Electrochimica Acta 168 (2015) 356–364

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Structure and transformation of oxy-hydroxide films on Ni anodes below and above the oxygen evolution potential in alkaline electrolytes

Sophia R. Mellsop[a], Alister Gardiner[b], Bernt Johannessen[c], Aaron T. Marshall[a,*]

[a] Department of Chemical and Process Engineering, MacDiarmid Institute for Advanced Materials and Nanotechnology, University of Canterbury, Christchurch, New Zealand
[b] Callaghan Innovation, Christchurch, New Zealand
[c] Australian Synchrotron, Victoria, Australia

ARTICLE INFO

Article history:
Received 18 February 2015
Received in revised form 30 March 2015
Accepted 4 April 2015
Available online 7 April 2015

Keywords:
Nickel
Nickel hydroxide
Nickel oxide
Oxygen evolution reaction
Electrocatalysis

ABSTRACT

The anodic behaviour of a nickel electrode has been investigated in KOH electrolytes below and above the oxygen evolution potential. As the literature reports a wide range of behaviours, initial repetitive cyclic voltammetry in 1 M KOH was compared to 30 wt% KOH (i.e., that used in alkaline water electrolysers) and it was found that a process in addition to the normal α-Ni(OH)$_2$/γ-NiOOH and β-Ni(OH)$_2$/β-NiOOH occurs in the more concentrated electrolyte. It is also confirmed that the initial hydroxide layer formed anodically from metallic nickel is not α-Ni(OH)$_2$, but a layer which is more readily reducible than α-Ni(OH)$_2$. At higher potentials, while in-situ XAS suggested that γ-NiOOH is not transformed to any further phase up to 0.665 V vs HgHgO in 1 M KOH, after extensive OER (at least 40 hrs) in 30 wt% at 50 mA cm^{-2}, an additional phase can be identified by cyclic voltammetry. Overall, during galvanostatic oxygen evolution, the nickel anodes follow an ageing behaviour characterised by a brief activation period, a short period of high activity (i.e., low overpotential) followed by deactivation and eventually stable but poor activity. While no clear evidence was obtained to identify the most active phase for oxygen evolution, it is likely that this is related to β-NiOOH and confined to the very surface of the electrode.

1. Introduction

Nickel is often used as a material for the oxygen evolution reaction (OER) in addition to other electrochemical technologies such as Ni-batteries and sensors [1–5]. While it is well known that the activity of nickel anodes towards the oxygen evolution reaction can decrease over time [6], and that the preparation procedure has a large influence on activity [7], the mechanisms involved are not fully understood.

There are four nickel oxide phases known to be present near the oxygen evolution reaction potential: α-Ni(OH)$_2$, β-Ni(OH)$_2$, β-NiOOH and γ-NiOOH. These four phases were first described by Bode et al. [8] (Fig. 1). α-Ni(OH)$_2$ has a hydrated disordered structure [9], and often contains foreign ions [10]. This α-Ni(OH)$_2$ phase does not have a well-defined structure and can vary depending on how the oxidised nickel layer was prepared [10]. Compared with the α-Ni(OH)$_2$ phase, β-Ni(OH)$_2$ is more structured, with more closely packed layers [5]. According to Bode's model, upon oxidation, β-Ni(OH)$_2$ is converted to β-NiOOH, whereas α-N(OH)$_2$ is converted to γ-NiOOH. The γ-NiOOH structure is not well-defined, but is known to contain intercalated alkali metallic cations and water molecules, and results indicate it is at a higher oxidation state than β-NiOOH [9,11]. It has been proposed that β-NiOOH converts to γ-NiOOH upon further oxidation [12,13].

Despite the utility of Bode's model, the interconversion between the oxidised nickel phases appears to be more complex than described in the model. For example, Raman spectroscopy indicates that β-NiOOH transforms into an undefined phase (not γ-NiOOH) above 0.52 V vs Hg/HgO in 0.1 M KOH [7], and results obtained by Ohligschlager and Schwitzgebel [13] suggest another intermediate β phase exists (β^*) at low alkaline electrolyte concentrations. Furthermore, much of the research has investigated the interconversion of the anodic nickel oxides at lower potentials and lower hydroxide electrolyte concentrations than used in industrial alkaline water electrolysers. Thus in this paper the phase changes are examined over a wide range of potentials, and in both 1 M and 30 wt% (6.8 M) KOH electrolytes, with the intent of relating

---

* Corresponding author.
E-mail address: aaron.marshall@canterbury.ac.nz (A.T. Marshall).

http://dx.doi.org/10.1016/j.electacta.2015.04.020
0013-4686/© 2015 Elsevier Ltd. All rights reserved.

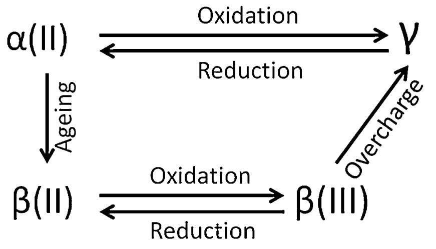

Fig. 1. Bode diagram of known nickel phases.

these results to the less understood structural changes that occur throughout galvanostatic oxygen evolution.

2. Experimental

1 cm^2 nickel foil electrodes (Sigma-Aldrich $\geq$ 99.9%) 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, and finally rinsed in deionised water. Contact with 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. Tests were performed in either 1 M or 30 wt% KOH solution in a thermostatically controlled PTFE cell at 25 °C. Nickel foil (30 cm^2) acted as the counter electrode along with a Hg/HgO (KOH) reference electrode. Cyclic voltammetry was performed at 50 mV s^{-1} from -0.1 V to 0.65 V (unless stated otherwise). Electrochemical impedance spectroscopy (EIS) was performed either at 0 V (to obtain the ohmic resistance between the reference and working electrodes) or 50 mA cm^{-2} (during galvanostatic oxygen evolution) over the frequency range 0.2 - 100,000 Hz at 5 mV rms. Unless stated otherwise the following pretreatment procedure was used: the freshly etched nickel electrodes were subjected to potentiostatic EIS at 0 V, and then the potential held at -100 mV for 2 hours. Prior to a galvanostatic ageing test, the electrode also had a cycling pretreatment step at 50 mV s^{-1} for 20 cycles between -0.1 V and 0.65 V.

