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A nanostructured bifunctional Pd/C gas-diffusion electrode for metal-air batteries

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ABSTRACT

Designing a bifunctional air electrode which catalyses both the oxygen reduction and oxygen evolution reactions is an essential part of progress towards fully rechargeable metal-air batteries, such as the iron-air battery which is environmentally friendly, low cost, and does not suffer risk of thermal runaway like lithium-ion batteries. This paper reports the development of a lightweight carbon-based bifunctional air electrode, catalysed by a small ($0.5\,\mathrm{mg\,cm^{-2}}$) loading of 30 wt.% palladium on carbon. The Pd-catalysed air electrode showed good bifunctional activity, with 0.53 V potential difference between oxygen reduction and evolution. The Pd/C air electrode showed improved catalytic activity at high current densities ($\geq 50\,\mathrm{mA\,cm^{-2}}$) and enhanced durability compared with two commercial Pt/C air electrodes produced by Gaskatel GmbH and Johnson Matthey. A stable oxygen evolution potential was maintained over 1,000 charge-discharge cycles.

1. Introduction

Metal-air batteries are currently of great research interest, particularly in the area of rechargeable batteries for electric vehicles [1]. This is because they use atmospheric oxygen as a source of energy, which allows the batteries to be lightweight as only a thin, low-density "air breathing" cathode is needed to catalyse the oxygen reactions. The anode can be made from a variety of metals, for example zinc, iron, aluminium or lithium. Heavy metals can be avoided entirely or used only in small amounts (e.g. 5 wt.%), giving the metal-air batteries a considerably lower density than lead acid batteries. The theoretical specific energy density of a metal-air battery (up to $12{,}000\,\mathrm{W\,h\,kg^{-1}}$) [2] is much greater than the energy density of the lithium-ion batteries currently used in rechargeable vehicles (up to $1{,}000\,\mathrm{W\,h\,kg^{-1}}$) [2], and metal-air batteries do not suffer from the thermal runaway safety issues of lithium-ion batteries [3].

One of the greatest challenges is to make a rechargeable metal-air battery that can be re-used for thousands of charging and discharging cycles. In terms of the choice of anode, iron-air batteries may be most suitable, because iron is less easily corroded than aluminium or lithium, and does not suffer the dendrite formation problems of zinc-air batteries during re-charging [4]. The air breathing cathode of a rechargeable iron-air battery also needs to be able to support repeated cycling without substantial degradation in performance.

A rechargeable air cathode must have good bifunctionality, i.e. be able to reduce oxygen during discharge and evolve oxygen during charge. The most efficient and cost-effective way of achieving this is to include a single bifunctional catalyst in the electrode, rather than one catalyst for each separate reaction. However, in practice, separate electrocatalysts are often used for the two reactions of the bifunctional electrode [5] because good bifunctional oxygen catalysts are rare, and often involve precious metals such as platinum and palladium. These metals and their alloys need to be used sparingly, or cheaper alternatives such as perovskites [6,7] or spinels [8–10] can be used.

Palladium oxygen catalysts have been reported in a number of studies, [11–17] A wide range of palladium loadings and particle sizes have been studied, and compared with state-of the-art platinum catalysts. A study performed in 1983 suggested that the catalytic activity per gram of platinum and palladium supported on graphite is similar if the metals are highly dispersed, i.e. the loading is small (<2 atomic% or <33 wt% in the catalyst layer), [15]. Another study suggested superior performance of palladium to platinum if used in a methanol fuel cell cathode with

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$\leq 2\,mg\,cm^{-2}$ catalyst loading [13]. Superior performance of Pd/C compared with Pt/C was also reported for palladium supported in thin graphite sheets, although the authors did not report the Pd catalyst loading [16]. A recent study from 2015 showed that 30 wt.% Pd supported on Vulcan had higher activity for the oxygen evolution reaction than 30 wt.% Pt on Vulcan, and also had improved durability during repeated cycling tests [17]. These studies provide some justification for using the cheaper palladium instead of platinum in applications where the catalyst loading is low and the catalyst particles are well- dispersed.

In the majority of the above studies the palladium and platinum catalysts were layer-deposited onto small glassy carbon rotating disk electrode, not a complete air electrode with a gas-diffusion layer, and the oxygen reduction reaction alone was studied rather than the bifunctional reactions (charge and discharge). It is apparent in the literature on bifunctional air electrodes in general that although a large number of publications study bifunctional catalysts deposited onto the surface of rotating disk electrodes (RDEs) in oxygen saturated solution (for recent publications see the references [6,18–22]), there is a much more limited number of publications which look at the properties of such catalysts when they are on the surface of complete gas diffusion electrodes [7–9,17,23].

In order to assess the practicality of using a particular catalyst it is important to study not only the characteristics on a RDE, but also *in-situ* on a gas diffusion electrode. This is because the activity of the catalyst is not the only important factor in the construction of a rechargeable air electrode: the interaction of the catalyst with the supporting layers of the electrode and the current collector, and the efficiency of oxygen transport to the catalyst through the gas diffusion layer, are also of importance. For instance, catalysts which appear to have a strong performance on a solid glassy carbon or gold RDE may not have such high activity when adsorbed onto high surface area gas diffusion layer [24].

