

## Enhanced Oxygen Evolution at 'Aged' Hydrous Nickel Oxide Electrodes in Alkaline Solution: Kinetics and Mechanism

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Electrochemical water splitting via alkaline water electrolysis is currently an extremely active research area of intense topical international interest. This is due to the need for the development of a clean, reliable and sustainable method for large scale production of high purity hydrogen gas for use as a fuel in a potential hydrogen economy. [1–3] However, one of the grand challenges fully utilising alkaline water electrolysis for hydrogen production is in the large anodic overpotential associated with the oxygen evolution reaction (OER). Over the past 30 years considerable research effort and resources have been focused on the development and improvement of novel anode materials, with the aim of achieving useful rates of the OER at the lowest possible overpotential and cost in order to improve the economic viability of this technology. Dimensionally stable anode (DSA®) electrodes, based on RuO<sub>2</sub> and IrO<sub>2</sub> replaced traditional graphite anodes and currently exhibit the lowest overpotential for the OER at practical current densities [4] Despite their excellent OER performance, the relative high cost of these materials, in particular iridium, combined with their poor long term chemical stability in alkaline media renders their long term use as anode materials for water electrolyzers impractical. Because of this problem we have attempted to overcome this problem by using oxides/hydroxides/ oxyhydroxides of first row transition metals which offer comparable OER performance but at significantly lower cost. [5,6]

In this work we have adapted an 'ageing' method, discovered initially for electrodeposited nickel hydroxide on gold support electrodes to further enhance the OER performance of hydrous nickel oxide films as presented recently in papers emanating from our research group. [7–13].

Briefly, the ageing method consists of repetitively cycling at a slow sweep rate the potential across the main Ni(II/III) redox peaks at a slow scan rate in aqueous base. The results of such a procedure are presented in fig.1 below. We suggest that the latter cyclic potential treatment allows rearrangement of the film to its thermodynamically most stable arrangement, since it is well established that hydrous oxides are metastable species in that initially the kinetically most accessible rather than the thermodynamically most stable form of the oxide is generated during the oxide growth procedure. Clearly, slow potential cycling facilitates this transformation as illustrated in fig.1 below. In fig 1 (b),

we note that the ageing process does not appear to affect the Tafel slope, whereas the opposite pertains for the electroprecipitated 'battery type' oxide. (fig 1 (d)). It is interesting to see the development of a potential independent OER rate at high overpotential for both fresh aged electroprecipitated nickel hydroxide. This is not noted for the fresh and aged hydrous oxide film.

Electrochemical ageing was found to significantly enhance the OER performance of the hydrous nickel oxide electrode (fig.1) with the OER overpotential decreasing by  $60 \pm 2$  mV and experiencing a 10 fold increase in OER rate for a fixed overpotential over that of an un-aged electrode. The OER turnover frequency for an aged electrode was found to be  $1.16 \pm 0.07$  s<sup>-1</sup> in comparison to  $0.05 \pm 0.003$  s<sup>-1</sup> for a hydrous nickel oxide electrode not subjected to ageing.

In this communication, results concerning the redox and catalytic properties of the hydrous nickel oxide films, both before and after aging, obtained using electrochemical techniques such as steady state Tafel plots, cyclic voltammetry, open circuit potential decay measurements and electrochemical impedance spectroscopy will be presented and compared with similar electroprecipitated nickel hydroxide. Surface imaging such as SEM will also be employed to detect any surface morphology changes due to ageing. The kinetics and mechanism of active oxygen evolution at both fresh and aged electrodes will be compared and defined.

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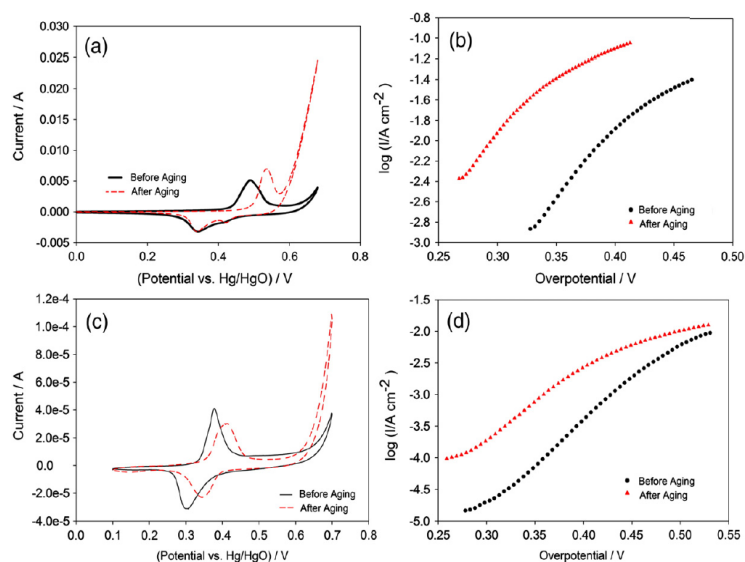


Fig. 1. (a) Typical cyclic voltammogram (b) Tafel plot of a hydrous nickel hydroxide electrode before and after electrochemical ageing by slow potential multicycling in 1 M NaOH across the Ni(II/III)/Ni(III/II) redox peaks shown. (c) Cyclic voltammogram (d) Tafel plot of an electroprecipitated 'battery type' nickel hydroxide electrode on an Au substrate before and after aging using the same slow potential multicycling regime. Potentials quoted against Hg/HgO. Scan rate 40 mV/s for cyclic voltammograms and 1 mV/s for Tafel plots.