 X-ray diffraction pattern for zinc metal.

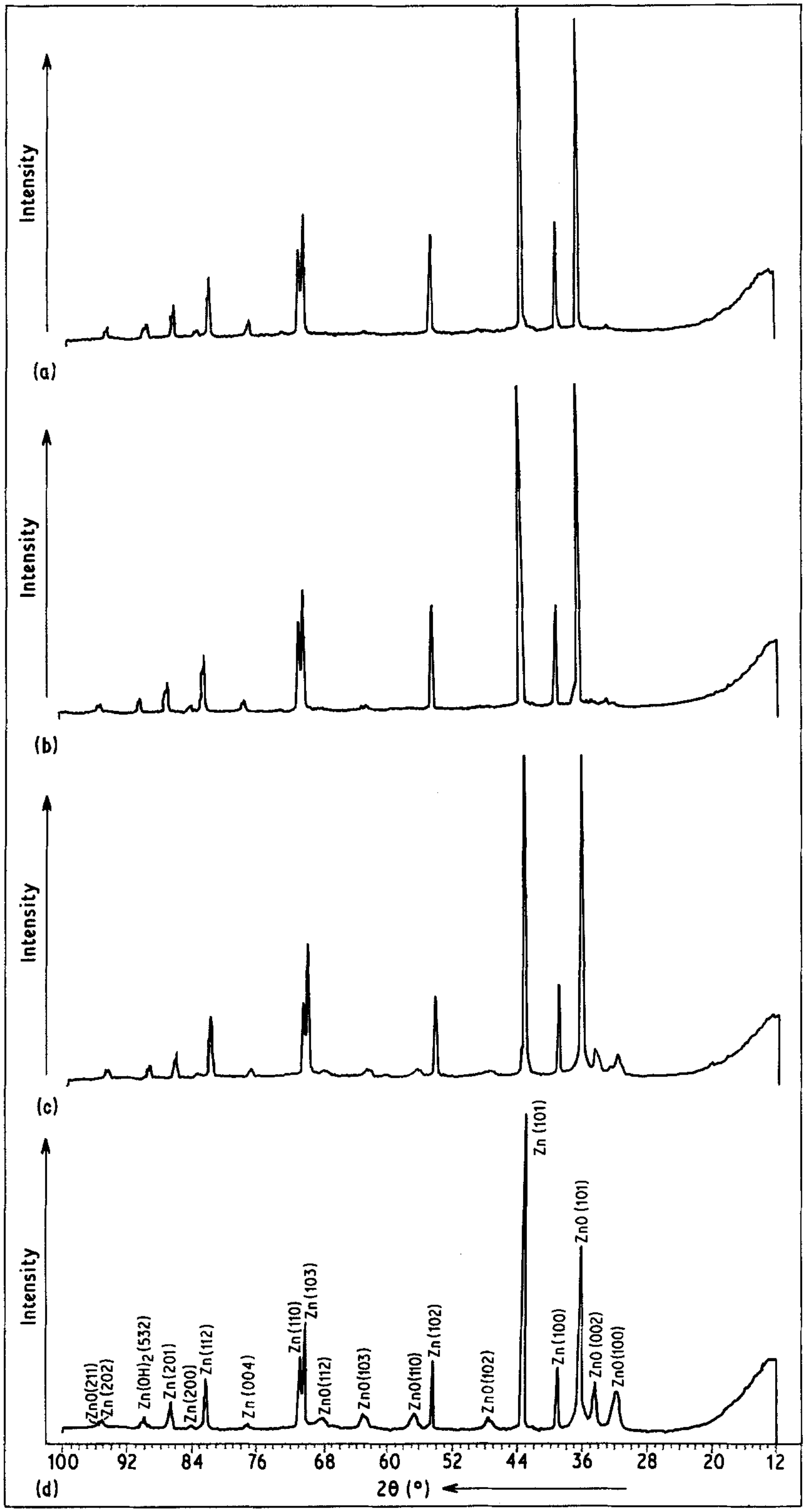

Figure 2 X-ray diffraction patterns for different ZnO layers formed at constant anodizing voltage (2 V) and different electrolyte concentrations: (a) 0.1 M KOH, (b) 0.5 M KOH, (c) 1.0 M KOH and (d) 2.0 M KOH.