For this reason, the supporting materials onto which the catalyst materials are absorbed must also be optimised. Carbon is usually the conductive supporting material of choice for air electrode catalysts due to its low density and high surface area. However, carbon has a tendency to undergo corrosion during repeated current cycling on an air electrode, particularly during the charging process where the air electrode is at positive (oxidising) potentials. The products of this corrosion process are oxygen-functionalised carbon such as $-COO^{-}$, or carbonates CO_3^{2-} formed via CO_2 generation [25,26]. As the carbon corrodes, oxidised particles may detach and dissolve into the electrolyte, leading to the loss of carbon and catalyst particles from the air electrode surface and a decrease in the electrochemical surface area [27,28]. The performance of carbon-based gas diffusion electrodes will therefore deteriorate over time. The development of carbon supporting materials with high corrosion resistance is vital to ensure that air electrodes have a good durability over many charge-discharge cycles.

This paper outlines the development of a palladium-catalysed bifunctional air-breathing electrode, and demonstrates how obtaining a good dispersion of palladium nanoparticles can create a stable catalyst with good activity at low catalyst loadings, such that only very small quantities ($0.5\,mg\,cm^{-2}$) of palladium are sufficient to give good performance. The choice of carbon materials and their role in ensuring the long-term durability of the air electrode are also discussed.

2. Experimental Details

2.1. Synthesis and characterisation of the Pd/C catalyst

The Pd catalyst was synthesized by means of a colloidal method, employing sulphites as complexing agents, as described elsewhere [29,30]. The carbon support (supplied by Imerys Graphite & Carbon, $220\,m^2\,g^{-1}$ specific surface area, subsequently referred to in this paper as C) was suspended in distilled water and stirred in an ultrasonic water bath at about 80 °C to form a slurry. An acidic solution containing an appropriate amount (to reach a final loading of 30 wt.% of Pd on the support) of $Na_6Pd(SO_3)_4$ was successively added to the slurry. The Pd sulphite complex solution was decomposed by adding H_2O_2 and successively increasing the pH to 5.5 to form colloidal PdO_x/C. The metallic oxide was reduced in a H_2 stream at room temperature (23 °C) to form the 30 wt.% Pd/C catalyst.

The catalysts were characterized by X-ray diffraction (XRD) using a Philips X-pert 3710 X-ray diffractometer with Cu Kα radiation operating at 40 kV and 30 mA. The peak profile of the (220) reflection in the face centred cubic structure of Pd was analysed by using the Marquardt algorithm, and it was used to calculate the crystallite size by the Debye-Scherrer equation. Transmission electron microscopy (TEM) analysis was made by first dispersing the catalyst powder in isopropyl alcohol. A few drops of this solution was deposited on carbon-film-coated Cu grids and analysed with a FEI CM12 microscope. The total metal content in the catalysts was determined by burning the carbon support in a thermal gravimetric experiment up to 950 °C in air.

Cyclic voltammetry was also performed in order to calculate the electrochemically active surface area (ESA) of the catalyst. A cell with a three-electrode assembly and an Autolab potentiostat-galvanostat were used to carry out the electrochemical characterization. The working electrode consisted of a thin layer of the catalyst deposited on a pyrolytic graphite disk (5 mm) polished to a mirror finish using an alumina suspension. The counter electrode consisted of a high surface Pt wire and the reference electrode was an Hg/HgO electrode filled with a $1\,mol\,dm^{-3}$ KOH solution (AMEL Electrochemistry, - 115 mV vs. SHE). An aqueous suspension consisting of $1\,mg\,cm^{-3}$ of the Pd/C catalyst was obtained by ultrasonically dispersing it in iso-propanol and Nafion ionomer (30 wt.%) (purchased from Ion Power). The Pd loading on the working electrode was $50\,\mu g\,cm^{-2}$. After preparation, the electrode was immersed into deaerated $1\,mol\,dm^{-3}$ KOH electrolyte, prepared from high purity reagents (Sigma–Aldrich) and ultrapure water. Cyclic voltammograms were carried out at scan rate of $20\,mV\,s^{-1}$, between -0.93 and 0.27 V vs. Hg/HgO (0 and 1.2 V vs. RHE). All the experiments were carried out at room temperature. The ESA was determined from the integration of the current involved in the reduction of the palladium oxide assuming $405\,\mu C\,cm^{-2}$ for the reduction of a monolayer of PdO_x and correcting by the double layer capacitance [31].

2.2. Construction of the gas diffusion electrode

The Pd/C gas diffusion electrode was composed of three main parts: a gas diffusion layer, a catalyst layer, and a current collector, which were bound together in a single step by hot-pressing. To make the gas diffusion layer, a carbon cloth of 0.11 mm thickness treated with 25 wt.% PTFE was purchased from FuelCell.com, and cut into a 5 × 5 cm piece. A paste was made from 80 wt.% of a $64\,m^2 g^{-1}$ low-surface area carbon (supplied by Imerys Graphite & Carbon, subsequently referred to in this paper as C1) mixed with 20 wt.% PTFE (DISP 30 solution, DuPont) and $10\,cm^3$ water per 1 g of solids. The paste was then rolled evenly over the carbon cloth to a thickness of approximately $100\,\mu m$.

To make the catalyst layer, the 30 wt. % Pd/C catalyst was sonicated for 15 minutes in a 5 wt.% Nafion ® solution in aliphatic alcohols (Sigma Aldrich), in a weight ratio of 3:2 for the catalyst: Nafion. The sonication resulted in a black viscous ink. The catalyst layer ink was spread evenly on top of the gas diffusion layer (which was not allowed to dry out, to prevent it from detaching from the