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Electro-deposition of Pd on Carbon paper and Ni foam via surface limited redox-replacement reaction for oxygen reduction reaction

Remegia M. Modibedi[a,*], Mkhulu K. Mathe[a], Rapelang G. Motsoeneng[b], Lindiwe E. Khotseng[b], Kenneth I. Ozoemena[a], Eldah K. Louw[a]

[a] Energy Materials, Materials Science and Manufacturing, Council for Scientific & Industrial Research (CSIR), Pretoria 0001, South Africa
[b] Eskom Center for electrocatalytic Research, South African Institute for Advanced Material Chemistry, Faculty of Science, University of the Western Cape, Bellville, Cape Town 7535, South Africa

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ABSTRACT

Pd nanostructured catalysts were electrodeposited by surface-limited redox replacement reactions using the electrochemical atomic layer deposition technique. Carbon paper and Ni foam were used as substrates for the electrodeposition of the metal. Supported nanostructured Pd electrodes were characterized using electrochemical methods and scanning electron microscopy. Carbon paper and Ni foam produced good quality deposits with some agglomeration on Ni foam. The EDX profiles confirmed the presence of Pd particles. Cyclic voltammograms of the electrodeposited Pd on substrates showed features characteristic of polycrystalline Pd electrodes. In the acidic electrolyte a very weak oxygen reduction reaction (ORR) activity was observed on Pd/Carbon paper electrode when compared to Pd/Ni foam electrode. The Pd/Ni foam electrode showed improved ORR activity in alkaline medium.

1. Introduction

Fuel cells continue to be investigated as alternative energy source because of the high energy demand worldwide. Fuel cells offer high efficiency with little or no pollution. Direct methanol fuel cells (DMFCs) have received extensive attention as potential power sources for portable and stationary applications [1–3]. The electrocatalytic reduction of oxygen is of great importance in fuel cells and sensors. The oxygen reduction reaction (ORR) involving the four electron transfer remains a challenge for DMFCs due to its slow kinetics. Research activities worldwide are focussed on improving the performance of ORR catalysts, reducing the amount of Pt required in DMFCs and in developing catalysts that are tolerant to methanol (methanol crossover). These activities are aimed at lowering the cost, increasing the efficiency, and improving the durability of fuel cells hence accelerating the commercialisation of fuel cells. Noble metals have proved to be the best electrocatalysts for the oxygen reduction reaction (ORR) [4–8]. Pt-M alloyed or mixed nanoparticles (M =Au, Pd, Ir, Rh, Re, Ru, or Os) on Pd (111) single-crystal and carbon-supported Pd nanoparticles for ORR has been reported [9]. Pd has attracted enormous attention since it is more abundant and cheaper than Pt [10,11].

In catalysis, it is well known that surface reactions are controlled by the atomic level details of the catalytic surface and hence the catalyst preparation method is important in tuning the morphology and composition of the catalyst. Various methods such as conventional physical and chemical, electrodeposition as well as sputtering methods are used in the preparation of catalysts [12]. The catalytic layer can be applied on the membrane or gas diffusion layer by different techniques, namely: rolling, spray-coating, brush-painting and printing methods [13] followed by drying and hot pressing. The electrochemical deposition method is well known for the fabrication of nanostructured catalysts for energy materials. In this report, Electrochemical Atomic Layer Deposition (EC-ALD) was identified as a potential catalyst fabrication technique. EC-ALD is the electrochemical deposition method that involves alternated electrodeposition of atomic layers of elements on a substrate, employing under-potential deposition (UPD) in which one element deposits onto another element at a voltage prior to that necessary to deposit the element onto itself [14]. These deposition processes are typically carried out at ambient temperatures and use small concentrations of precursor solutions (typically in millimolar levels). Different solutions are used to deposit each element separately. EC-ALD is an attractive technique because of the inherent advantages of sequential electrochemical deposition with self-limiting

* Corresponding author. Tel.: +27128412516; fax: +27128412135.
E-mail addresses: mmodibedi@csir.co.za, mmalewane@gmail.com (R.M. Modibedi).

