

## REDUCTION OF MANGANESE DIOXIDE ON GOLD ELECTRODE

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The zinc-manganese cell and its modifications are the most common chemical sources of electricity due to low production costs of these cells and the availability of the electrode materials, which are more environment-friendly than the chemicals used for the production of other batteries [1]. Even though over a hundred years have passed since the discovery of the Leclanché cell, there is still a lot of interest in the manganese dioxide reduction process, because some problems related to the mechanism of this process still remain unresolved, e.g. the rate of the process and the behavior of the products of the electrode reaction.

Lee *et al.* [1,2], Petitpierre *et al.* [3] and Nijjer *et al.* [5] have considered the influence of the pH, temperature and working solution composition on the electrochemical behavior of manganese dioxide. During the initial stages of cathodic reduction of MnO<sub>2</sub> they observed a sharp and intense single peak. During this process a thin layer of scarcely conducting film is formed on the surface of the manganese dioxide. The layer, which properties depend on the pH and the composition of the working solution, limits the rate of the reduction of manganese dioxide. As a result, the further reduction process produces a flattened current peak in a wide potential range. This behavior has been reported by Bodoardo *et al.*, [4] in 0.5 M sulfuric acid solution.

In this work, the electrochemical reduction of electrodeposited MnO<sub>2</sub> on Au electrode has been investigated in sulfuric acid solution with various concentrations of Mn (II) ions, using the voltammetry technique. Scanning Electron Microscope and Scanning Tunneling Microscope have been used to study the structure of the deposit.

The unusual effect of hysteresis, not reported before, has been observed on the cyclic voltammetric curves of manganese oxide deposition and reduction on Au electrode (Fig. 1) This effect occurs under certain experimental conditions (sweep rate range, H<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub> concentration) and has prompted a detailed investigation of the electrochemical behavior of MnO<sub>2</sub>. It was found that the presence of the hysteresis depends on the number of sweep segments and on the scan rate. The conditions of MnO<sub>2</sub> electrodeposition (electrolyte composition, scan rate, temperature, stirring) were varied for the purpose of optimization of the electrochemical behavior of this oxide.

In a thin layer cell, consisting of Au electrode immersed in H<sub>2</sub>SO<sub>4</sub> + MnSO<sub>4</sub> solution, and separated from the bulk H<sub>2</sub>SO<sub>4</sub> solution by Nafion® membrane, the hysteresis observed (Fig. 2) for the deposition/reduction of MnO<sub>2</sub> is even more pronounced than for the solution studies (Fig. 1). Also, in a thin layer cell, the shape and the potential range of these oxidation/reduction peaks are different. These results suggest that the hysteresis can be related to the surface rather than bulk effects and might originate from the difficulty of permeation of Mn<sup>2+</sup> ions through the surface oxide layer.

### Acknowledgements

The authors acknowledge financial support by Polish State Committee for Scientific research (KBN) grant No. 3 T09A 947 18

### References.

- [1] J.A. Lee, W.C. Maskell, F.L. Tye, J. Electroanal. Chem., 79 (1977) 79.
- [2] J.A. Lee, W.C. Maskell, F.L. Tye, J. Electroanal. Chem., 110 (1980) 145.
- [3] J. Petitpierre, C. Comminellis, E. Platiner, Electrochim. Acta, 35 (1990) 281.
- [4] S. Bodoardo, J. Brenet, M. Maja, P. Spinelli, Electrochim. Acta, 39 (1994) 1999.
- [5] S.Nijjer, J. Thonsad, G.M. Haarbeg, Electrochim. Acta, 46 (2000) 395.
- [6] J.Caja, A.Czerwinski, H.B.Mark Jr, Analyt.Chem., 51 (1979) 1328

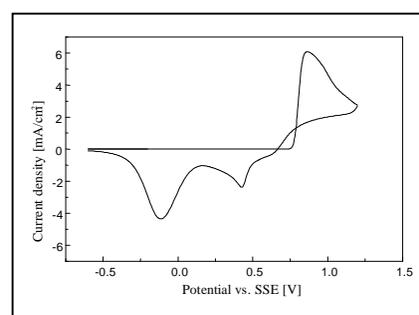


Fig1. Cyclic voltammogram of gold electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.5MnSO<sub>4</sub> solution, T=298K, v=5mVs<sup>-1</sup>

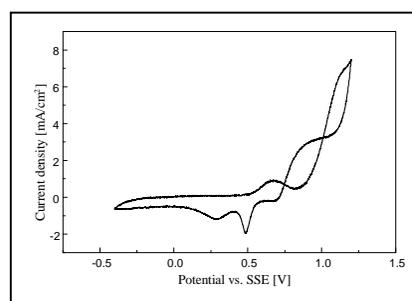


Fig.2 Cyclic voltammogram of gold electrode in thin layer 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.5MnSO<sub>4</sub> solution, T=298K, v=5mVs<sup>-1</sup>