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Comparison of the Spinels Co_3O_4 and $NiCo_2O_4$ as Bifunctional Oxygen Catalysts in Alkaline Media

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ABSTRACT

Data from experiments with both rotating disc electrodes (RDEs) and gas diffusion electrodes (GDEs) are used to investigate the properties of the spinels, Co_3O_4 and $NiCo_2O_4$, as bifunctional oxygen electrocatalysts. Emphasis is placed on catalyst compositions and electrode structures free of carbon. Oxygen evolution and reduction occur at surfaces where the transition metals are in different oxidation states but the surface can be repeatedly cycled between these two states without significant change. It is shown that carbon-free, $NiCo_2O_4$ catalysed GDEs can be fabricated using structures based on stainless steel cloth or nickel foam. Those based on nickel foam can be cycled extensively and allow both O_2 evolution and reduction at current densities up to 100 mA cm^{-2}.

1. Introduction

Electrocatalysts that can support both oxygen reduction and oxygen evolution at high current densities are critical components of proposed metal/air secondary batteries and reversible fuel cells. Spinels have been widely proposed as bifunctional oxygen electrocatalysts in alkaline media [1–6], but their performance at practical current densities is seldom reported. One reason is that to operate as a bifunctional electrode at high current densities, the electrocatalyst must be placed into a GDE structure that allows both a high flux of O_2 to the catalyst sites during battery discharge and effective removal of O_2 away from these sites during battery charge. Dispersal of the gas away from the interelectrode gap, ie. into the gas space behind the catalyst layer is much preferable. Moreover, this performance must be achieved with a GDE without carbon components since carbon is prone to corrosion in strong alkali at the potentials for oxygen evolution, particularly at elevated temperatures [7–11].

Our target is the design of an electrode free of both precious metal and carbon powder that supports both oxygen reduction and oxygen evolution at high current densities. Spinels, especially Co_3O_4 and $NiCo_2O_4$ have been selected as non-precious metal catalysts for such electrodes [12–14] and this paper compares the performance of these two oxides as a bifunctional oxygen electrocatalyst. The comparison is based on experiments with RDE and the paper also contains performance data for GDE based on the preferred catalyst.

2. Experimental

2.1. Catalyst Preparation

The preparation of the two spinels was described in the previous paper [14]; characterisation of the spinel powders using XRD, SEM, TEM and surface area determination is presented in the Supplementary Information to the paper [14]. Pt black (Fuel Cell Grade) was purchased from E-TEK.

2.2. Instrumentation

All electrochemical experiments were carried out with Autolab PGSTAT instruments with NOVA and GPES software packages. The rotation rates of the electrodes were controlled by Pine Instrument Rotators, type CPR or MSR.

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2.3. Electrochemical Cells and Electrolyte

Experiments were carried out in beaker cells (volume ~ 200 cm^3) with a polymer cover and a water jacket. Water, temperature controlled with a Grant TC120 recirculator with a 5 litre reservoir, was passed through the jacket. The counter electrode was a Pt gauze in the same compartment and the reference electrode a laboratory fabricated Hg/HgO/KOH electrode inside a Luggin capillary. The KOH concentration in the reference electrode was always the same as used in the solution under study. With 1 M KOH, the potential of the reference electrode is + 866 mV vs NHE.

For experiments with disc electrodes, the working electrode was a 0.2 cm^2, glassy carbon disc electrode (Pine Instruments AF3 M electrode) coated with a catalyst layer without carbon powder applied as an ink. To prepare the ink, 2 mg catalyst in 6 cm^3 of deionised water was placed in an ultrasonic bath (Fisherbrand FB15046) for 30 minutes followed by 2 minutes shear force stirring in a homogeniser (Fisher Powergen 1000). The ink was applied to pre-polished (with alumina slurries of 1.0 μm then 0.05 μm particle size on a microcloth), glassy carbon discs in 3 × 15 μl aliquots with drying with an IR heat lamp between applications. Finally, a thin film of Nafion was drop cast over the catalyst layer using 15 μl of 1 wt % Nafion in water (prepared from aqueous Nafion solution, 10 % solids (Ion Power GmbH)) and the coating again dried. This final layer was found to greatly enhance the stability of the coating and improve the reproducibility of experimental data. The final catalyst loading on the glassy carbon disc was 75 $\mu g\,cm^{-2}$.

The gas diffusion electrodes (GDEs) were based on 12 mm diameter discs that were mounted inside a PTFE holder so that the $NiCo_2O_4$/PTFE layer was adjacent to the electrolyte and an area of 0.5 cm^2 was exposed to both electrolyte and gas phase. Electrical contact was made with a fine Ni mesh and Ni wire on the gas side. Oxygen gas was passed to the rear of the GDE with a feed rate of 3.3 $cm^3\,s^{-1}$ controlled via a flowmeter. Two types of GDE were fabricated:

