



Short communication

The fabrication of a bifunctional oxygen electrode without carbon components for alkaline secondary batteries



Stephen W.T. Price^{a,*}, Stephen J. Thompson^a, Xiaohong Li^b, Scott F. Gorman^b,
Derek Pletcher^a, Andrea E. Russell^a, Frank C. Walsh^b, Richard G.A. Wills^b

^aChemistry, University of Southampton, Southampton SO17 1BJ, UK

^bEnergy Technology Group, University of Southampton, Southampton SO17 1BJ, UK

HIGHLIGHTS

- Fabrication and development of a carbon free bifunctional gas diffusion electrode.
- Good stability and overpotentials on cycling at 50 mA cm⁻² for >50 cycles.
- Operational up to current densities of 100 mA cm⁻².

ARTICLE INFO

Article history:

Received 3 December 2013

Received in revised form

5 February 2014

Accepted 15 February 2014

Available online 26 February 2014

Keywords:

Carbon free gas diffusion electrode (GDE)

Bifunctional electrode

Oxygen evolution/reduction

Alkaline

ABSTRACT

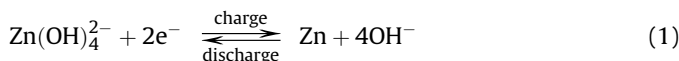
The fabrication of a gas diffusion electrode (GDE) without carbon components is described. It is therefore suitable for use as a bifunctional oxygen electrode in alkaline secondary batteries. The electrode is fabricated in two stages (a) the formation of a PTFE-bonded nickel powder layer on a nickel foam substrate and (b) the deposition of a NiCo₂O₄ spinel electrocatalyst layer by dip coating in a nitrate solution and thermal decomposition. The influence of modifications to the procedure on the performance of the GDEs in 8 M NaOH at 333 K is described. The GDEs can support current densities up to 100 mA cm⁻² with state-of-the-art overpotentials for both oxygen evolution and oxygen reduction. Stable performance during >50 successive, 1 h oxygen reduction/evolution cycles at a current density of 50 mA cm⁻² has been achieved.

© 2014 Elsevier B.V. All rights reserved.

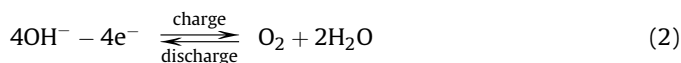
1. Introduction

A successful renewable energy economy will require energy storage to manage the time differences between generation and customer demand. One solution is offered by flow batteries [1–3] although none of the systems extensively studied offer ideal behaviour and economics. Secondary metal/air batteries, particularly zinc/air [4–6], merit development. In a zinc/air battery, the electrode reactions are:

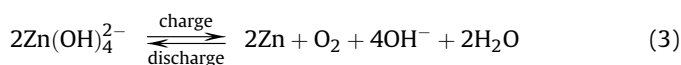
negative electrode



positive electrode



battery



The battery has an open circuit potential of ~1.65 V. Clearly, one requirement is a bifunctional oxygen electrode, ie. an electrode that supports both oxygen evolution and reduction with low overpotentials.

A recent communication [7] described a novel procedure for fabrication of a bifunctional oxygen electrode for alkaline secondary metal/air batteries. In this procedure, a nickel metal powder/PTFE gas diffusion electrode (GDE) is preformed within a nickel foam prior to the deposition of a catalyst layer by dip coating and thermal treatment. This paper now reports the influence of the

* Corresponding author.

E-mail addresses: stephen.price@diamond.ac.uk (S.W.T. Price), a.e.russell@soton.ac.uk (A.E. Russell).

numerous parameters in the fabrication procedure on the performance of these electrodes.

While the choice of electrocatalyst to minimise overpotentials is clearly important, it needs to be recognised that a gas diffusion electrode suitable as a bifunctional oxygen electrode must have a series of additional properties. It must have a structure that provides an effective barrier to crossover of both gas and electrolyte while permitting a high flux of oxygen to the catalyst centres during discharge and release of oxygen to the gas side during charge. Also there must be low resistance, current pathway between catalyst centres and external contacts that prevents IR drops and an uneven current distribution. The target is to design electrodes that have the physical and mechanical properties to allow their scale-up and implementation in flow cells with electrode areas up to 1 m².

The design of the GDEs was based on a number of conclusions from preliminary experiments and the literature.

- Nickel cobalt spinel, NiCo₂O₄ was selected as the electrocatalyst [8–14]. Preliminary experiments showed that it gave overpotentials for both oxygen evolution and reduction that were at least comparable to other electrocatalysts including precious metals. However, it had the advantage that it was prepared in a simple procedure and this could be achieved at a relatively low temperature where other components of the GDEs were stable. This is essential for application of the spinel catalyst after the formation of the gas diffusion layer.
- Carbon materials within the GDEs (powder and paper) were avoided since the literature has concluded that carbons corrode under the forcing conditions of oxygen evolution [15–18] and this was also our experience.
- The polymer selected as binder in the GDEs was PTFE. Cation conducting polymers were considered unsuitable because of the key role of hydroxide ion in the battery chemistry and no anion conducting polymers with the appropriate properties have been located.

The medium chosen was 8 M NaOH at 333 K. Sodium hydroxide is substantially cheaper than potassium hydroxide and allows a significant increase in the zincate concentration (1.2 M cf 0.5 M). The use of the elevated temperature leads to large decrease in the overpotentials for the electrode reactions as well as increasing the solubility of the sodium zincate; it is also a typical steady state temperature for a large scale electrolysis cell system.

