Mesoporous PdBi film as efficient electrocatalyst for ethanol oxidation reaction

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Abstract

Developing electrocatalysts that can completely oxidize ethanol oxidation is critical for commercializing direct ethanol fuel cells. Here, we tailored synthesis of mesoporous PdBi films by employing an electrochemical-assisted micelle assembly approach. The as-prepared film exhibited superior electrocatalytic activity and stability toward ethanol oxidation reaction, which is promising for practical applications.

Direct ethanol fuel cells (DEFCs), that can convert the chemical energy stored in liquid ethanol into electricity, are the most promising way to relieve or even resolve the energy and environmental crisis caused by the excessive consumption of fossil fuels. This is because ethanol is environmental-friendly, naturally available from biomass, as well as being easy to store and transportation [1–5]. The energy density of DEFC directly depends on the oxidation state of ethanol. A complete oxidation of ethanol to CO$_2$ and H$_2$O with 12e exchange in the desired electrocatalytic process greatly favors a high energy density of DEFC, but it is difficult to accomplish [6–10]. Therefore, great efforts have been made to establish good electrocatalysts that can electrocatalyze ethanol oxidation efficiently. Palladium (Pd) was proved to be a superior component for ethanol oxidation reaction (EOR) in alkaline electrolyte [11–18]. Intense studies have elucidated that the combination of Pd with other metals (like Au, Co, Ni, Bi, and so on) endows Pd electrocatalyst with higher utilization efficiency, better stability, and better anti-poisoning ability [19–22]. Alloying Pd with Bi has shown promoting effects toward EOR due to the synergistic effect between Pd and Bi [21].

The structure of electrocatalysts is another important factor that influences the electrocatalytic performance of Pd-based materials [23–25]. Among all the nanostructures, mesoporous constructions have attracted great attention due to the relatively high surface area, favorable mass transportation, and large amount of accessible active sites [11, 12, 26–28]. Yamauchi et al established a facile micelle assembly approach for tailored synthesis of various mesoporous Pd-based nanostructures with different porous constructions, including films and nanoparticles [27–31]. Replicating the micelle structure is capable for creating various porous constructions by tailoring the micelle constructions, which provides the basis and versatility for the synthesis of mesoporous materials with different compositions. Therefore, we aimed to fabricate mesoporous PdBi film by using the electrochemical-assisted micelle assembly approach in order to optimize the electrocatalytic performance of Pd toward EOR.

In the present work, the mesoporous PdBi films were electrochemically deposited on an Au-coated Si (Au–Si) substrate by applying a constant external potential of $-0.2$ V for 600 s. The aqueous electrolyte solution contains pore-directing agent Pluronic P123 (2.5 wt% P123) and metal precursors (10 mM of PdCl$_2$ and 2 mM of BiCl$_3$). It is important to keep the electrolyte acidic by utilizing HCl to avoid the serious hydrolysis of BiCl$_3$ [29, 32]. A study on the pH effect to the BiCl$_3$ hydrolysis shows that 600 mM of HCl is helpful to get clear and homogeneous electrolyte without any hydrolysis (figure S1 (available online at stacks.iop.org/JPMATER/4/034001/mmedia)). Therefore, the concentration of HCl in the electrolyte was kept at 600 mM in the present work in order to obtain uniform mesoporous PdBi films.
Figure 1. (a), (b) Top-view SEM images, (c) TEM image and (d) HRTEM images of the obtained film. (e) HADDF-STEM image and (f), (g) elemental mapping images of the obtained film.

The nano-structures of the as-prepared films were firstly studied by scanning electron microscope (SEM) and transition electron microscope (TEM). The top-surface SEM results show that the film possesses bumpy surface with plenty of nanobulges (figure 1(a)). A higher magnification of the surface clears shows that mesopores with a pore size of 10 nm and pore wall thickness of 6.6 nm well distribute all over the film (figure 1(b)). In the present work, triblock copolymer Pluronic P123 takes a vital effect in creating porous structures in the film. Proper interaction force between the micelles and the metal ions and the stableness of the micelles is of great importance because it strongly influences the metal growth manner and determines the final structures [11, 33–36]. In the case of P123 triblock copolymer, the hydrophilic poly(ethylene oxide) block can interact with the metal-aqua complexes with hydrogen bonding and the micelle is stable enough to guide the growth manner of PdBi metals into porous constructions [29]. The film scratched from the Au–Si surface was casted on the copper grid for further TEM characterization. The TEM images observed at the edge of the film show the difference in the darkness, evidencing the porous constructions (figure 1(c)). Close observation by high-resolution TEM displays clear lattice fringes of highlycrystalline products, suggesting the formation of metallic walls (figure 1(d)). The porous structures could be further confirmed by the high-angle annular dark-field scanning TEM measurement (figure 1(e)). All the results consistently supported the claim that the present approach is efficient for obtaining porous films. To assess the composition of the film, the corresponding elemental mapping was carried out, and both Pd and Bi elements are found to be uniformly distributed in the film (figures 1(f) and (g)), indicating the formation of the PdBi alloy. The atomic ratio of Pd to Bi in the mesoporous film is determined to be 83.5:16.5 by energy-dispersive x-ray spectroscopy.