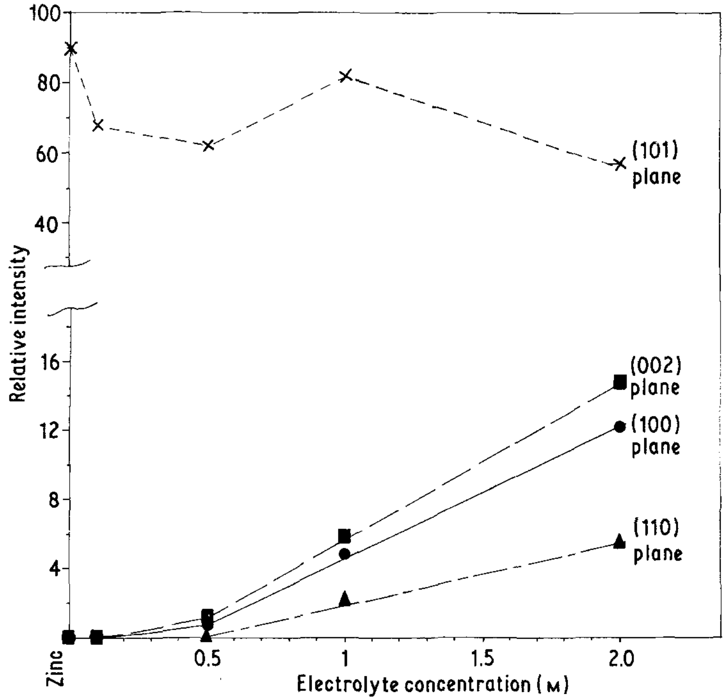

Figure 3 The dependence of the diffracted X-ray intensity from different planes of ZnO film on the electrolyte concentration (KOH) at an anodizing voltage of 2 V.

were connected to the measuring circuit, which consists of a stabilized direct current power supply (0 to 300 V) and a sensitive milliammeter. The potential across the cell electrodes was measured using a sensitive digital voltmeter.

Two types of anodizing electrolytes were used: potassium hydroxide and sodium borate in aqueous solutions with different concentrations of 0.1, 0.5, 1 and 2 M. The films formed on zinc metal in the electrolyte solutions after an interval of 30 min were examined using a Siemens X-ray diffractometer,* type D500, with copper target and nickel filter ($K\alpha = 0.15417$ nm). Measurements were carried out at room temperature and the results were found to be highly reproducible.

3. Results and discussion

3.1. Anodic oxidation

Fig. 1 shows the X-ray diffraction pattern of the starting material, metallic zinc. Upon immersion of metallic zinc in a solution a few zinc atoms lose some electrons and dissolve as ions [15]. These ions will meet the constituents of the electrolyte and the possible reactions are [16]

$$Zn \longrightarrow Zn^{2+} + 2e^-, \qquad (1)$$

$$Zn + 2H_2O \longrightarrow H\,ZnO_2 + 3H^+ + 2e^- \qquad (2)$$

and

$$Zn + 2H_2O \longrightarrow ZnO^{2-} + 4H^+ + 3e^-, \qquad (3)$$

where the ZnO so formed is a partially ionic material [17].

Fig. 2a to d shows X-ray diffraction patterns for different layers formed at a constant anodizing voltage (2 V) and different electrolyte concentrations. The curves show an increase in the relative intensity for zinc oxide with increasing electrolyte concentration (Fig. 3). Moreover, the same behaviour was observed when the anodizing voltage increases at a fixed concentration of the electrolyte solution (1 M KOH), as shown in Figs 4 and 5.

Fig. 6 shows the variation of the intensity of diffracted X-rays from planes of zinc and zinc oxide with electrolyte concentration at a fixed anodizing voltage (2 V). It is clear from the curves that the rate of dissolution of zinc and zinc oxide at the (1 0 1) plane increases with the concentration, while for the (1 0 0) plane the growth of ZnO appears and the dissolution of zinc increases. Similar results were observed for other planes, such as (1 1 0), (1 0 2), (1 0 3) and (1 1 2), as shown in Table I.

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*Obtained from Services Laboratory, National Research Centre, Eldokki, Cairo.

