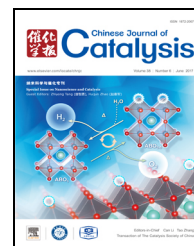


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Fabrication, characterization and electrochemical properties of porous palladium bulk samples with high porosity and hierarchical pore structure

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ABSTRACT

In the present study, porous bulk palladium samples were prepared by sodium chloride salt powder spacer incorporation and removal combined with dealloying. The obtained porous Pd bulks were characterized by X-ray diffraction, field-emission scanning electron microscopy and N₂ adsorption isotherm measurements. The prepared porous Pd bulk samples showed a hierarchical pore structure, a high porosity of ~88%, a high surface area of ~54 m²/g, and a compression strength of ~0.5 MPa. Electrochemical measurements were performed to evaluate the electrocatalytic properties of the porous Pd bulk samples, revealing their effectiveness for ethanol oxidation.

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1. Introduction

Palladium materials are widely used in hydrogen storage and separation applications [1,2], catalysts [3–6], and sensors [7–9]. In particular, supported Pd shows excellent performance in the electrochemical oxidation of ethanol and methanol and combustion of methane [3,6,10]. Metal nanoparticles of conventional Pd-supported catalysts are often unstable in many applications and aggregate, resulting in degradation of the catalysis properties [11]. Compared with typical Pd foil, conventional supported Pd and powder samples [12–14], porous Pd materials have many advantages such as a high surface area, a connected pore channel network, and a structure which is sta-

ble to the aggregation effects that occur in powders [1,15]. In addition, bulk porous Pd has applications in a broad range of fields, and is considered a promising candidate material for functional devices.

Recently, considerable research efforts have focused on fabricating porous Pd materials with high porosity, hierarchical pore structures and large surface areas. Hierarchical porous structures have been shown to have more effective electrocatalytic properties toward the oxygen reduction reaction compared with monolithic nanoporous structures [16–18]. Powder sintering routes using spacer materials such as sodium chloride have been reported by Li et al. [19]. The porosity of the prepared porous materials can be easily adjusted by changing the

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amount of spacer material added. However, the surface area of the resultant porous Pd is relatively low.

Dealloying methods have also been used as a simple way to form nanoporous metals [20,21]. Nanoporous Pd with connected pore/ligaments and a large surface area has been successfully fabricated by dealloying techniques [22,23]. However, it is difficult to fulfill key requirements for high performance porous Pd materials, such as a bulk (millimeter-sized) self-supporting hierarchical pore structure, with the use of this method [16,17]. Spark plasma sintering (SPS) has been used extensively and shows clear benefits over conventional methods [24,25]. In previous studies, mechanical alloying and SPS methods have been used to fabricate CuAl and PdAl alloys [26,27]. Bulk nanoporous metallic materials have been successfully prepared from the resultant SPS sintering alloy precursors by dealloying. Thus, we expect that, the use of soluble salts, such as NaCl, as spacer materials in the SPS sintering process combined with chemical dealloying, may allow for bulk hierarchical porous metallic materials to be obtained.

Here, we present a novel processing technique that allows for fabrication of porous Pd bulk samples with a hierarchical self-supported porous structure (millimeter- and nano-sized), which has high porosity. Moreover, the electrochemical properties of the prepared porous Pd bulk samples were also studied.

2. Experimental

PdAl mechanical alloying (MA) powder was obtained by ball milling of Al (>99.9%, ~2 μm , ST NANO, China) and Pd (>99.95%, Northwest Institute for Non-ferrous Metal Research, China) with a composition of Al-20 atom% Pd under vacuum. The PdAl alloy composites were prepared by spark plasma sintering (SPS) of the PdAl MA powder with various amounts of NaCl powder added (~50 μm , 10 vol.%, 20 vol.%, 30 vol.%, denoted as PA1, PA2, PA3, respectively). The power/salt mixtures were subjected to SPS sintering in a Dr SPS-1050 apparatus in a tungsten carbide mold. A sintering temperature of 600 $^{\circ}\text{C}$ and a pressure of 30 MPa and a holding time of 30 min were chosen. The resultant PdAl alloy composites were wire cut and ground with SiC paper. The PdAl alloy composites were immersed in deionized water to extract the NaCl particles, and chemically etched in 0.5 mol/L HCl solutions at room temperature. The dealloyed samples were rinsed with ethanol and deionized water.

