

## Preparation of zinc oxide films by a humid air plasma<sup>†</sup>

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The surface of zinc metal exposed to a humid air plasma gives rise to an oxide layer which was identified by the linear sweep voltammetry technique. The quantity of zinc oxide (ZnO) layer formed increases with exposure time and the humid air gas flow. The humid air plasma treatment of a zinc surface can be proposed as a new technique to prepare zinc oxide.

**Keywords:** humid air plasma, zinc oxide layers, cathodic reduction

Zinc oxide (ZnO) films are attractive materials because of their transparency in the visible range and their electrical conductivity.<sup>1</sup> Both properties vary with the oxide composition, namely with the O/Zn ratio. Recent interest for ZnO films arose from their use as transparent electrodes because of their cheap and low temperature preparation in contrast with the high cost of the In<sub>2</sub>O<sub>3</sub> or SnO<sub>2</sub> transparent films.<sup>2</sup> The ZnO films are obtained by means of several techniques. Among them, sputtering techniques are used to yield good quality films.<sup>3</sup> Chemical bath deposition, electrodeposition and oxygen plasma treatment<sup>4-6</sup> are also used.

The electrochemical behaviour of Zn has been studied for several years.<sup>7</sup> The kinetics and mechanism of the electrochemical oxidation of the metal in alkaline solutions were carefully investigated and proved of particular interest in view of the technical applications of zinc such as cathodic protection and batteries. Studies of zinc electrodisolution and passivation showed that many compounds such as Zn(OH)<sup>-</sup><sub>ad</sub>, Zn(OH)<sub>ad</sub>, Zn(OH)<sub>2</sub><sup>-</sup> and Zn(OH)<sub>3</sub><sup>-</sup> form in alkaline media.<sup>8</sup> The thermal oxidation ( $T = 673$  K) and pure inductive oxygen plasma treatment of zinc foils were studied.<sup>9,12</sup> The formation of ZnO was controlled by means of optical (UV-vis-NIR, FTIR and photoluminescence) and electrochemical methods.<sup>9-12</sup>

The oxidising character of the species created in an humid air plasma was investigated through previous studies: for example, treatments of copper foils and industrial waste waters.<sup>13,14</sup> In a plasma, a number of processes take place (*e.g.* dissociation by electron impact, ionization, molecular excitation). In the case of a humid air plasma, these induce the formation of activated species such as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O, OH<sup>\*</sup> and NO<sup>\*</sup> which were identified by emission spectroscopy in the 230–650 nm range.<sup>14</sup>

In the present work, we used a new plasma set-up, the gliding arc or "Glidarc", proposed by Czernichowski *et al.*<sup>15</sup> This kind of arc was modelled by Fridman *et al.*<sup>16</sup> more recently and was classified as a non thermal plasma because the energy of the electrons is markedly higher than that of the heavy species. The resulting plasma presents, among others, the interesting characteristic of being a source of highly oxidising species like OH<sup>\*</sup>:  $E^\circ(\text{OH}^*/\text{H}_2\text{O}) = 2.85$  V *vs* standard hydrogen electrode (SHE) and O<sub>3</sub>:  $E^\circ(\text{O}_3/\text{O}_2) = 2.85$  V *vs* SHE.<sup>12,13</sup> The oxidising properties of these activated species generated in the gliding arc discharge in humid air are used to treat the zinc foils surface.

This paper is devoted to the preparation of zinc oxide films by exposing metal foils to a humid air plasma. The excited particles formed in the plasma react at the zinc surface and form an oxide film which is characterised by the linear sweep voltammetry technique. The gliding arc treatment of a surface metal was proposed as a new technique to prepare metal oxides.

### Materials and experimental procedures

The experimental device has already been detailed.<sup>13</sup> The glidarc reactor includes two diverging aluminum electrodes disposed symmetrically around a blowing nozzle (diameter 1 mm). This nozzle is fed by wet air obtained by bubbling a compressed air flow through a water-filled Durand flask. A discharge takes place between the electrodes raised to a convenient voltage (9 kV). In this work, the air flow rate was fixed at 600 Lh. The sample was positioned normally to the gas flow on a stainless scaffold equipped with a system of cooling. The distance between the treated sample and the tips of the electrodes was carefully fixed ( $d = 1.5$  cm).