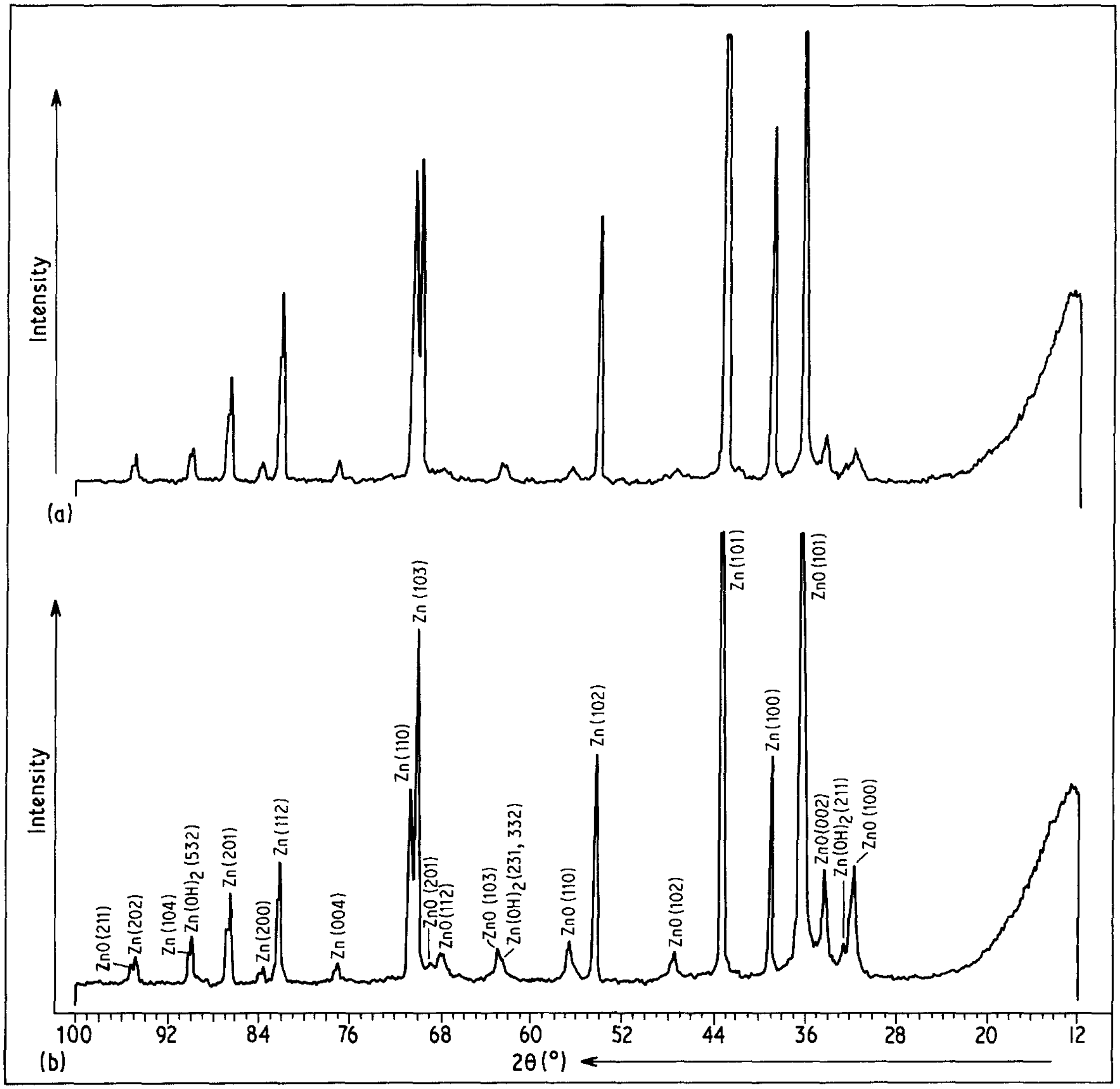

Figure 4 X-ray diffraction pattern for different ZnO layers formed at a fixed electrolyte concentration of 1.0 M KOH and different anodizing voltages: (a) 1 V and (b) 3 V.

TABLE I Calculated X-ray diffraction intentities* from zinc and zinc oxide planes for different electrolyte concentrations and at a constant anodizing voltage of 2 V

KOH concentration	(1 1 0) face		(1 0 2) face		(1 0 3) face		(1 1 2) face	
	Zn	ZnO	Zn	ZnO	Zn	ZnO	Zn	ZnO
Pure zinc	4.9	–	5.6	–	8.8	0.2	3.05	–
0.1	5.25	–	6.25	–	7.3	0.3	3.6	–
0.5	5.5	–	6.4	–	7.6	0.35	3.6	–
1.0	4.6	0.55	5.05	0.45	8.2	0.55	3.8	0.4
2.0	4.5	1.05	4.25	0.8	6.6	0.95	3.1	0.65

*Arbitrary units.