The samples were characterized with a field-emission scanning electron microscope (FE-SEM, Hitachi S4800) equipped with an X-ray energy spectrometer (EDS). X-ray diffraction (XRD) patterns were recorded by an X-ray diffractometer (DX-2000) with $\text{Cu } K_{\alpha}$ radiation. The compressive strength tests were performed on an Instron mechanical testing machine (Instron 4302) with a crosshead speed of 0.5 mm/min. All specimens used in the compressive tests were cut to a size of 5 mm \times 5 mm \times 10 mm. At least three specimens were tested for each sample. The specific surface areas of Pd samples were measured with an N_2 adsorption apparatus. Electrochemical measurements were performed in a standard three-electrode

cell (500 mL) using an electrochemical workstation (CHI660E) with a Pt plate electrode as a counter electrode and a saturated calomel electrode (SCE) or a Hg/HgO reference electrode. The porous Pd bulk samples were used as the working electrode. Cyclic voltammetry was measured in 1 mol/L H_2SO_4 solution. The ethanol electro-oxidation performance was characterized in a mixture of 1.0 mol/L KOH with different concentrations of ethanol. The electrolytes were de-aerated by N_2 . Electrochemical experiments were performed at ambient temperature. The current density was calculated by reference to the geometric area of the work electrode

3. Results and discussion

3.1. Characterization of the Pd alloy composite

Fig. 1 shows the density of the Pd alloy composites. As the amount of added NaCl was increased from 10 vol.% to 30 vol.%, the density of the prepared PdAl composites decreased. The addition of more spacer may be beneficial for decreasing the density of the bulk; however, too much spacer may lead to formation of defects and even collapse of the structure. To obtain robust PdAl alloy composites, the amount of NaCl added should be maintained below 30 vol.%. An XRD pattern of PA2 is shown in Fig. 2. The diffraction peaks could be assigned to PdAl₃, Al, and NaCl, indicating that a PdAl alloy composite was successfully prepared. Notably the presence of the NaCl particles does not disrupt the formation of PdAl alloy. The mechanism of SPS remains unclear, despite several decades of study and development [25]. The presence of plasma during the SPS process has been realized as an important hypothesis [28,29]. However, experiments performed by Mukherjee et al. indicated that there is no plasma, sparking or arcing present during the SPS process. Joule heating effects and electromigration of point defects or other current effects are now considered to be the primary reason for enhanced sintering in conducting powders and thermal exchange in non-conductive powder [25,30,31]. Thus, only thermal exchange can take place between the PdAl mechanical alloying powders and NaCl particles, ensuring that

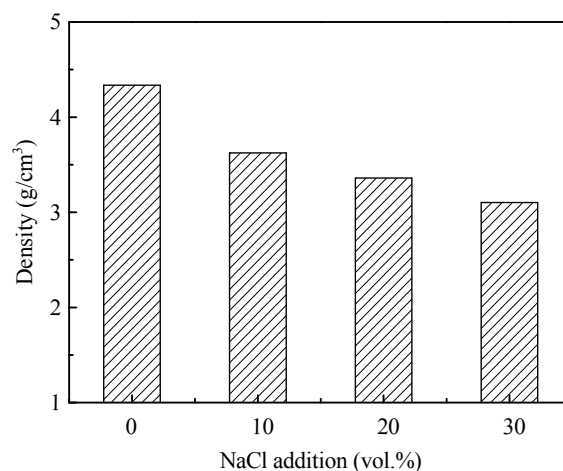


Fig. 1. Density of PdAl alloy composites as a function of the amount of added NaCl.

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