The zinc samples were supplied by the Goodfellow company. The chemical composition (ppm) of the industrial starting metal was: Al, 3 ; Ag, 7 ; Cd, 10 ; Ca, 2 ; Cu, 20 ; Sn, 5 ; Fe, 20 ; Mg, 1 ; Au, 1 ; Pb, 25 ; Si, 2. The samples ( $\cong 1$  cm<sup>2</sup> surface area) were mechanically polished with different gringing papers (400, 800, and 1200 grade) rinsed in absolute ethanol and dried immediately with nitrogen gas before being exposed to the humid air plasma.

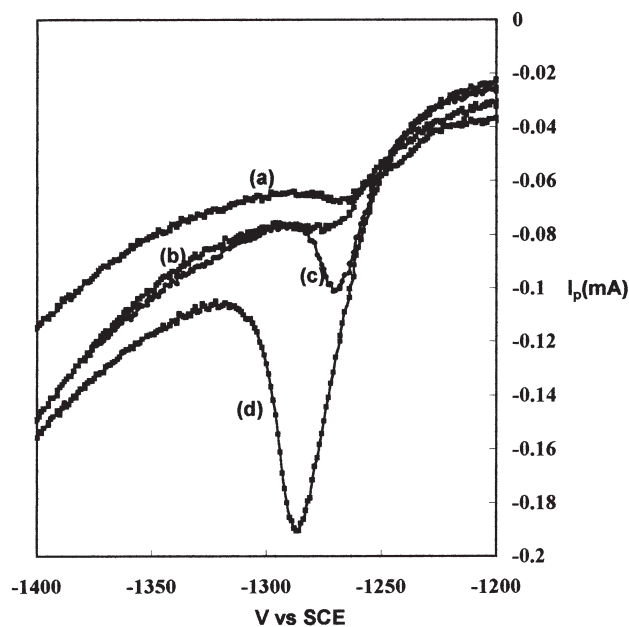
The electrochemical measurements were performed at room temperature (*i.e.* around 18 °C) in a three-electrode glass cell. The potentials are referred to a saturated calomel electrode (SCE). The selected electrolyte is a (0.1 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 510<sup>-3</sup> M LiClO<sub>4</sub> + 0.2 M H<sub>3</sub>BO<sub>3</sub>) solution at pH = 9.2 since the solubility of zinc oxide is a minimum in these conditions.<sup>6,17</sup> The voltammetry curves are recorded on a PAR 273 potentiostat with a potential sweep rate of 1 mV/s<sup>-1</sup> from -1.2 to -1.5 V *vs* SCE. Before each run the electrolyte was carefully purged with nitrogen gas.

### Results and discussion

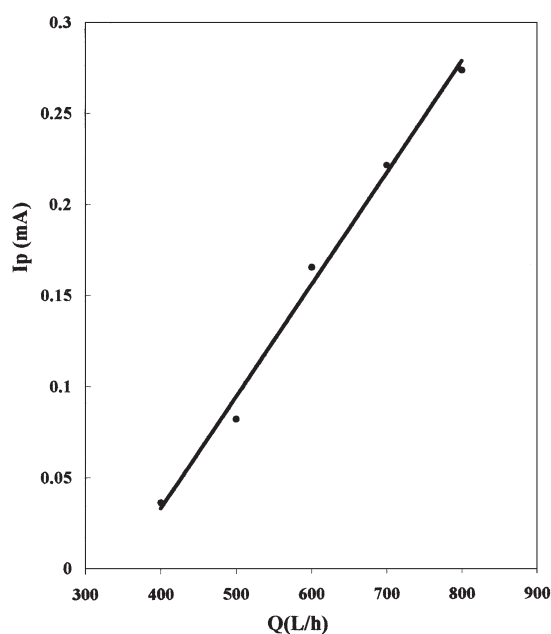
This paper is devoted to the surface oxidation of zinc foils operated by humid air plasma treatment in controlled conditions of injected power, gas flow, and position of the treated zinc sample. Figure 1 illustrates the typical curves (current (*i*/mA)) versus applied potential (*E*/V) of zinc samples treated for 1 min or more. All the cathodic curves present a single peak in the range -1.2 to -1.5 *vs* SCE which is attributed to the reduction of zinc oxide to metal:  $\text{Zn(II)} + 2e^- \rightarrow \text{Zn(0)}$ .

