

## Anodic dissolution of zinc in organic solutions of chlorides

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The electrochemical dissolution and deposition of zinc has been intensively investigated in aqueous environments. Simple model of the mechanism is based on a two-step consecutive mechanism where the intermediate product  $Zn_{ad}^+$  is adsorbed on the metal surface [1,2]. Wiart proposed more complicated mechanism of electrochemical process of zinc's dissolution and deposition [3,4]. In this model both of two parallel paths i.e. the catalytic and consecutive mechanism were considered. A predominant process is the catalytic reaction that is similar to the Heusler's mechanism of iron dissolution [5].

Our investigation of electrochemical dissolution of zinc (polycrystalline and monocrystalline samples) was performed in anhydrous, organic media (methanol and acetonitrile solutions with different concentration of chloride anions). The influence of the crystallographic orientation on the mechanism of zinc dissolution was studied by means of Scanning Electron Microscopy (SEM) and microscopic observation.

Mechanism of zinc dissolution in anhydrous organic solvents is similar to the mechanism in aqueous media however the stability of monovalent cations and then stability of adsorbed intermediate product in these solvents are much higher than in aqueous environments. Our investigation demonstrates the strong inhibition of anodic and cathodic reactions by the anodic, intermediate product. In organic solvents the solubility of corrosion products is also lower than in aqueous solutions. Stability of surface species and mechanism of desorption or dissolution play very important role in the electrochemical processes on zinc electrode in organic environments. The shapes of polarisation curves are similar to those obtained for polycrystalline as well as monocrystalline samples of zinc in environments with different concentration of LiCl and LiClO<sub>4</sub> respectively [6].

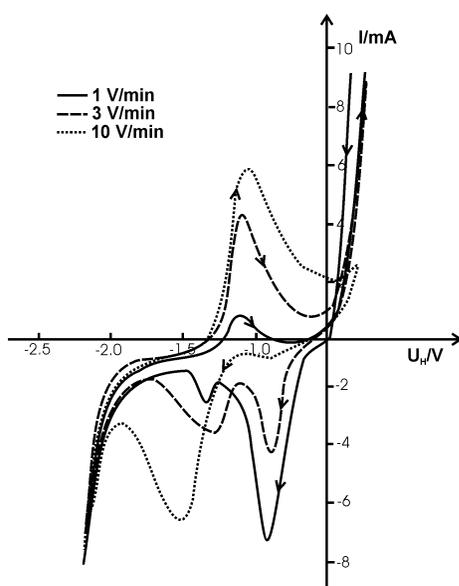


Fig. 1 Cyclic voltammograms (scan rate 1, 3, 10 V/min) obtained during the polarisation of Zn (0001) in electrolyte

CH<sub>3</sub>OH-LiClO<sub>4</sub>.

The first anodic peak or anodic plateau, which is commonly observed at polarisation curve in acetonitrile solution, corresponds to the adsorption of anodic intermediate product (Fig. 1). At the higher overpotential the sudden desorption of intermediate product is observed. For the monocrystalline samples the higher value of desorption potential was observed at the surface with loose-packed atoms sample (11 $\bar{2}$ 0) than at the surface of close-packed (0001). The better adsorption on the (11 $\bar{2}$ 0) surface sample is connected with being gaps where the product can be "anchored". The comparison of cyclic voltammograms and etching morphology tests of samples with two crystallographic orientations, readily lead us to conclusion that the domination of catalytic process is closely related to the structure or/and quality of surface preparation [7].

The confirmation of the anisotropic etching is the shapes of the pits on both of the electrodes that are distinctly crystallographic in appearance according to the plane configuration (Fig.2).

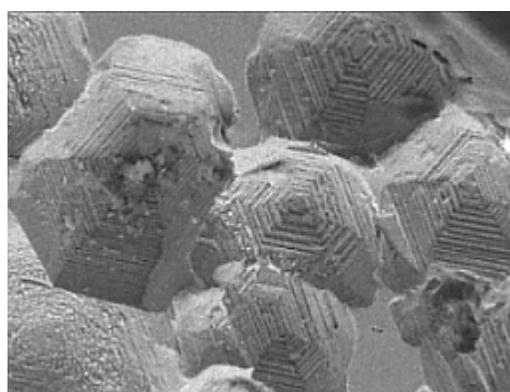
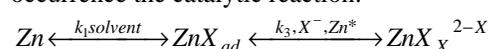


Fig.2 SEM micrograph of Zn (0001) surface etched in electrolyte CH<sub>3</sub>CN-0.1m LiClO<sub>4</sub>; potential of etching E<sub>1</sub>=-0.622V t<sub>1</sub>=1800s; E<sub>2</sub>=-0.178V, t<sub>2</sub>=5400s.

The performed measurements and the analysed data are the confirmation of the predicted hypothesis of occurrence the catalytic reaction:



as a predominant path of the mechanism of anodic dissolution of zinc in organic media .

### References

- [1] L. Gaiser, K.E. Heusler: *Electrochim. Acta*: 15, 161, 1970
- [2] K.E. Heusler, L. Knoedler: *Electrochim. Acta*, 18, 855, 1973
- [3] C. Cachet, B. Saidini, R. Wiart: *Electrochim. Acta*, 33, 3, 405, 1988
- [4] C. Cachet, R. Wiart: *J. Electrochem. Soc.*, 129, 103, 1981
- [5] K.E. Heusler: *Ber. Bunsenges. Phys. Chem.*, 62, 582, 1958
- [6] J. Banaś: *Corrosion of Zinc in Organic Solvents*, Mat. de 13<sup>o</sup> Congresso Brasileiro de Engenharia e Ciencia dos Materiais, 06 a 09 dezembro 1998, Curitiba (PR)
- [7] J. Światowska, J. Banaś: *The anodic dissolution of zinc monocrystals in anhydrous methanol solutions of chlorides*, Medzinarodna konferencia pre doktorandov, skolitelov a pracovnikov z praxe, 19-20 oktobra, Sulov