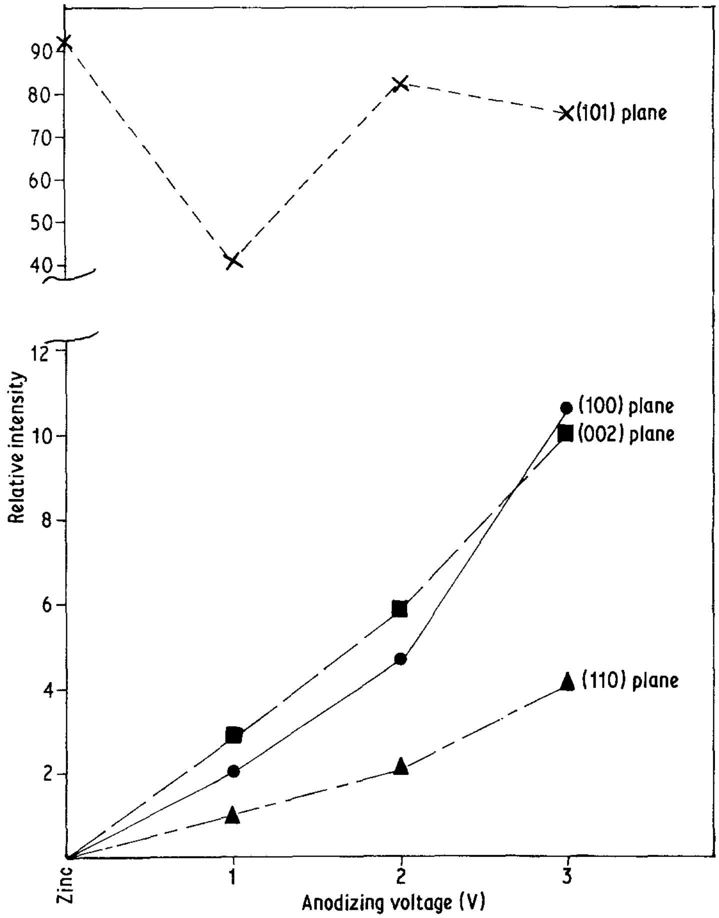

Figure 5 The dependence of the diffracted X-ray intensity from different planes of ZnO layers on the oxidation voltage at constant electrolyte concentration (1.0 M KOH).

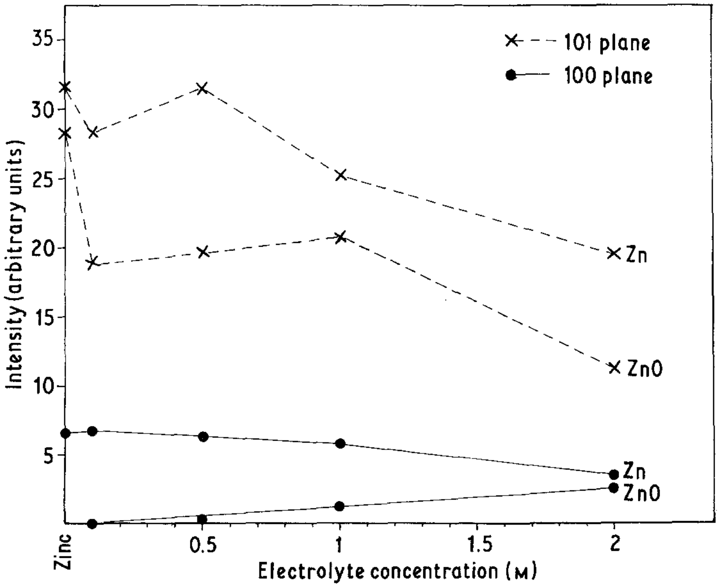

Figure 6 The dependence of the diffracted X-ray intensity from different planes of Zn and ZnO on the electrolyte concentration.