2. Experimental

2.1. Chemicals

Nickel powder (2–10 μm particle size determined by SEM) was supplied by Huizhou Wallyking Battery Ltd, China. Two sources of nickel foam were used – Goodfellow Metals (thickness 1.9 mm, 20 pores cm⁻¹) and Changsha Lyrun New Material Co. Ltd (thickness 1.6 mm, 43 pores cm⁻¹). Nickel nitrate (Aldrich, 99.999%), cobalt(II) nitrate (Aldrich, ≥98%), sodium hydroxide (Fisher, 97%), polytetrafluoroethylene (PTFE, Aldrich, 60 wt% dispersion in H₂O) were used as received.

An electrode prepared from nickel cobalt spinel, NiCo₂O₄, powder was used for comparison. The powder was prepared by a thermal decomposition procedure. Ni(NO₃)₂·6H₂O (14.54 g) and Co(NO₃)₂·6H₂O (29.1 g) were dissolved in methanol (100 ml) and heated at 338 K to evaporate solvent. The dried powder sample was calcined at 648 K for 20 h. The resulting black powder was characterized by SEM, TEM, EDAX, XRD, BET analysis and particle size analysis and a further paper [19] will discuss the data in detail as well as comparing spinel powders from several preparation

procedures. Here, we note that samples from repetition of the preparation led to materials with well-defined XRD patterns characteristic of a spinel structure, a ratio of Ni:Co close to 1:2 (determined by both EDAX and elemental analysis), BET surface area of ~10 m² g⁻¹ and particles sized below 5 μm.

2.2. Preparation of gas diffusion electrodes

The procedure for making the bifunctional oxygen gas diffusion electrodes (GDEs) is illustrated with a particular example. The first stage led to a porous nickel powder/PTFE layer on nickel foam. The nickel foam (a disc, diameter 12 mm) was ultrasonicated in acetone for 20 min, acid etched in 1 M HCl at 353 K for ~1 h and then washed with water and ultrasonicated in water for 15 min. Nickel powder (150 mg) and 60% PTFE solution (75 mg) were mixed with isopropanol (0.5 cm³) and water (0.5 cm³). The paste was then ultrasonicated for 20 min and homogenised for 4 min to form an ink before drying to a paste with a ratio of Ni:PTFE of 10:3. The Ni/PTFE paste (200 mg wet weight ~ 120–150 mg dry weight) was spread uniformly over the Ni foam disc and pressed in a Specac hydraulic press at 1.5 kN cm⁻² and 298 K for 30 s. The second step was to form the catalyst layer. The nickel powder/PTFE coated nickel foam was soaked in a solution containing 1 M Ni(NO₃)₂ and 2 M Co(NO₃)₂ in 50/50 isopropanol/water, dried at 298 K for ~60 s and then heat treated at 648 K in air for 10 min to form the NiCo₂O₄ spinel. The dip, dry and heat cycle was repeated 3 times before the sample was calcined at 648 K for 3 h. The procedure always had the two stages but a number of parameters within it (eg. ratio of Ni:PTFE, loading, dipping solution, thermal treatment) were varied as set out in the results section. For comparison, some GDEs were prepared where NiCo₂O₄ spinel powder was used instead of Ni powder; these were fabricated in a single stage.

Fig. 1 reports SEM images of the NiCo₂O₄ coated Ni powder/PTFE GDEs. Fig. 1(a) shows the uniform surface of the electrodes exposed to the electrolyte when mounted in the cell; an SEM images of the gas side clearly show that foam structure is maintained. Fig. 1(b) shows a cross section SEM image; there is 50 μm dense layer on the electrolyte side and the fill of the foam decreases away for this surface to give open foam. Fig. 2 shows high resolution SEM images of the surface of the NiCo₂O₄ coated Ni powder/PTFE GDE along with the Ni/PTFE layer before deposition of the spinel catalyst. It can be seen that before the coating with catalyst, the surface consists of small angular particles of nickel while after coating, rather unstructured, ‘fluffy’ patches of the spinel catalyst are dispersed over the surface.

2.3. Electrochemical experiments

Electrochemical experiments were carried out in a water jacketed glass cell (volume 200 cm³), see Fig. 3, with a GDE, a platinum gauze counter electrode and a laboratory prepared Hg/HgO reference electrode placed inside a compartment with a Luggin capillary. The GDE disc (diameter 12 mm) was mounted inside a PTFE holder, see Fig. 3(b) with the NiCo₂O₄ coated Ni powder/PTFE layer adjacent to the electrolyte. The area of the GDE exposed to the electrolyte was 0.5 cm² and electrical contact was made with a circle of Ni wire around the perimeter of the disc on the gas side. A Grant TC120 recirculator with 5 L reservoir maintained the electrolyte temperature at 333 K. O₂ was passed to the rear of the GDE with a feed rate of 200 cm³ min⁻¹, controlled via a flow meter. The electrolyte was 8 M NaOH at 333 K. Current cycling was carried out under galvanostatic control at current densities in the range 10–100 mA cm⁻². All current densities are based on the geometric area of the electrode (0.5 cm²) exposed to the electrolyte and gas

Download English Version:

<https://daneshyari.com/en/article/1286876>

Download Persian Version:

<https://daneshyari.com/article/1286876>

[Daneshyari.com](https://daneshyari.com)