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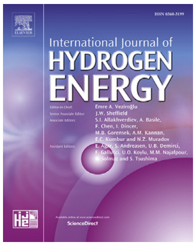

Pd_xNb_y electrocatalysts for DEFC in alkaline medium: Stability, selectivity and mechanism for EOR

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ABSTRACT

Pd_xNb_y/C binary electrocatalysts supported on Vulcan carbon XC72 were prepared by the sol-gel method. The materials are characterized by transmission electron microscopy, X-ray diffraction analysis, inductively coupled plasma–mass spectrometry and contact angle measurements. The electrocatalytic activity for ethanol electrooxidation reaction was studied by cyclic voltammetry, chronoamperometry, Tafel slope and accelerated durability testing. The direct ethanol performance and the products after the experiments were studied by Fourier transform infrared spectroscopy. Pd_1Nb_1/C (50:50 wt%) shows superior activity for ethanol oxidation compared to the other electrocatalysts prepared in this work. All electrocatalysts containing Nb show the highest current exchange density. The Tafel slope results suggest that the Nb modified the Pd-electrocatalyst to obtain a reaction path with high selectivity with only a single determining step with low production of the intermediates for the ethanol oxidation reaction. The best performance is obtained using Pd_1Nb_1/C 18.11 mW cm^{-2}. The Pd_1Nb_1/C electrocatalyst displays the highest production of CO_2 and the lowest production of acetaldehyde. Pd_1Nb_1/C shows the highest peak current density during 1000 cycles of the experiment and the lowest mass loss of Pd after the cycling test. We find that the Nb modifies the Pd electrocatalysts from the bifunctional mechanism and reduces the loss of Pd during the accelerated durability test.

Introduction

Research has been conducted all over the world to provide technologies for the conversion of chemical energy into electric energy with reduced heat losses. Different types of fuel cells have been developed and investigated as promising technologies for such energy conversion. A direct liquid fuel cell (DLFC) has great potential because it does not require fuel

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reforming or an ultrapure gas tank. In addition, it is compact and suitable for mobile applications.

DLFCs are divided into specific fuel cell (FC) subgroups, for example, direct ethanol fuel cells (DEFCs), which use ethanol as fuel at the anode and the existing oxygen from the atmospheric air at the cathode. These devices are ideal for portable applications such as electronic device chargers because they operate at room temperature and are easy to manipulate [1].

Ethanol has numerous advantages compared to other alcohols such methanol, which is more toxic and volatile [2,3]. Ethanol exhibits easy handling compared to glycerol and ethylene glycol [4]. In addition, ethanol can be produced from a renewable source (biomass) such as maize or sugarcane crops [5–7].

Furthermore, the ethanol oxidation reaction (EOR) that provides $12e^-$ per molecule in the complete reaction is a goal that still remains to be achieved. This difficulty is due the cleavage of the C–C bonds for the oxidation of ethanol to CO_2, which requires selective anode catalysts [5–7]. Therefore, the main intermediates of this reaction are acetaldehyde and acetate in the alkaline medium [8,9].

Palladium (Pd) has been shown to be the best catalytic metal for ethanol oxidation reaction (EOR) in alkaline medium for fuel cells. This metal shows a high power density per mg of catalytic metal [10]. However, the cost of Pd is too high to be commercially employed in these devices [10]. In addition, intermediate products formed from the EOR, for example, CO, poisoning the Pd surface and hindering the ethanol molecules from approaching the active sites to undergo oxidation. This limitation is a major challenge today for Pd and platinum (Pt)-based electrocatalysts [10]. The stability and durability of these Pd-based electrocatalysts is another unsolved problem. For these reasons, the search for non-noble metals as co-catalysts has become the focus of several researchers.

