INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–10

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Rapid fabrication of Cu/Pd nano/micro-particles porous-structured catalyst using hydrogen bubbles dynamic template and their enhanced catalytic performance for formic acid electrooxidation

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ARTICLE INFO

Article history:
Received 21 December 2013
Received in revised form
5 March 2014
Accepted 14 March 2014
Available online xxx

Keywords:
Cu/Pd porous structures
Hydrogen bubbles template
Galvanic replacement
Electro-oxidation
Formic acid

ABSTRACT

In this work, a self-supporting Pd–Cu bimetallic film with 3D porous structure was electrodeposited at the surface of glassy carbon electrode (GCE) using a facile double-template fabrication process, including hydrogen bubble templating method and galvanic replacement reaction, and its performance investigated as a catalyst for formic acid oxidation (FAO). The structure of the Cu/Pd porous film was characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The electrocatalytic activity of the as-prepared catalysts with high surface areas were evaluated in sulfuric acid solution containing 1 M formic acid using cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The Cu/Pd porous structure exhibited significantly high current densities of formic acid oxidation compared to the Cu/Pd particles film catalyst. The effects of galvanic replacement time and concentration of formic acid on the catalytic activity of as-prepared electrode for FAO were comparatively investigated.

Introduction

Energy storage devices including fuel cell, Li-batteries etc. have been developing especially today [1,2]. Among them, direct formic acid fuel cells (DFAFCs) has been receiving much attention as one of the most attractive energy sources [3]. Pd-based electrocatalysts have recently attracted great attention as promising anode catalyst for DFAFCs [4–9]. In contrast to the commonly used Pt catalysts, Pd catalysts can catalyze FAO via a more direct pathway, bypassing the strongly bound CO intermediate [5,6]. Therefore, considerable efforts have currently been directed to developing novel Pd catalysts.

Recent studies in the field of FAO have been focused on increasing catalyst activity and durability through various approaches. It has been demonstrated that formic acid oxidation was more facile on Pd alloyed with a less expensive metal M (M = Fe, Co, Ni, and Cu etc.) [10–13] than on pure Pd and the catalyst deactivation was much slower. For example; Xu et al. [11,14] fabricated the Pd–Cu alloy particles with

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http://dx.doi.org/10.1016/j.ijhydene.2014.03.081

