



Electrocatalytic oxygen evolution on nickel oxy-hydroxide anodes: Improvement through rejuvenation



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ABSTRACT

The ageing and rejuvenation behaviour of nickel oxy-hydroxide anodes for alkaline water electrolysis is investigated. The anodically formed oxy-hydroxide material is known to age over time causing a decrease in performance. However, this deactivation can be mitigated by temporarily reducing the potential for brief periods. This work looks at continuous rejuvenation of nickel anodes in 30 wt.% KOH solution and it is shown that rejuvenation at 0.5 V vs. Hg/HgO for 10 minutes every 100 minutes can prevent ageing of the anode, thus maintaining a low overpotential during galvanostatic oxygen evolution at 50 mA cm⁻². It is suggested that the short potentiostatic rejuvenation periods at regular intervals prevents the ratio of Ni(IV) to Ni(III) from increasing, thereby maintaining the intrinsic activity of the material. The rejuvenation potential must be above 0.36 V vs. Hg/HgO to ensure it is effective in obtaining good performance (i.e. the material must not reduce to Ni(II)). These findings suggest that electrolysis systems using nickel anodes could benefit from direct coupling to fluctuating power sources such as solar or wind, where the variability in their power output could facilitate the rejuvenation of the nickel anode. We estimate that by using the rejuvenation steps, an energy saving of 9% is possible in an alkaline water electrolyser using nickel anodes.

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1. Introduction

Water electrolysis has long been investigated as a way of producing very pure hydrogen gas from a renewable energy sources. Much of the research has focussed around developing electrocatalysis to improve the efficiency of electrolysers. Important factors to consider when choosing an electrocatalyst include its stability, performance, and cost. Many researchers have investigated nickel oxides as the electrocatalyst for the anodic oxygen evolution reaction [1–7], as it is much less costly than options such as iridium or ruthenium oxide and has reasonably good performance, with a potentials of approximately 750 mV vs. Hg/HgO at a current density of 50 mA cm⁻² [8], and Tafel slopes as low as 38 mV. However, the performance stability under anodic conditions can be an issue, resulting in the performance of the electrocatalyst decreasing over time [6,8]. As the loss in performance of nickel oxide anodes is generally accepted to be related to structural changes in the oxide, much of the research into nickel oxide electrocatalysts has involved

investigating the structure of the electrocatalyst [6,9–12]. Traditionally four phases are thought to be present as shown in the Bode diagram [13] (Fig. 1). The true map of phases and their transformations is likely to be more complex [8] based on recent research [8,14–19]. For example, raman spectroscopy suggests that at the onset of oxygen evolution, NiOOH transforms to another phase [15] and similarly our cyclic voltammetry work suggested that after extensive oxygen evolution (at least 40 hours at 50 mA cm⁻²) an additional phase forms [8]. Many authors have also suggested that over-oxidation causes Ni(IV) to form [6,20–23], although there is currently little direct evidence of the formation of NiO₂ or other Ni(IV) species.

Work by Lu and Srinivasan, and Osaka and Yatsuda [6,7] has shown that the activity of a deactivated nickel oxide anode can be recovered by briefly decreasing the potential of the anode to values where minimal oxygen evolution occurs (1.5 V vs RHE). This rejuvenation can increase the current density by as much as 3–7 times, compared to that just prior to the rejuvenation process [6]. Lu and Srinivasan [6] also showed that longer rejuvenation times at low potentials, gave larger performance recoveries. One explanation for the ageing or loss in activity (which can be reversed by rejuvenation) is simply that the thickness of the poorly conductive

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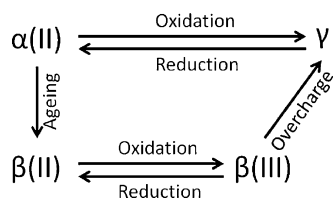


Fig. 1. Bode diagram of known nickel phases.

nickel oxide layer increases during the oxygen evolution reaction, thus increasing the ohmic resistance of the electrode. However the work of Lu and Srinivasan appears to rule this out as the main cause, and instead it has been suggested that the activity is improved by a thin layer of more highly active electrocatalyst (perhaps β -NiOOH) forming on the surface of the oxide during rejuvenation, and it is this which controls the specific activity, rather than the structure of the bulk oxide [6]. Here the rejuvenation of a nickel oxide electrode is investigated as a way of improving the activity for the oxygen evolution reaction. Specifically, the role of rejuvenation potential, time and frequency is examined, as well as the implications of the ageing and rejuvenation of nickel oxide anodes on the measurement of steady-state polarisation data.

2. Experimental

Nickel foil electrodes (Sigma-Aldrich $\geq 99.9\%$), with a surface area of 1 cm^2 , were cleaned in acetone for 5 minutes, ultrasonicated in water, etched in 1 M hydrochloric acid solution with 5.25 g L^{-1} of hydrogen peroxide for 15 minutes, then finally rinsed in deionised water. Contact to the nickel foil was achieved by spot welding a nickel wire (0.5 mm diameter) to a corner of the foil. This wire was insulated from the electrolyte using an inert thermosetting polymer.