X-ray photoelectron spectroscopy (XPS) was performed for surface analysis using a Kratos Axis DLD spectrometer with monochromated Al K-α source, and CasaXPS was used to fit peaks to the data. Materials analysed with XPS underwent long-term galvanostatic oxygen evolution measurements for 0 - 100 hours at 50 mA cm^{-2}. The samples were removed immediately after galvanostatic-ageing, rinsed in DI water, then isopropanol, and then dried in an oven at 50 °C for 10 minutes.

In-situ x-ray absorption spectroscopy (XAS) measurements were performed at the Australian Synchrotron using nickel thin films (approximately 20 nm thick) prepared by thermal evaporation of Ni onto pyrolytic graphite foils. The XAS data was recorded in fluorescence mode using a 100-element Ge fluorescence detector using an electrochemical cell similar to that described by Holstein and Rosenfeld [14], with a Pd counter electrode and AgAgCl reference electrode. The potential of the thin Ni film was controlled with a Digi-Ivy DY2100 potentiostat. A Ni reference foil was measured simultaneously with the fluorescence data, and α-Ni(OH)$_2$ and NiO powders were also used as reference compounds.

3. Results and Discussion

3.1. Cyclic-Ageing and Phase Changes

Repetitive cyclic voltammetry was used to understand the phase changes occurring on the nickel electrode surface. Much of the recent literature associated with electrochemical oxidation of nickel used electrolytes of $\leq$ 1 M OH$^-$, so in order to allow comparisons between existing literature and the measurements reported here at 30 wt% KOH, cyclic voltammetry was first performed in 1 M KOH (Fig. 2). Two overlapping peaks are seen on the cathodic sweep at approximately 0.38 V (C1) and 0.35 V (C2), and overlapping peaks are seen in the anodic direction at 0.45 V (A1) and 0.48 V (A2). In existing literature, C1 and A1 are typically associated with the α-γ reaction, and C2 and A2 are associated with the β-β reaction [7,12]. The β-β reaction occurs at lower potentials in the cathodic direction because the γ-NiOOH phase is more accessible to anions and the β-NiOOH phase is more thermodynamically stable [15]. The individual peaks may be deconvoluted by fitting Gaussian peaks to the voltammetry data (Fig. 3), in a similar way to that used when interpreting electrochemical behaviour of Ni in QCM studies [13,16]. It is important to stress that the use of Gaussian peaks is only to illustrate the possible potential and charge associated with the overlapping redox processes, and is not assumed to theoretically described cyclic voltammetry peaks [17]. Despite this, the fits do result in a consistent ageing pattern over all electrodes tested which provides further insights into which processes dominate the voltammetric behaviour over time (Fig. 4). It is clear that as the cycling proceeds, the A1 peak decreases continuously and is practically gone after approximately 150 cycles (Fig. 4a). This is consistent with the Bode model, which shows that the α-Ni(OH)$_2$ phase develops into β-Ni(OH)$_2$ upon ageing, and also the findings of others which show the net anodic peak (of the overlapping α-γ and β-β processes) shifts to higher potentials upon cycling [7,15,18]. The transition process from α-Ni(OH)$_2$ to β-Ni(OH)$_2$ is described well by Bernard [19], with an initial fast decrease in the quantity of alkali metal ions exchanged during potential cycling due to a

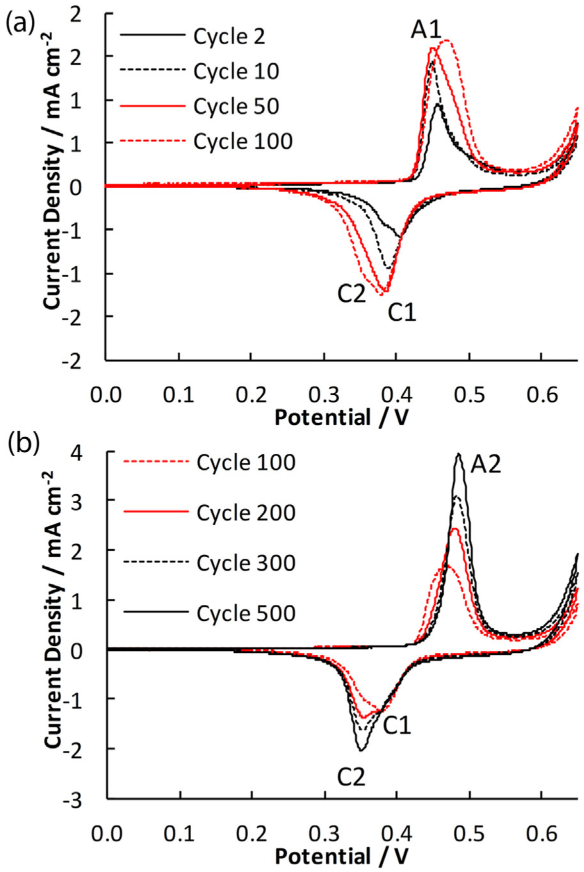

Fig. 2. Cycles 2-100 (a) and 100-500 (b) of cyclic voltammograms performed at 50 mV cm^{-2} between -0.1 V and 0.65 V in 1 M KOH.