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# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

## Materials & Chemical Sciences Division

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### *In Situ* Laser Raman Spectroscopy of Zinc Film Formation in Alkaline Media

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December 1989

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Extended Abstract

***IN SITU* LASER RAMAN SPECTROSCOPY OF  
ZINC FILM FORMATION IN ALKALINE MEDIA**

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December 1989

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# IN SITU LASER RAMAN SPECTROSCOPY OF ZINC FILM FORMATION IN ALKALINE MEDIA

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## INTRODUCTION

Previously we have discussed the use of Raman spectroscopy as an *in-situ* technique for the identification of surface species and the study of photo-induced transformation of anodic film formation on copper in alkaline media [1,2]. Here we review our Raman results on the physical and chemical nature of zinc anodic film formation in 1M KOH. It is generally believed that ZnO forms on zinc anodes at high pH. However, it is still a matter of discussion whether Zn(OH)<sub>2</sub> or ZnO constitutes the passive film. Since the solubility of Zn(OH)<sub>2</sub> and ZnO are similar in this pH range, it is unclear which compound is formed. Most authors support a dual-layer film model for the structure of the anodic film. This idea (originally proposed by Powers and Breiter [3]) suggests that a flocculent Zn(OH)<sub>2</sub> film forms on the electrode during active dissolution, followed by a more compact ZnO layer upon passivation. McKubre and MacDonald [4] have stated that the flocculent film may be necessary for ZnO formation. Raman/potential-sweep experiments were undertaken to (1) identify the species present in the surface film, (2) determine whether chemical transformation of the film occurs, and (3) examine the processes that accompany the active/passive transition.

The Raman spectrometer used in this study is identical to that discussed previously [1,2]. Solutions of 1M KOH saturated with ZnO powder were centrifuged and deoxygenated prior to their injection into the Raman cell, which was kept free of oxygen during the experiments. Zn (1000) single crystals (surface area 1.6 cm<sup>2</sup>) were polished to a mirror finish prior to their use as substrates.

## RESULTS

The electrode potential was swept anodically at 1 mV/sec beginning at the open circuit potential (about -1.38 V vs. Hg/HgO in 1M KOH). Initially the current increases linearly with voltage, but it levels off at more anodic potentials (see Figure 1). A maximum current density of 28 mA/cm<sup>2</sup> is observed at around -1.02 V, beyond which the current decreases by an order of magnitude.

The Raman spectra of reagent grade ZnO and  $\epsilon$ -Zn(OH)<sub>2</sub> powder (Alpha products) were determined for comparison to our *in-situ* observations. X-ray diffraction patterns of these powders match those of

JCPDS standards. The ZnO powder exhibits a number of Raman bands in the 200-800 cm<sup>-1</sup> range, in agreement with the spectra presented by Hugo-Le Goff *et al.* [5] (see Figure 2). Attempts to observe the Raman spectra of  $\epsilon$ -Zn(OH)<sub>2</sub> proved unsuccessful. The compound inelastically scatters light primarily by fluorescence. This finding should be contrasted with that of Hugo-Le Goff, whose Zn(OH)<sub>2</sub> standard was made by chemical precipitation. We found that the Raman spectra of the compound made in the manner described by these authors is in agreement with their published results, but that the X-ray diffraction pattern of the material is characteristic of neither the  $\epsilon$ ,  $\gamma$ , or  $\beta$  allotrope of Zn(OH)<sub>2</sub>.

As the potential is increased from -1.38 to -0.95 V vs. Hg/HgO in 1M KOH there is a general featureless increase in the level of scattering (Figure 3). We associate this phenomenon with fluorescence from an  $\epsilon$ -Zn(OH)<sub>2</sub> layer whose thickness is increasing with potential. If the cell is set to open circuit from this potential range, the level of fluorescence decreases with time, indicating that the film dissolves when the supply of reactant is removed. *Ex-situ* Raman analysis of an electrode that was carefully removed from the electrolyte while being held at an active potential also shows fluorescence of the surface. After rinsing the electrode with distilled water, the Raman spectra show bands at locations associated with the presence of ZnO, though the relative size of these bands is different from those of the powder standard (Figure 4). X-ray diffraction data clearly show that the surface layer present after rinsing is ZnO. X-ray diffraction is sensitive to long-range order while Raman spectra depend strongly on the local order of the molecular point group. Several explanations for the band size discrepancy will be discussed. We conclude that the film in the active dissolution region is mostly  $\epsilon$ -Zn(OH)<sub>2</sub>, which either dehydrates or is dissolved when rinsed (thereby exposing an underlayer of ZnO). Furthermore, the rate of  $\epsilon$ -Zn(OH)<sub>2</sub> film formation is not related to the charge passed but mimics the current as a function of potential, indicating that the rate of film formation is matched by its rate of dissolution.

As the potential is swept into the passive region ( $E > 1.0$  V), the level of featureless scattering decreases and the size of a band at 560 cm<sup>-1</sup> (now visible) increases (Figure 5). If the cell is set to open circuit starting from a passive potential, the intensity of this band decreases, completely disappearing after about 150 seconds. If potential control is maintained and the sweep direction is reversed, ZnO is detected by Raman spectroscopy at potentials anodic of -1.25 V (which is 150 mV anodic of the equilibrium potential). The fact that the film readily dissolves on open circuit suggests that the rate of ZnO film formation is balanced by its rate of formation in the passive region. The formation of the ZnO layer at the metal/film interface is possibly induced by the starvation of the surface for hydroxide ion. Once formed, the electrically insulating film can greatly reduce the supply of reactants, causing the soluble  $\epsilon$ -Zn(OH)<sub>2</sub> outer layer to dissolve into the electrolyte.