(a) Steel cloth collector – Discs (diameter 12 mm) were cut from a stainless steel filter cloth (Type BMT50 - United Wire Ltd) and cleaned. They were placed in acetone in an ultrasonic bath (Fisherbrand FB15046) for 20 minutes, acid etched in 1 M HCl, washed well with water and dried. $NiCo_2O_4$ powder (100 mg), and 60% PTFE solution (50 mg) were mixed with isopropanol (0.2 cm^3) and water (1 cm^3). For some GDEs, sodium sulphate (10 mg) was added as a pore-former. The mixture was then ultrasonicated for 20 minutes and homogenised (Fisher Powergen 1000) for 2 minutes to form an ink with a ratio of $NiCo_2O_4$: PTFE of 10:3 by mass. The ink was then sprayed onto the steel cloth with an airgun (Iwata CM-B spray-gun) and dried with a hot air gun. The spray coating was repeated to obtain the desired loading with the cloth heated by a hot air-gun between catalyst-film applications. The electrodes were then compressed with a pressure of 4 $kg\,cm^{-2}$ at a temperature of 450 K for 5 minutes. Finally, the whole structure was dipped three times into a solution of 2 M $Co(NO_3)_2$ + 1 M $Ni(NO_3)_2$ for 5 minutes with drying between dips before heating to 648 K for 3 hours. While not essential, the final in situ deposition of a $NiCo_2O_4$ layer was found to improve reproducibility of the GDE performance. The treatment probably led to protection of the stainless steel surface and certainly the heat treatment led to PTFE migration through the structure and consequent improvement in catalyst adhesion to the cloth, as well as increased hydrophobicity and/or increased porosity to gas. The final $NiCo_2O_4$ loading was 10 - 20 mg cm^{-2}.

(b) Ni foam current collector - Discs (diameter 12 mm) cut from a nickel foam sheet (thickness 1.9 mm, 20 pores/cm – Goodfellow Metals) were first cleaned. They were ultrasonicated in acetone for 20 minutes, acid etched in 1 M HCl at 353 K for ~ 1 hour and then washed with water and ultrasonicated in water for 15 minutes. $NiCo_2O_4$ powder (150 mg), and 60 % PTFE solution (75 mg) were mixed with isopropanol (0.5 cm^3) and water (0.5 cm^3). The paste was then ultrasonicated for 20 minutes and homogenised for 4 minutes to form an ink before drying to a paste with a ratio of $NiCo_2O_4$: PTFE of 10:3 by mass. The $NiCo_2O_4$/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. As with the stainless steel cloth GDEs, in a final stage, the whole structure was dipped three times into a solution of 2 M $Co(NO_3)_2$ + 1 M $Ni(NO_3)_2$ for 5 minutes with drying between dips before heating to 648 K for 3 hours.

3. Results

3.1. Oxidation States in the Spinel

Fig. 1 shows cyclic voltammograms for Co_3O_4 and $NiCo_2O_4$ coated glassy carbon disc electrodes in 1 M KOH at 298 K, recorded with a potential scan rate of 10 mV s^{-1} between the potentials for oxygen evolution and reduction. The dominant features on the forward scans are well-formed oxidation peaks at slightly less positive potentials than that for O_2 evolution. Nickel, cobalt and

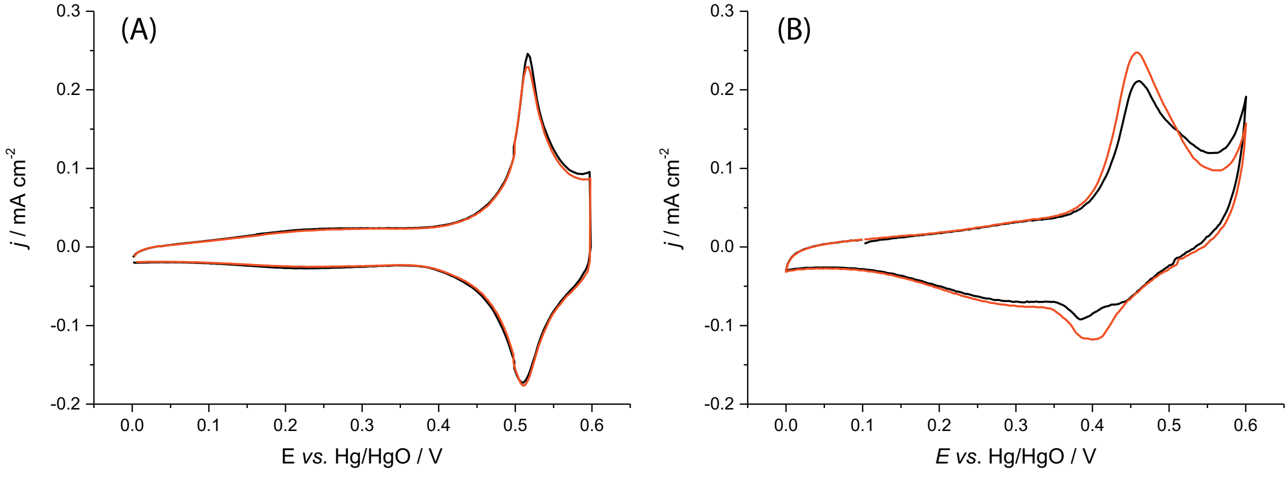

Fig. 1. Cyclic voltammograms - 1st (black) and 10th cycles (red) for (A) Co_3O_4 and (B) $NiCo_2O_4$ layer in 1 M KOH. Temperature 298 K. Potential scan rate 10 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)