

## The Oxygen Evolution Reaction at Manganese Dioxide Films in Base: Kinetics & Mechanism

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Alkaline water electrolysis has been proposed as an environmentally inoffensive route to the production of the large volumes of hydrogen gas required by a possible hydrogen economy [1-5]. In practice, the efficiency of water electrolysis is limited by the large anodic overpotential of the oxygen evolution reaction (OER) [5]. Over the past thirty years, considerable research effort has been devoted to the design, synthesis and characterization of OER anode materials, with the aim of achieving useful rates of active oxygen evolution at the lowest possible over-potential, in order to optimize the overall electrolysis process. Currently, the optimal OER anode materials are RuO<sub>2</sub> and IrO<sub>2</sub>, since these oxides exhibit the lowest overpotentials for the OER at practical current densities [6]. However, the high cost of these materials and their poor long term stability in alkaline solution renders their widespread commercial utilisation both uneconomical and impractical [7]. For these reasons, the oxides of the first row transition metals (e.g. manganese, iron, cobalt and nickel) offer a compromise solution. Even though they are not as electrocatalytically active, their relatively low cost and long term corrosion resistance in alkaline solution makes them attractive OER anode materials [7-11].

In the present work, we focus on the redox properties and electrocatalytic behaviour with respect to anodic oxygen evolution of manganese dioxide electrodes in aqueous alkaline solution. These films can be prepared simply via thermal decomposition of a manganese nitrate salt [12]. The structure and morphology of the thermally decomposed oxide materials are examined using thin film XRD, high resolution SEM and TEM. The redox behaviour of the resulting oxide films is investigated as a function of substrate and annealing temperature using cyclic voltammetry. Interestingly, the voltammetric profile for the manganese dioxide film is strongly dependent on the nature of substrate, as evident from Fig. 1. The kinetics of the OER at manganese dioxide coated substrates have been studied using a range of electrochemical techniques including steady-state polarization and open circuit potential decay curves and electrochemical impedance spectroscopy. In particular, Tafel slopes and reaction orders with respect to hydroxide

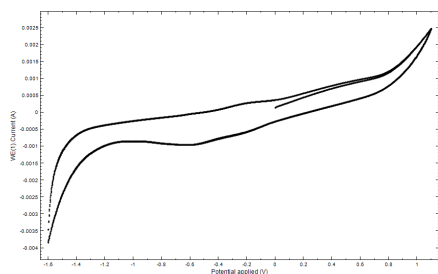
ion activity are determined. Based on the available kinetic data, a reaction mechanism utilizing the active surface group concept, as outlined by Lyons and Doyle [13] for iron and nickel oxide layers, is proposed.

### Acknowledgements

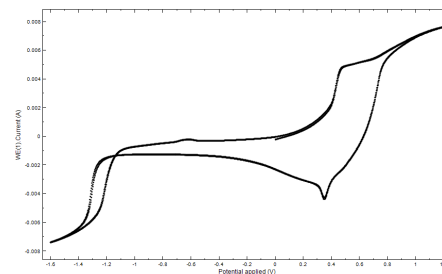
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### References

- [1] K. Zeng and D. Zhang, *Prog. Energy Combust. Sci.*, 36 (2010) 307.
- [2] H. Tributsch, *Int. J. Hydrogen Energy*, 33 (2008) 5911.
- [3] G. W. Crabtree, M. S. Dresselhaus and M. V. Buchanan, *Phys. Today*, December 2004, 39–44.
- [4] J. Ohi, *J. Mater. Res.*, 20 (2005) 3180.
- [5] D. E. Hall, *J. Electrochem. Soc.*, 130 (1983) 317.
- [6] A. Michas, F. Andolfatto, M. E. G. Lyons and R. Durand, *Key Eng. Mater.*, 72-74 (1992) 535.
- [7] K. Kinoshita, *Electrochemical Oxygen Technology*, Wiley-Interscience, New York, 1992.
- [8] M. E. G. Lyons and M. P. Brandon, *Int. J. Electrochem. Sci.*, 3 (2008) 1386.
- [9] M. E. G. Lyons and M. P. Brandon, *Int. J. Electrochem. Sci.*, 3 (2008) 1425.
- [10] M. E. G. Lyons and M. P. Brandon, *Int. J. Electrochem. Sci.*, 3 (2008) 1463.
- [11] M. E. G. Lyons, R. L. Doyle and M. P. Brandon, *Phys. Chem. Chem. Phys.*, DOI: 10.1039/c1cp22470k
- [12] D. Galizzioli, F. Tantarini, S. Trasatti, *J. Appl Electrochem* 4(1974)57-67.
- [13] M. E. G. Lyons, R. L. Doyle, I. Godwin, M. O'Brien, and L. Russell, *J. Electrochem. Soc.*, 159 (2012) H932.



(a)



(b)

Figure 1. (a) Cyclic voltammograms recorded of titanium substrate with MnO<sub>2</sub>. (b) Cyclic voltammograms recorded of nickel substrate with MnO<sub>2</sub>.