Wide angle x-ray diffraction (XRD) is further employed to study the crystal structure of the as-prepared mesoporous film. To get better XRD profiles, a square carbon paper with side length of 2.0 cm was employed as the substrate for electrodeposition. Except the electrolyte containing both Pd and Bi precursors, an electrolyte without Bi precursors was also used for the electrodeposition. The film obtained by using Pd precursor only is found to be porous film without any cracks and bumps. A statistically analysis of the pores reveals that the pores are uniform in pore size (12.6 nm) and pore wall thickness (7.3 nm) (figure S2). The XRD patterns for both samples are displayed in figure 2. The peak centered at 54.5° is ascribed to the (004) plane of carbon paper substrate. The diffraction peaks centered at 40.2°, 46.7°, 68.2°, 82.1° and 86.7° can be well assigned to the diffraction peaks of (111), (200), (311) and (222) facets of face-centered-cubic (fcc) Pd crystals, confirming the formation of mesoporous Pd film. In comparison to the mesoporous Pd
film, the XRD peaks show obvious left-shift for the mesoporous PdBi film, evidencing the formation of PdBi alloy by incorporating Bi atoms with larger atom size to the Pd crystal lattice. A crystalline grain size was calculated to be 6.9 nm by Scherrer equation based on the most intense (111) peak centered at 38.5°, which is consistent with the average grain size (7.0 nm) statistically by TEM images (figure S3).

As a proof-of-concept application, the obtained mesoporous PdBi film is directly used as the electrode for EOR. The obtained mesoporous Pd film and commercial Pd black (PdB) are used as benchmark to investigate the electrocatalytic performance toward EOR. The electrochemical surface area (ECSA) of all the samples was firstly measured by cyclic voltammetry in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹ in potentials ranging from −0.2 to −1.2 V (vs. Ag/AgCl) (figure S4). The ECSA values are calculated by using the oxide reduction charge assuming that the conversion factor for an oxide monolayer reduction is 420 µC cm⁻² on smooth surface [29]. The ECSA values for mesoporous PdBi film and mesoporous Pd film with deposition time of 600 s are estimated to be 30.24 cm² and 21.58 cm², respectively. The typical cyclic voltammetric curves for EOR catalyzed by both electrocatalysts are shown in figure 3(a). To better comparison, all the current was normalized by the ECSA of the samples. The peak current density of mesoporous PdBi film and mesoporous Pd film toward EOR is 9.7 mA cm⁻² and 8.4 mA cm⁻², greatly exceeding that of PdB (2.6 mA cm⁻²). It indicates that the mesoporous structures largely increase the intrinsic activity of Pd catalyst. The better electrocatalytic performance of mesoporous PdBi film relative to mesoporous Pd film can be ascribed to the incorporating of Bi atoms tune the electronic structure of the Pd, which is very important for enhance the activity and durability of the Pd-based electrocatalyst [8, 37]. More importantly, the anodic current of the mesoporous PdBi film rapidly increased under the positive scan relative to the mesoporous Pd film (figure S5). Further experiments were carried out to check the stability of the films during electrocatalyzing EOR. By keeping a constant potential of 0.1 V, the current responses were recorded for both samples. The oxidation current density of mesoporous PdBi film kept exceeding that of mesoporous Pd film for the whole timescale (figure 3(b)), suggesting that the incorporating Bi to Pd impedes better stability. To confirm the structure stability, the top-surface structures of both films after long-term stability tests were checked by SEM. No aggregation or collapse was observed for both samples (figures 3(c)–(f)). All the results clearly demonstrate that the mesoporous PdBi film is a superior electrocatalyst for EOR both in activity and stability.

In summary, we have successfully developed an electrochemical-assisted micelle assembly approach for the fabrication of mesoporous PdBi films. The as-prepared film shows evenly distributed mesopores all over the film. Benefiting from the porous structures and the incorporating of Bi, the mesoporous PdBi film exhibited superior electrocatalytic performance toward ethanol oxidation. The synergistic effect of porous structure and alloying is promising to establish good electrocatalysts toward the DEFC applications.

1. Experimental section

1.1. Preparation of meso-PdBi film

The electrochemical fabrication of mesoporous PdBi films was performed by using a CHI 760E electrochemical analyzer with a standard three-electrode cell system, including an Ag/AgCl (saturated KCl) electrode as the reference electrode, a platinum wire as the counter electrode, and gold-coated silicon (Au–Si)
substrate as the working electrode. The electrolyte used for electrochemical deposition was prepared by mixing 2 ml of 5 wt% Pluronic P123 with 0.5 ml of 80 mM PdCl$_2$, 0.1 ml of 80 mM BiCl$_3$ and 0.4 ml of 6 M HCl aqueous solution. A constant potential of $-0.2$ V vs. Ag/AgCl was then used for electrodepositing the mesoporous PdBi films. The obtained films were then soaked in ethanol for 24 h to thoroughly remove the surfactants, and then dried with nitrogen gas for further characterizations.

1.2. Preparation of meso-Pd film
The electrodeposition of mesoporous Pd film is same to the above-mentioned method for mesoporous PdBi film deposition, except changing the electrolyte to 2 ml solution containing 2.5 wt% Pluronic P123 and 40 mM PdCl$_2$

1.3. Electrochemical measurement
Electrochemical measurements were performed using a CHI 760E electrochemical analyzer. The three-electrode cell consisted of a reference electrode (Hg/HgO electrode), a counter electrode (Pt wire) and the mesoporous PdBi film (or mesoporous Pd film) as a working electrode. Before electrocatalytic study, the film electrode was activated by cyclic voltammetric measurements between $-1$ V and 0.6 V at a scan rate of 50 mV s$^{-1}$ for ten segments. EOR was carried out in 1.0 M KOH solution containing 1.0 M ethanol.
Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author upon reasonable request.

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