A Gamry Instruments Reference 3000 potentiostat was used for electrochemical analysis. The electrochemical tests were performed in 30 wt% KOH solution in a thermostatically controlled PTFE cell at 25°C . Nickel foil (30 cm^2) was used as the counter electrode along with a Hg/HgO(KOH) reference electrode. All potentials are referenced to the Hg/HgO (30% KOH). Unless stated otherwise the following pretreatment procedure was used on the nickel electrodes: the freshly etched nickel electrodes were subjected to potentiostatic electrochemical impedance spectroscopy (EIS) at 0 V (to obtain the ohmic resistance between the reference and working electrodes) over the frequency range 0.2 - 100,000 Hz at 5 mV rms before the potential was held at -100 mV for 2 hours (to ensure the electrode surface was covered in the α -Ni(OH)₂ phase), then cycled at 50 mV s^{-1} for 5 to 20 cycles between -0.1 V and 0.65 V .

All rejuvenation measurements involved galvanostatic oxygen evolution at 50 mA cm^{-2} coupled with potentiostatic rejuvenation periods at open circuit potential (OCP), 0.5 V, or 0.2 V. Cyclic voltammetry was performed at the end of all oxygen evolution/rejuvenation measurements at 50 mV s^{-1} from -0.1 V to 0.65 V . Slow linear scanning voltammograms discussed in Section 3.3 were performed at a rate of 0.2 mV s^{-1} following the initial electrode pretreatment and 40–80 hours of galvanostatic oxygen evolution at 50 mA cm^{-2} . All potential measurements were corrected for the uncompensated IR drop post measurement using the value determined by EIS.

3. Results and Discussion

3.1. Galvanostatic Ageing and Rejuvenation

When a nickel electrode is subjected to continuous potential cycling (e.g. cyclic voltammetry), a change in the oxide structure is

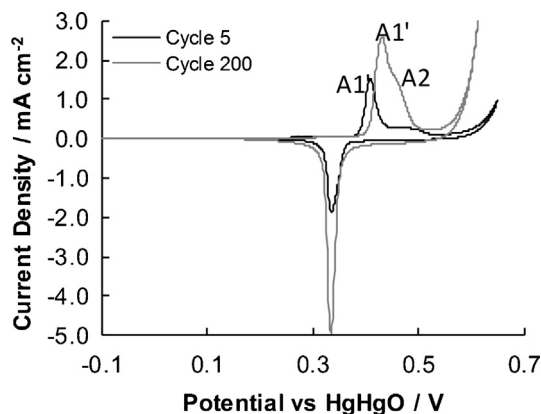


Fig. 2. Cycle 5 and 200 of cyclic voltammograms performed at 50 mV s^{-1} between -0.1 V and 0.65 V following a pretreatment of potentiostatic EIS at 0 V over the frequency range 0.2 - 100,000 Hz at 5 mV rms and constant potential at -100 mV for 2 hours.

known to occur [1,8,24]. Here the cyclic voltammogram after 200 cycles is noticeably different to that after only 5 cycles (Fig. 2). It is well known that this cycling causes a transition from the α -Ni(OH)₂ / γ -NiOOH solid-state redox couple to the β -Ni(OH)₂ / β -NiOOH couple [1,8,24]. During cycling, the peak labelled A1, decreases in size while A1' and A2 grow. A2 stops growing at 200 cycles while A1' continues to grow. While it is unclear whether A1' or A2 corresponds to the oxidation of β -Ni(OH)₂ to β -NiOOH, galvanostatic oxygen evolution after cycling (data not shown) reveals that at least one of these peaks corresponds to the formation of a more active phase compared to the γ -NiOOH phase (which forms from α -Ni(OH)₂, peak A1). This is consistent with the recent work which clearly shows that potential cycling can improve the activity of a nickel oxide electrode towards the oxygen evolution reaction [2].

For an electrode which has only undergone 5–20 cycles during the initial electrode pretreatment (and thus is only in the α -Ni(OH)₂ / γ -NiOOH structure), a very characteristic ageing behaviour is observed during galvanostatic oxygen evolution (Fig. 3a). The galvanostatic ageing can be split into five periods: an initial decrease in overpotential (period 1), a period of good performance (period 2), a slow increase in overpotential (period 3), a steep increase in overpotential (period 4), and finally a stable high potential (period 5). While it is clear that initially only the α - γ phases are present at the start of galvanostatic ageing, once period 4 is reached, a second pair of peaks appear in the voltammograms (A3 and C3) (Fig. 3b). By comparing the voltammogram from this galvanostatically aged α -Ni(OH)₂ / γ -NiOOH anode with that in Fig. 2, it is clear that peaks A3 and C3 arise from a different solid-state redox pair to those found after ageing by cyclic voltammetry. We suggest that peaks A3 and C3 result from the formation of a structure containing Ni(IV) [8].

While nickel oxide anodes (initially with the α/γ structure) are slowly deactivated during galvanostatic oxygen evolution, it is observed that the activity can be partially recovered if the potential is temporarily decreased to 0.5 V before return back to the galvanostatic oxygen evolution (Fig. 4). An example of this is given in Fig. 4, where oxygen evolution at 50 mA cm^{-2} is interrupted after 40 hours by a 10 minute rejuvenation step at 0.5 V. Just prior the the rejuvenation step, the anode potential is 0.82 V (and increasing), whereas immediately after the rejuvenation step the potential is about 0.8 V (and approximately stable for 5–10 hours), i.e. a rejuvenation of 20 mV. This rejuvenation affect is also seen in other work [6,7] and has been suggested to be related to a rapid change in the surface of the oxide, upon decreasing the potential, to a form which is more intrinsically active toward the oxygen evolution reaction [6]. This active oxide layer is said to have a higher ratio of Ni(III) to Ni(IV) than the layer before rejuvenation, and is consistent with the

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