

## Methanol Oxidation as Anode Reaction in Zinc Electrowinning

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### INTRODUCTION

Electrowinning is an energy demanding process in which the electrolysis of metal accounts for the major part of the energy consumption. The lead anodes used in zinc electrowinning today are not dimensionally stable and have a high overvoltage for oxygen evolution. By replacing the oxygen evolution in sulphate based electrolytes with methanol oxidation the anode potential could be lowered significantly. This would reduce the energy consumption as well as enabling the use of new and more stable types of electrodes. Several studies have been done on methanol oxidation reaction (MOR) in zinc electrowinning with various types of electrodes [1-6]. In this study different types of electrodes were compared regarding their activity and stability for MOR in zinc electrowinning environment. The influence of zinc, methanol concentration and temperature on the anode performance was studied. Different methods for reactivating the electrodes were also tested.

### EXPERIMENTAL

The experiments were carried out in a cell with a Rotating Disk Electrode (RDE) connected to a potentiostat. The standard electrolyte contained sulphuric acid, 160 g/l, to which zinc and various concentrations of methanol were added. Tests have also been performed in perchloric acid. Four different electrodes have been used: Pt and PtRu on Ti (Permascand), porous Pt and porous PtRu. The porous electrodes had a catalyst loading of 0.07 mg/cm<sup>2</sup> Pt and 0.14 mg/cm<sup>2</sup> PtRu (1:1) respectively and contained 40% Nafion<sup>®</sup>. They were prepared by a method previously used at the department [7]. The activity of the electrodes was studied with cyclic voltammetry and the stability was studied during galvanostatic and potentiostatic tests.

### RESULTS AND DISCUSSION

The cyclic voltammetry made on the four different electrodes showed that the porous PtRu electrode had the highest activity for MOR. Increasing methanol concentration and temperature improved the activity for MOR at the electrodes whereas zinc addition decreased the activity to some extent. Figure 1 shows cyclic voltammograms recorded on the porous PtRu electrode in electrolyte with and without zinc. Galvanostatic tests were performed with the porous PtRu at a current density of 400 A/m<sup>2</sup> at 30°C. The potential increased with time and finally O<sub>2</sub> evolution started. After the O<sub>2</sub> evolution the electrode surface had changed and became more active to MOR. Due to deactivation of the electrode with time during galvanostatic tests a reactivation procedure was necessary. Different reactivation methods are found in the literature [3,4]. Fig. 2 shows one method tested in this study, Periodic Current Reversal (PCR). PCR was used with good result and the electrodes were almost completely reactivated.

In order to elucidate what causes the deactivation of the electrodes potentiostatic tests were done. Tests were performed at two different potentials, 0.5 V and 0.7 V vs

SHE, with the four different electrodes. The deactivation of the porous electrodes was compared with the metallic coated electrodes to see how the surface structure and composition of the electrodes affected the deactivation. The current decreased fast with the porous PtRu electrode, despite the high activity observed in the cyclic voltammogram. The platinised titanium displayed the smallest decrease of current of all the electrodes during the galvanostatic tests.

This study shows that the activity of several electrodes are sufficient for MOR to be used in zinc electrowinning but further studies of the deactivation mechanism are needed to establish their stability for longer periods of time.

### ACKNOWLEDGEMENTS

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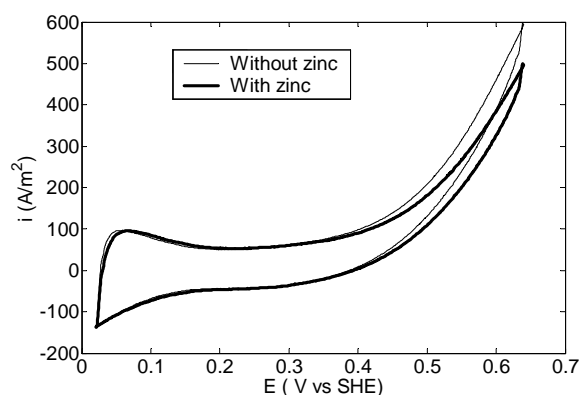


Figure 1. Cyclic voltammetry on porous PtRu in 160 g/l H<sub>2</sub>SO<sub>4</sub>, 1 M CH<sub>3</sub>OH, T = 30°C, scan rate 100 mV/s, without (—) and with (---) 160 g/l ZnSO<sub>4</sub>.

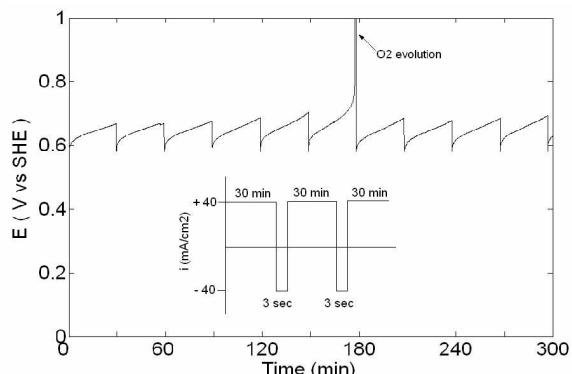


Figure 2. Galvanostatic tests with PCR at 400 A/m<sup>2</sup> in 160g H<sub>2</sub>SO<sub>4</sub>/l, 160 g/l ZnSO<sub>4</sub>, 1 M CH<sub>3</sub>OH and T = 30°C.

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