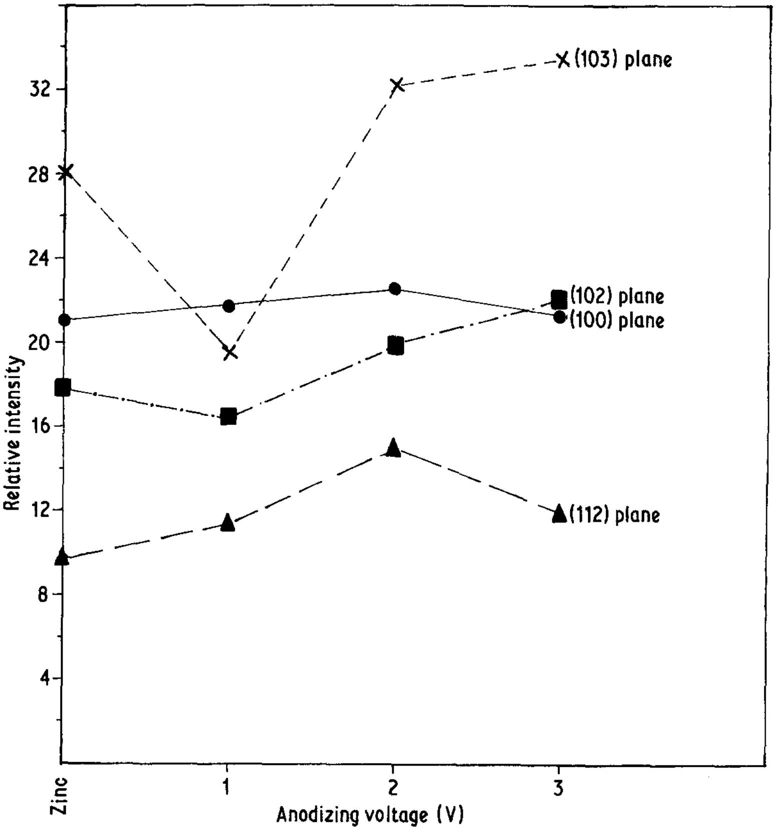

Figure 7 The variation of the diffracted X-ray intensity with the oxidation voltage for different zinc planes.

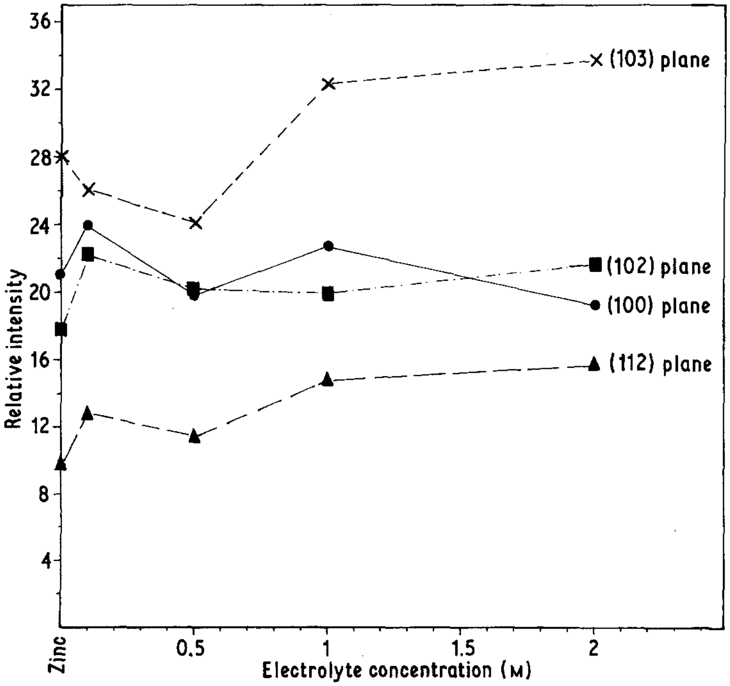

Figure 8 The dependence of the diffracted X-ray intensity on the electrolyte concentration for different zinc planes.