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<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.



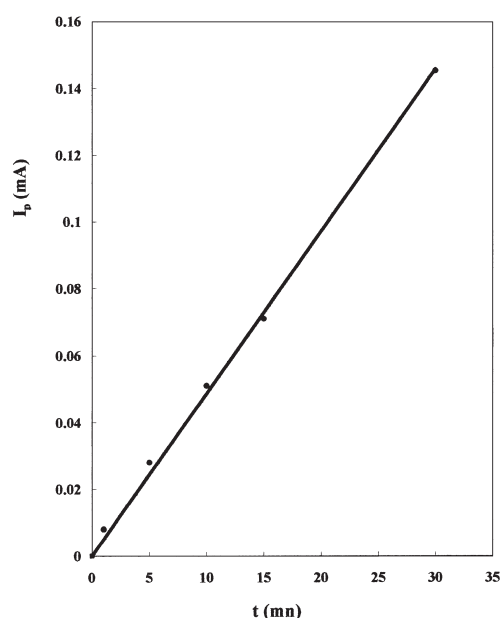
**Fig. 1** Cathodic reduction curves of zinc oxide formed by an humid air plasma oxidation of zinc foils for different exposures ( $d=1.5$  cm,  $\Phi = 600$  L.h<sup>-1</sup>): (a) 2; (b) 5; (c) 10 and (d) 30 min.



**Fig. 2** Variation of the intensity of the reduction peak for given treatment time exposures ( $d=1.5$  cm,  $\Phi = 600$  L.h<sup>-1</sup>).

The position of the peak potential is close  $-1.29$  V vs SCE and agrees with the literature value for the standard potential (*i.e.*  $E^\circ(\text{Zn}(\text{OH})_2/\text{Zn}) = -1.48$  V vs SCE) with respect to the acid–base properties on the relevant species, the ionic strength and the junction potentials corrections.<sup>6</sup>

However, one observes a slight shift of the peak potential towards the more negative potential as the treatment time increases. This shift is limited to a few tens of mV and may be correlated to the increase of the thickness of the ZnO films, which becomes more difficult to reduce as the layer gets thicker.<sup>6</sup> As expected, the peak intensity  $I_p$  is also affected by the plasma treatment time  $t$ , which is also related to the film thickness. The  $I_p$  values increase with  $t$  and the plot  $I_p$  against



**Fig. 3** Variation of the intensity of the reduction peak for given humid air gas flow at fixed treatment time and distance ( $d = 1.5$  cm,  $t = 30$  min).

$t$  is reasonably linear (Fig. 2). Since the formation of zinc oxide on the metal surface results from the plasma treatment, and since the peak intensity  $I_p$  is related to the quantity of oxide formed, the oxidising effect of the plasma observed directly depends on the exposure time, in the same way as for the electrolysis processes.

We now consider the influence of the working parameters of the plasma treatment on the oxidation kinetics and special attention is devoted to the humid air gas flow  $\Phi$  at fixed treatment time (30 min). As shown by Fig. 3, the peak intensity  $I_p$  is strongly affected by the gas flow. The  $I_p$  increases as gas flow increases. This effect, which confirms previous results, is interpreted in terms of plasma efficiency, since for higher  $\Phi$ , the plasma efficiency is higher.

This new preparation technique already used in the case of copper is also successful for zinc.<sup>13</sup> It thus seems suitable to prepare in a few minutes a zinc oxide film, whose thickness depends on the working conditions. A comparison between the plasma treatment and the classical thermal oxidation can be derived from these experiments on the basis of the peak intensity of the oxide layer formed: for example  $I_p = 0.145$  mA results from a 30 min humid air plasma treatment or from 720 min during thermal treatment ( $T = 673$  K).<sup>9,12</sup> It clearly appears that the plasma treatment leads to similar quantity of zinc oxide for much shorter times, which illustrates the well known efficiency of this process.

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