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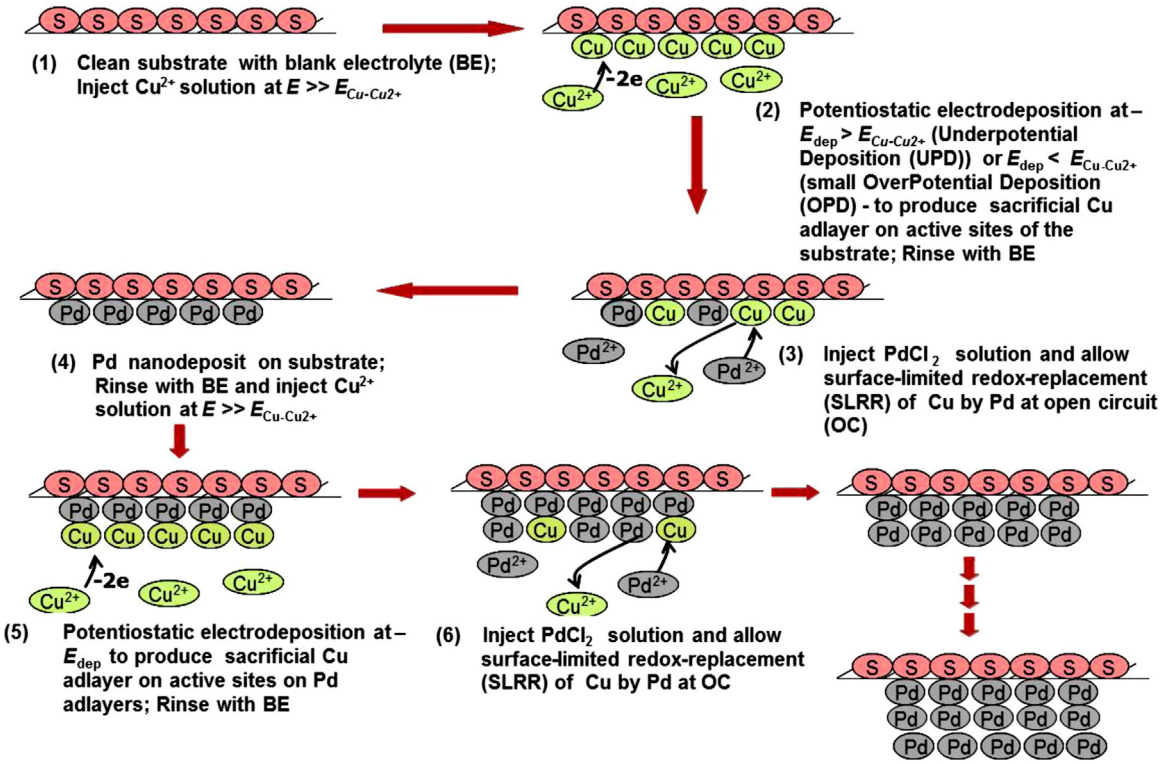

Fig. 1. Sequential layer-by-layer electrodeposition of Pd using Cu as a sacrificial metal.

growth of deposits, features that may allow, for instance, fine-tuning of catalytic properties in relation to ratios of constituent elements, by way of stopping the growth of deposits at appropriate points. Khosravi et al. [15] coated the carbon paper with Au in order to perform Cu UPD for the deposition of Pt also aiming at reducing the Pt loading needed for FC. These carbon paper supported Pt/Au catalysts were evaluated for the electro-oxidation of methanol as well as the oxygen reduction reaction (ORR). The fabrication of Pd on nanoporous gold film electrode was explained by Kiani et al. [11]. Ni foam was used by Bidault et al. [16] as electrode substrate for the ORR catalysts. Mkwizu et al. [17] demonstrated the synthesis of bimetallic multilayered nanostructures of platinum-based nanostructures involving Pt, Ru and Au using EC-ALD and derivatives of this layer-by-layer electrodeposition on model substrates with unique electrocatalytic properties for alcohol oxidation and oxygen reduction reactions in half-cell tests.

In the pursuit to improve reproducibility while overcoming the loss of catalytic activity during the catalyst preparation process, Pd nanostructures are grown directly on fuel cell gas diffusion layers following the established method [17] and then evaluated for ORR in acidic and alkaline electrolytes.

2. Experimental

2.1. Materials and reagents

The chemicals used in the preparation were Pd solution (1 mM $PdCl_2$ pH = 1, SA Precious Metals), copper sulphate solution (1 mM $CuSO_4.5H_2O$ pH = 1, Merck) were prepared in perchloric acid (0.1 M $HClO_4$, Merck). The chemicals were used as received without any further purification. All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ cm. The substrates used were carbon paper TGPH090 (PEMEAs) and Ni foam (Celmet, Japan: thickness = 1.6 mm, surface area = 7500 m^2/m^3, cell size = 0.5 mm, 48–52 cells per inch). Ni foam was cleaned in acetone, HCl and isopropanol followed by distilled water. Compressed air was used to dry the substrate.

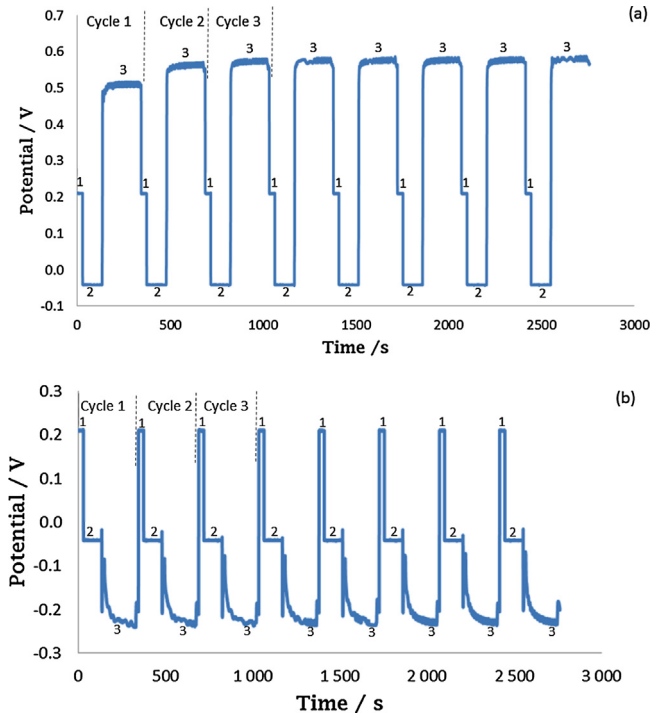

Fig. 2. Time-potential curves recorded during sequential layer-by-layer electrodeposition of Pd on (a) Carbon paper and (b) Ni foam.