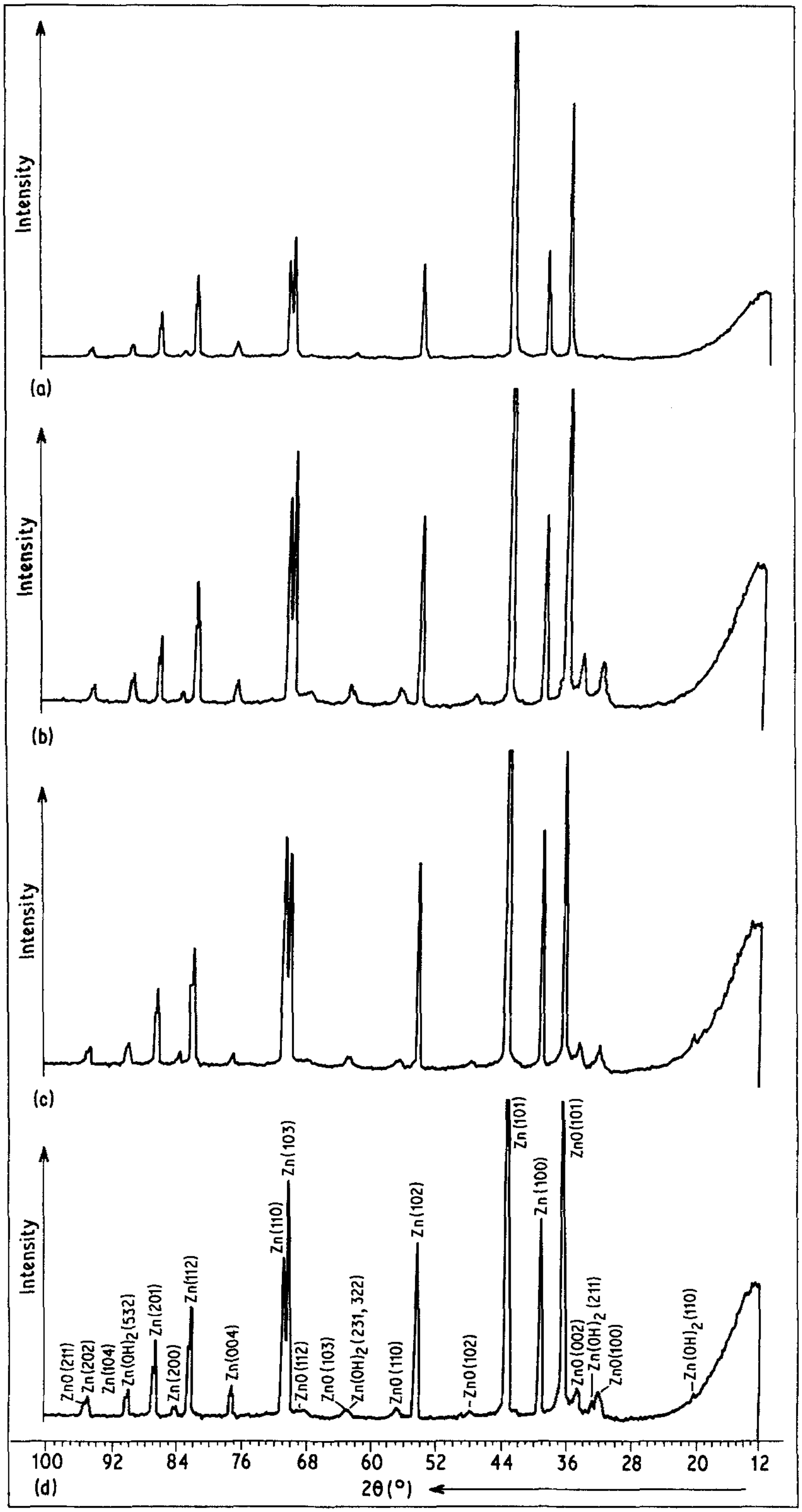

Figure 9 X-ray diffraction patterns for self polarization in (a) 0.1 M Na borate, (b) 0.1 M KOH, (c) 0.1 M KOH + 10 vol% H_2O + 90 vol% methyl alcohol and (d) 0.1 M KOH + 10 vol% H_2O + 90 vol% ethyl alcohol.