These auxiliary metals would act by the bifunctional mechanism or electronic effect with the purpose of oxidizing the adsorbed intermediates in the surface of the catalytic metals and release the active site for the oxidation of a new molecule of the fuel [10–12]. Some binary electrocatalysts such as PdRu/C, PdIr/C, PdAu/C, PdSn/C and others have been proposed to improve the electrocatalytic activity, tolerance to impurities in the ethanol (and intermediate products from EOR), stability and durability of the materials [13–17]. Alvarenga and collaborators [12] showed that the EOR activity of Pd nanoparticles is strongly correlated with electronic properties and managed to use a lower onset potential in the EOR. Chen et al. [18] reported the use of PdRu/C for the oxidation reaction of bioethanol and evaluated the impurities' tolerance.

The most important properties for the catalyst are nanoparticle stability, durability and capability for the oxidation of CO to CO_2 [19]. Therefore, in order to proceed with the use of bioethanol as a fuel in FCs, we need to improve the tolerance of Pd to impurities/poisoning with the aid of an auxiliary metal. It has been shown that there is no low-cost auxiliary metal that exhibits all the desired effects (such as high stability and CO-tolerance). Nevertheless, there have been reports of auxiliary metals that obtain some desired effects, for example, Ru enhanced the surface area [20]; Sn improved the CO-tolerance by an electronic effect [21]; and other noble metals, e.g., Ag, Au, and Rh, or non-noble metals such as Fe, Co, Ni, Cu and Mn have also been shown to improve the catalytic activity [22–31].

In this work, we present the synthesis of Pd and Nb electrocatalysts supported on carbon Vulcan XC72 by a simple and fast sol-gel method. We characterized the fabricated electrocatalysts by SEM/EDX, ICP-MS, TEM, XRD, and contact angle measurement techniques. The electrochemical activity, stability and mechanism were evaluated, and finally, the electrocatalysts were applied in the DEFC experiments.

Materials and methods

Preparation of the electrocatalysts

The electrocatalysts were prepared by a modified sol-gel method [32]. First, 57.8 mg (125 μmol) of Pd-acetylacetonate (99% Sigma-Aldrich®, product by USA) and 58.7 (215 μmol) mg of $NbCl_5$ (99% Sigma Aldrich® product by Germany) were mixed with 6 mL of isopropyl alcohol (Synth®) and 2 mL of acetic acid (Synth®). Then, 160 mg of Vulcan XC72 carbon was added. The sol-gel solution was homogenized by magnetic stirring and heated for 60 min to dryness. The samples were submitted to heat treatment in the muffle under N_2 atmosphere. The samples were heated at the rate of 5 °C min^{-1} in three steps: for the Pd_1Nb_1/C sample, at 110 °C for 15 min, at 400 °C for 60 min and then cooled at the rate of 10 °C min^{-1} until the sample reached room temperature. For other electrocatalysts, the same procedure was followed but with changes in the quantities of reagents, which were 115.6, 28.9 and 86.7 mg for Pd-acetylacetonate and 0, 88.1 and 29.3 mg for Niobium(V) chloride for these electrocatalysts Pd/C, Pd_1Nb_3/C and Pd_3Nb_1/C, respectively.

Electrochemical measurements

Electrochemical cell

The materials were electrochemically characterized, and their catalytic activity was evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) using an Autolab 302N potentiostat. The electrolyte was KOH (1.0 mol L^{-1}) with or without ethanol (1.0 mol L^{-1}). A conventional electrochemical cell with a three-electrode configuration was used and included a 1.0 cm^2 platinum electrode as the counter electrode, Hg/Hg_2Cl_2 (SCE) as the reference electrode and the investigated electrocatalyst supported on a glassy carbon electrode as the working electrode.

The three electrodes were arranged in a 40 mL cell that contained the N_2-degassed (to reduce the O_2 intervention) electrolyte solution. For the analysis in the presence of ethanol, 2.34 mL of ethanol (99.5% Dinâmica®, Brazil) was added into the working solution to obtain a concentration of 1.0 mol L^{-1} for both the CV and CA tests. All experiments were carried out at room temperature.

Preparation of the working electrode

For the preparation of the electrocatalyst, we used approximately 8 mg of the metal/carbon mixture. Next, we added 1 mL of high purity deionized water (resistivity 18.2 MΩ cm, Millipore water purification system, Millipore, Bedford, MA,

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