Dimensionally Stable Anodes (DSA®) for Electrochemical Water Splitting: OER Kinetics and Mechanism at RuO$_2$/ NiO$_x$ Modified Electrodes in Aqueous Base

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One of the grand challenges facing 21st century society is finding a clean, sustainable and reliable source of energy to fuel society's ever increasing demands. Hydrogen generation via alkaline water electrolysis has been proposed as a major contender in meeting these stringent demands [1-5] due to the virtually unlimited source of base fuel needed for this process. One of the major issues limiting the wide spread use of alkaline water electrolysis is the high overpotential associated with the oxygen evolution reaction (OER).

Currently, the optimal OER anode materials are RuO2 and IrO2, 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 offer a compromise solution. Although 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].

Building on the seminal works by Trasatti and Burke [12-15], the present paper focuses on the kinetics and mechanism of thermally prepared binary oxides based on RuO$_2$/ NiO$_x$ of well-defined composition. Fundamental electrochemical techniques such as steady state Tafel analysis, open circuit potential decay, electrochemical impedance spectroscopy and reaction order studies are employed to probe the reaction mechanism at the binary metal oxide surface and to investigate the interplay between both oxides. The OER mechanism is interpreted in terms of the surfaquo group model developed in our group [16]. The turnover frequency for the mixed oxide films is evaluated and compared to a selection of other well established oxidative water splitting catalytic systems (both heterogeneous and homogeneous). We conclude that the introduction of the surfaquo group as a mechanistic concept provides a useful bridge between heterogeneous catalysis and molecular catalysis.

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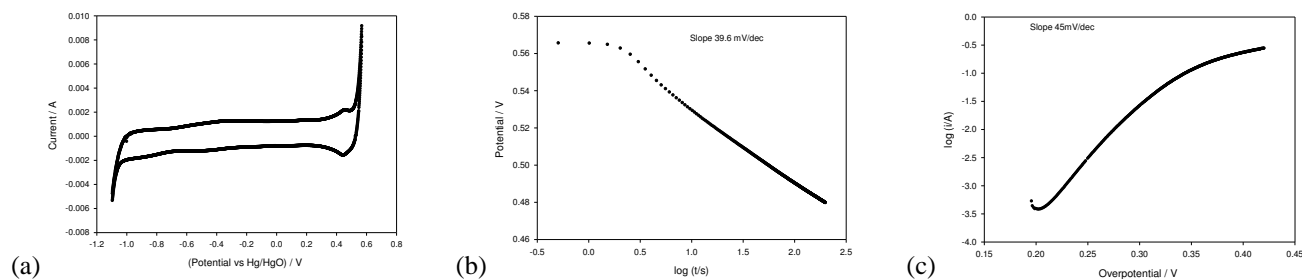[16] M.E. G. Lyons and R. L. Doyle, Int. J. Electrochem. Sci., 7 (2012) 9488 - 9501

Figure 1. (a) Cyclic Voltammogram of RuO$_2$ on Ti substrate in 1 M NaOH. (b) Open Circuit Potential Decay Plot of RuO$_2$ on Ti substrate in 1 M NaOH. (c) Tafel Plot of RuO$_2$ on Ti substrate in 1 M NaOH.