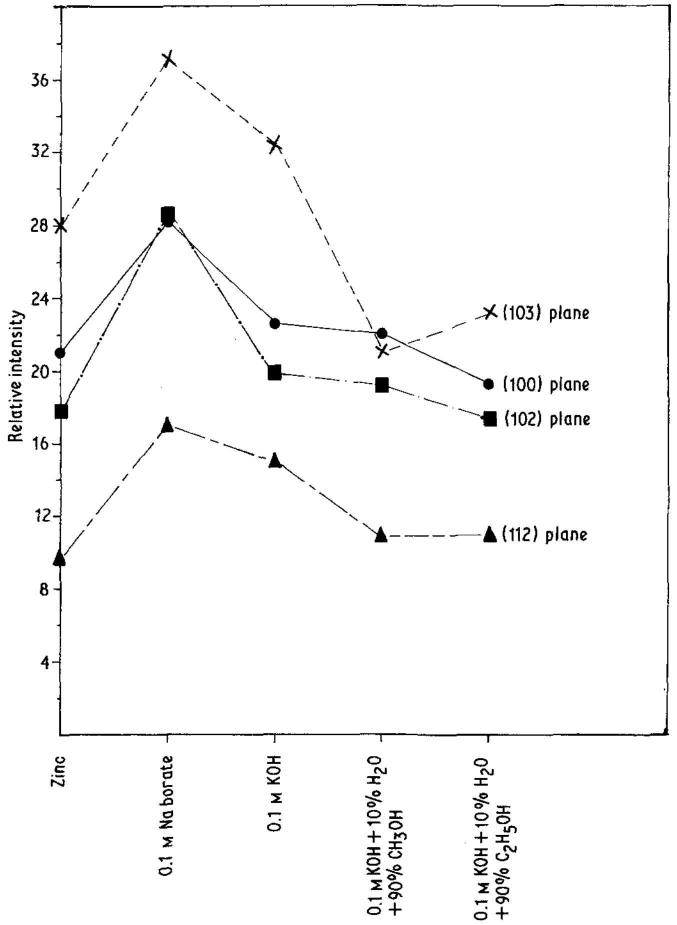

Figure 10 The dependence of the diffracted X-ray intensity for different zinc planes on the type of self-polarization solution.

Zinc oxide films obtained have a black colour which may be attributed to the affect of anode potential and electrolyte concentration. It was observed that the increases in anode potential and electrolyte concentration favour an oxide darker in colour. This black colour results from various types of lattice defects and imperfections. Some of the lattice defects are the result of the introduction of interstitial atoms such as excess zinc and other deviations from the stochiometric composition.

Hubber [6] suggested that anodized zinc consists of ZnO with varying excess of metallic zinc. This assumption was verified in Figs 7 and 8 which show the dependence of the relative intensity of diffracted X-rays from zinc planes on the anodizing voltage and electrolyte concentration, respectively. The relative intensity varies with the applied voltage as well as the electrolyte concentration.

3.2. Self-polarization

The most serious problem for photoelectrochemical cells is the strong tendency of semiconductors to be photodecomposed when immersed in a corrosive medium like an electrolyte. Such decomposition reactions are well known [18, 19], and they are caused by either electrons or holes [20]. Some examples are:

(a) anodic oxidation,

$$\mathrm{ZnO} + 2h^+ + \mathrm{aq.} \longrightarrow \mathrm{Zn}^{2+}\,\mathrm{aq.} + \tfrac{1}{2}\mathrm{O}_2, \quad (4)$$

(b) cathodic reduction,

$$\mathrm{ZnO} + 2e^- + \mathrm{aq.} \longrightarrow \mathrm{Zn} + 2\mathrm{OH}^-. \quad (5)$$

According to Hampson and Tarbox [21], when the electrode undergoes polarization, the initial step will be the production of soluble zincate. If there is a net accumulation of zincate at the anode the depletion of the OH^- concentration will cause the zincate to precipitate either as oxide or

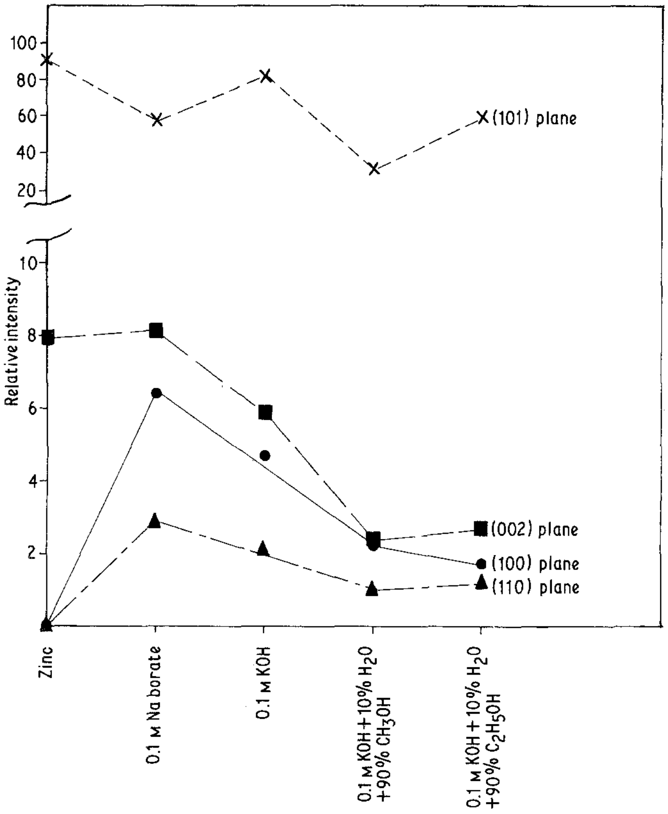

Figure 11 The dependence of the diffracted X-ray intensity for different ZnO planes on the type of self-polarization solution.

hydroxide. At the same time the hydroxyl ion adsorbed on the new positively charged ZnO surface combines with the latter as [22]

$$ZnO^+ + OH^- \longrightarrow ZnO^+ \cdot OH^- \longrightarrow ZnO \cdot OH. \quad (6)$$

This inhibits the anodic oxidation reaction. Therefore, to sustain the reaction it is necessary to remove the hydroxyl group, this can be achieved by using an organic medium.

