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Pd–Ni–Cu–P metallic glass nanowires for methanol and ethanol oxidation in alkaline media

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ABSTRACT

We demonstrate that $Pd_{43}Ni_{10}Cu_{27}P_{20}$ bulk metallic glass (BMG) nanowires, prepared by a facile, scalable top-down nanomolding approach, can be used as high surface area electrocatalysts for alkaline alcohol fuel cell applications. These nanowires exhibit higher activity for methanol and ethanol oxidation in alkaline media compared to pure Pd, quantified by cyclic voltammetry. Furthermore, the Pd-BMG nanowire electrocatalyst has a 300 mV lower onset potential for CO oxidation suggesting improved poisoning resistance beyond pure Pd. The Pd-BMG electrocatalyst activation energies for methanol and ethanol oxidation of 22 and 17 kJ mol^{-1} are lower than the pure Pd values of 38 and 30 kJ mol^{-1}, respectively. Unique properties of BMGs (homogeneity, viscosity, surface tension) facilitate the formability into high surface area electrocatalysts at low processing temperatures. The high electrical conductivity and chemical/physical stability suggest that these materials are ideal candidates for widespread commercial use including energy conversion/storage, hydrogen production, and sensors.

1. Introduction

With the recent advancements in anion exchange membranes, that can serve as an analog to Nafion® and prevent the use of corrosive KOH liquid electrolyte [1–5,56], alkaline fuel cells have reemerged as a promising power source technology for portable electronic devices and electric vehicles. One advantage of alkaline fuel cells over proton exchange membrane fuel cells

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is that non-noble metals (i.e. Ni, Cu, Co, Fe) can be used with or without noble metal electrocatalysts (i.e. Pt, Ag, Pd). Non-noble metals can be used because they are chemically more stable in alkaline media [6]. Often, liquid fuels such as alcohols are considered over hydrogen for fuel cell applications due to the preexisting liquid infrastructure and higher volumetric energy densities [7,8]. However, alcohol oxidation over conventional electrocatalysts still presents significant challenges, such as CO poisoning and alcohol crossover, which considerably limits the performance of direct alcohol fuel cells [6,8–10].

Previous studies have shown that Pt and Pd-based alloys are good electrocatalysts for alcohol oxidation in alkaline media [11–15]. Alloying these noble metals with more oxophilic elements can lower the electrocatalysts electronic binding energy by facilitating the adsorption of OH− at lower potentials and promoting the oxidation of the organic species [8,9]. The improved performance of binary and ternary electrocatalysts including Pt–Ru [16,17], Pt–Sn [17,18], PtSnRu [17], PtSnNi [18], PtRuNi [19], PtRuMo [20], PtCuCo [21], PtPd [22], PdNi [6,23], PdCo [6], PdAu [24], PdAg [25], and PdCu [25] have been extensively studied in both acidic and alkaline media. In addition, a majority of these electrocatalysts are supported on carbon to provide a high surface area, yet the carbon tends to corrode over time under fuel cell operating conditions [26].

Recently, we demonstrated a facile and scalable top down approach, to prepare nanowire structures using bulk metallic glasses (BMGs) [27,28]. Bulk metallic glasses exist in a wide range of compositions [29] and we have shown that these materials can be thermoplastically formed into complex geometries over a length scale ranging from ~10 nm to a few centimeters [30–32]. We note that these length scales are comparable to supported electrocatalysts that we have previously developed [33,34]. The absence of grain boundaries and dislocations in the BMG amorphous structure results in a homogeneous and isotropic material down to the atomic scale, which displays very high strength and elasticity combined with good corrosion resistance [29]. Previously, we have shown that platinum based BMGs have excellent durability and high alcohol oxidation activities, but Pt-BMG nanowires are not optimal for alkaline fuel cells due to the Pt content [27].

Here we report the fabrication of platinum-free ordered $Pd_{43}Ni_{10}Cu_{27}P_{20}$ BMG nanowires, where the composition of the Pd-BMG is dictated by the glass forming ability (or the ability to be molded into nanowires) of the material [35]. We show that this material is active for CO, methanol, and ethanol oxidation in alkaline media, demonstrating the potential of applying these nanowires as effective electrocatalysts for alkaline fuel cells.

2. Experimental

2.1. Bulk metallic glass synthesis

The synthesis of $Pd_{43}Ni_{10}Cu_{27}P_{20}$ bulk metallic glass used here is similar to our previous work with BMG alloys [27,31]. Briefly, alloying of the high-purity constituents was carried out in a vacuum sealed quartz tube using induction melting. Subsequently, the alloys were fluxed with B_2O_3 and vitrified by water quenching from a temperature of 1000 °C, which is 250 °C above the thermodynamic liquids temperature. The parameters for thermoplastic forming experiments were selected on the basis of the crystallization and viscosity data of the metallic glasses. Commercially available nano-porous anodized aluminum oxide (AAO) molds were used as a template for nanomolding in this work. For the molding of very high aspect ratio nanostructures, the metallic glass was thermoplastically formed from T_g (where T_g is the glass transition temperature) to T_x (where T_x is the onset of crystallization) under a constant load of 50 kN. The metallic glass nanowires were released from the AAO template by etching with 1 mol L^{-1} KOH solution for 30 min.

2.2. Physical characterization

Transmission electron microscopy (TEM) was carried out on a JEOL 3010 HREM instrument operating at 300 kV. Scanning electron microscopy (SEM) was conducted on a Hitachi SU-70 instrument at 10 kV.

2.3. Electrochemical characterization

The electrochemical measurements were conducted in an electrochemical cell from PINE Instruments using a custom rotating disk electrode setup with a multichannel potentiostat (Bio-Logic Instruments) and rotation control (AFR – Pine Instruments). Potentials were determined using a mercury–mercury oxide (MMO) reference electrode and a Pt-mesh counter electrode. The cyclic voltammetry (CV) tests were performed on the working electrode by cycling the voltage between −0.9 V and 0.3 V vs. MMO in nitrogen purged 1 mol L^{-1} aqueous KOH solution at room temperature (~25 °C). The CO oxidation experiments were conducted by purging the solution with CO for 30 min with the potential held at −0.95 V and then purging the electrolyte with nitrogen for 60 min to form a monolayer of CO on the surface of the electrode. The scan rate for all tests was 20 mV s^{-1} and current density was normalized to the working electrode's geometric surface area (0.196 cm^2).

3. Results & discussion

3.1. Physical characterization of the bulk metallic glass

The $Pd_{43}Ni_{10}Cu_{27}P_{20}$ BMG (Pd-BMG) nanowires are fabricated in a highly reproducible process following a previously described CMOS (complementary metal–oxide–semiconductor) compatible method [30,31,35,36]. Briefly, the Pd-BMG is placed on an anodized aluminum oxide (AAO) template (Fig. 1a) and heated into its supercooled liquid region and a pressure (150 MPa) is applied. The Pd-BMG fills the nanopores of the AAO template (Fig. 1b), which is subsequently dissolved in KOH solution (Fig. 1c) to expose the Pd-BMG nanowires (Fig. 1d). The SEM images in Fig. 2a–c demonstrate the Pd-BMG nanowires as well-isolated and ordered in a narrow distribution of length and diameter. Fig. 2c-insert confirms the amorphous state of the Pd-BMG with the electron diffraction pattern (inset) showing a diffused halo. The nanowires used in this study had an average length and diameter of approximately 2 μm and 20 nm,