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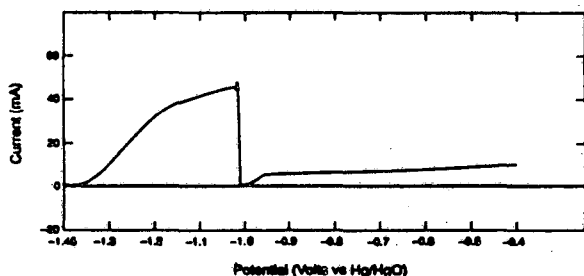


Figure 1. Current vs. potential during a 1 mV/sec potential sweep of Zn in 1M KOH. (XBL 898-7281)

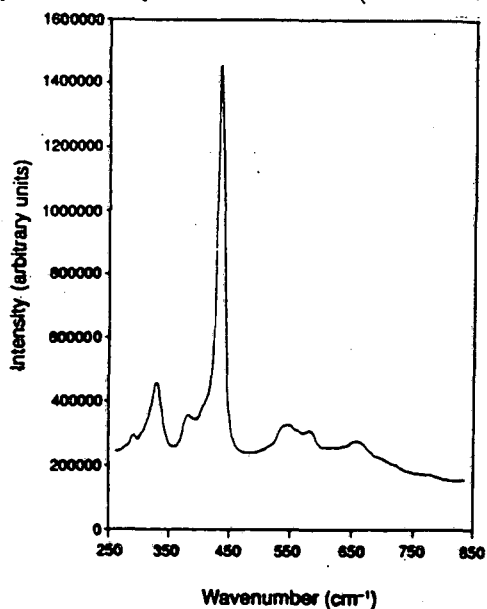


Figure 2. Raman spectrum of ZnO powder. (XBL 898-7278)

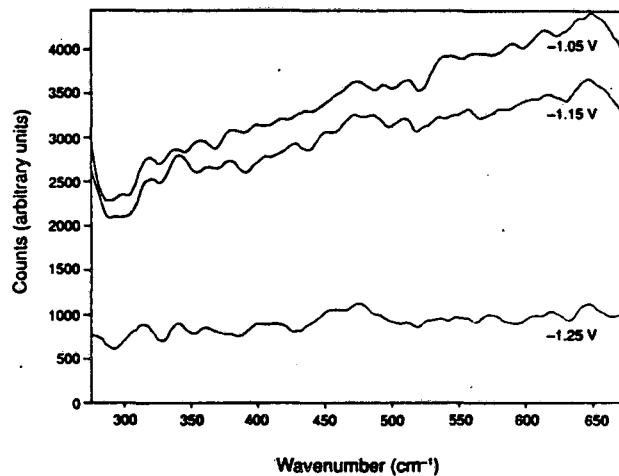


Figure 3. Raman spectra of Zn surface at selected potentials during potential sweep shown in Figure 1. (XBL 898-7273)

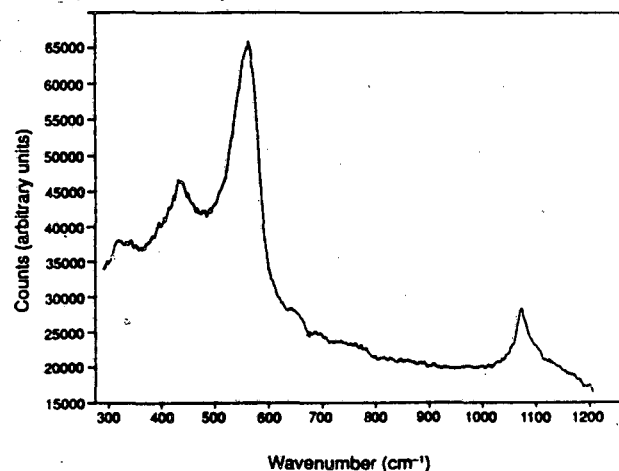


Figure 4. Raman spectrum of surface removed from the electrolyte and rinsed in distilled water after being anodized by a potential sweep at 1 mV/sec to -1.1 V vs. Hg/HgO. (XBL 898-7274)

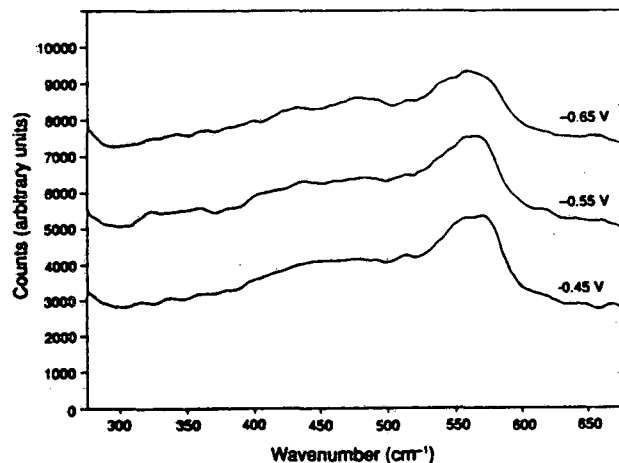


Figure 5. Raman spectra of Zn surface at selected potentials during potential sweep shown in Figure 1. Spectra are offset to allow readability. [XBL 898-7271A (part)]

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