To investigate the effect of organic media on the characteristics of zinc oxide electrodes, methyl and ethyl alcohols are added to the electrolyte in the following concentration: 90 vol% alcohol, 10 vol% water, 0.1 M KOH; 0.1 M sodium borate solution was also used as an electrolyte. Changes in structure and intensity observed in Figs 9 to 11 indicate that the relative intensities diffracted from both the zinc and zinc oxide planes is modified when self-polarization is carried out in mixed electrolyte and organic media and the formation of hydroxyl group is inhibited.

From Equations 4 to 6 it is clear that ZnO

TABLE II The change of the relative X-ray diffraction intensities for different planes after self-polarization for 287.1 h

	hkl	X-ray diffraction intensities*	
		Annodized only	After 287.1 h
Zinc oxide	101	82.41	70.45
	100	4.74	1.46
	002	5.92	1.92
	110	2.17	0.7
	103	2.17	0.64
Zinc hydroxide	110	–	4.02
	111, 210	–	1.05
	101, 200	–	1.87
	211	1.97	1.4
	231, 322	–	0.7

*Arbitrary units.

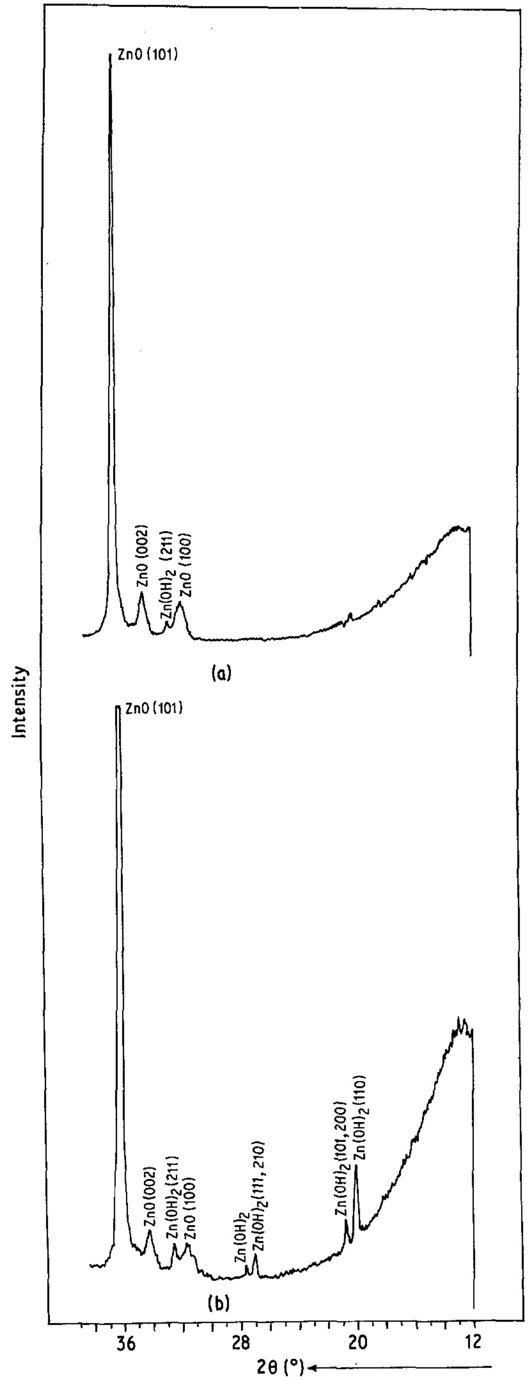

Figure 12 X-ray diffraction patterns for: (a) layer just anodized, (b) layer after 287.1 h self-polarization interval.

decomposes either to zinc or zinc hydroxide. It is noticeable that the composition depends on the time interval of self-polarization. Fig. 12 shows a comparison between the X-ray diffraction patterns for two specimens, one only anodized and the other subjected to self-polarization for 287.1 h. Table II indicates that the relative X-ray diffraction intensity from ZnO decreases after prolonged self-polarization, while zinc hydroxide crystal planes appear. Experimental observations emphasize that this behaviour is due to the self-polarization effect and it is not related to a process of hydration.

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