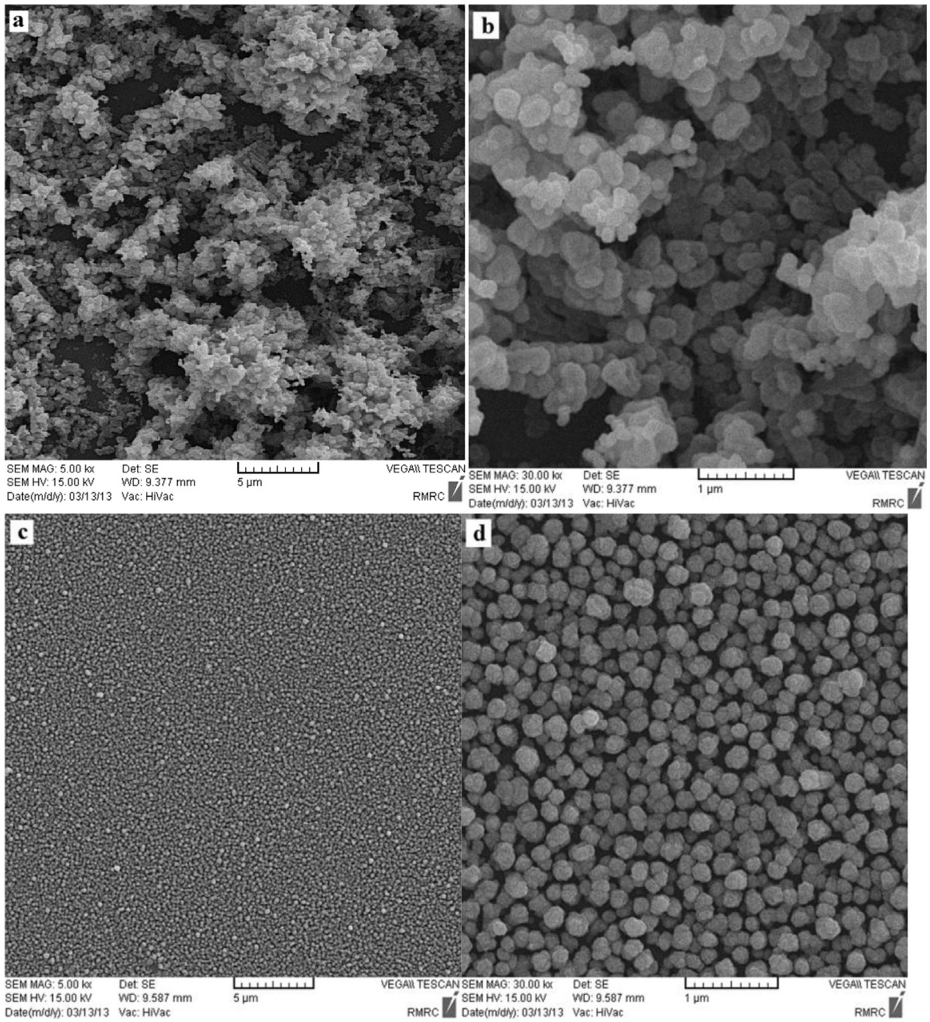

Fig. 1 – Low (a, c) and high (b, d) magnification SEM images of Cu/Pd porous structure (a, b), Cu/Pd particles film (c, d).

superior electrocatalytic activity and stability for formic acid oxidation. Han et al. [15] presented a facile one-pot synthesis of highly monodisperse Pd–Cu bimetallic alloy nanoparticles through the co-reduction of Pd and Cu precursors in non-hydrolytic solutions by using tri-octylamine and oleic acid. The alloying effect can be largely understood in the frame work of the d-band theory [16]. The addition of the second metal changes the electronic structure of Pd, decreases the Pd d-band center and therefore weakens the adsorption of inhibiting reaction intermediates. Another approach to enhance ability of Pd catalysts involves the design of novel Pd nano and microstructures with higher activity for formic acid oxidation such as 3D porous materials [7,17].

In recent years, numerous efforts have been performed for the preparation of porous materials due to their large surface area and, as a result, higher catalytic activity. Because of their large surface area, 3D porous materials have attracted increasing interests in the fields of catalysis [18–20], fuel cell [21], battery [22], sensor [23–25] and adsorbent [26]. One of the most intensive topics concerning their synthesis is to tailor the properties of the porous materials, including their porosity, mechanical stability, and specific surface area. Nanoparticle-based, templating (substrate-based), dealloying [12,27,28] and decoration techniques have been applied to yield porous structure [29]. Among them, the most popular approach to prepare such materials with controlled characteristics is the template assisted method. Notably templating can pre-define size and shape of porous structure [30] and the H_2 bubble technique presents a green and attractive template for preparing 3D nano, micro-porous structure materials [31–33], attributed to its low cost, ease of operation and facile elimination of bubbles. In gas bubble dynamic template process, the hydrogen bubbles arising from the electrochemical reduction of H^+ in the deposition process functions as the dynamic template for metal electrodeposition. Metal is electrodeposited and grows within the interstitial spaces between the hydrogen bubbles to form a porous film of metal on the substrate. It overcomes troublesome procedures to remove the traditional template, e.g. the drawback of using hard templates lies in the requirement to apply strong chemical treatment.

Based on above considerations, in this work, we report the application of 3D porous Cu film with the flower-like structure as a support for loading of Pd by galvanic replacement method

Please cite this article in press as: Ojani R, et al., Rapid fabrication of Cu/Pd nano/micro-particles porous-structured catalyst using hydrogen bubbles dynamic template and their enhanced catalytic performance for formic acid electrooxidation, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.03.081