



Preparation and characterization of palladium-hydride-coated titanium as a reference electrode for the supercritical carbon dioxide emulsion electrochemical system



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ARTICLE INFO

Article history:

Received 27 September 2014

Received in revised form 21 December 2014

Accepted 23 December 2014

Available online 26 December 2014

Keywords:

reference electrode

hydrogen sorption/desorption

palladium hydride

rest potential

aqueous supercritical carbon dioxide

emulsion solution

ABSTRACT

This work develops a new reference electrode for the electrochemical system using an aqueous supercritical carbon dioxide (sc-CO₂) emulsion solutions. Here, the Watts nickel bath is employed to be the standard testing electrolyte. A porous Pd-coated Ti (denoted as Pd/Ti) electrode is prepared by electroplating, which is subjected to the hydrogen sorption (including adsorption and absorption) reaction in 0.5 M H₂SO₄ for forming a palladium hydride-coated titanium (denoted as PdH_x/Ti) electrode. The hydrogen sorption/desorption behavior on Pd/Ti is characterized by cyclic voltammetry and rest potential against time analyses. These results reveal that PdH_x/Ti is a reliable reference electrode with a reproducible and stable PdH_x potential (longer than 10 h) in normal aqueous electrolytes at room temperature. The equilibrium potential of this PdH_x/Ti electrode is about 65 ± 15 mV (vs. RHE) in the Watts Ni bath. Although the hydrogen desorption rate is enhanced by elevating the solution temperature, all of the results confirm that the *in-situ* formed PdH_x/Ti electrode can be practically utilized as a reference electrode in the Watts Ni bath containing the sc-CO₂ emulsion medium.

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1. Introduction

Recently, increased attention on the supercritical carbon dioxide (sc-CO₂) media has been paid for industries and academic researches because of several benefits such as low surface tension and adjustable transport properties through controlling the pressure and temperature [1]. Furthermore, much attention on sc-CO₂ has been paid on the extraction of caffeine and spice in the food industry [2] and medicine purification in pharmaceutical applications [3,4]. Because of the extremely low surface tension, sc-CO₂ makes it possible to dissolve organic substances and extract solvent out of pores within nanostructure without damaging the structure in the drying process [5,6]. In addition, CO₂ is nontoxic and inexpensive, which makes CO₂ a popular substance for the supercritical fluid applications.

Since 2000s, electroplating gradually becomes a key technology for fabricating electronic devices in integrated circuit industries and micro-components of micro- electromechanical systems [7,8]. However, quality of the electroplated deposits strongly depends on roughness of the substrates. Meanwhile, hydrogen evolution is an inevitable side reaction of electroplating in aqueous electrolytes [9], which easily causes the formation of defects within/on the deposit films owing to the adhesion of hydrogen bubbles. In order to resolve these problems, some researches tried to electroplate metals, alloys, or oxides from aqueous electrolytes containing sc-CO₂ and proposed a new technique, called electroplating using sc-CO₂ emulsion (EP-SCE) [10,11]. This new electroplating technique provides several attractive advantages, such as low surface tension, adjustable mass transport properties, and most importantly, high solubility of hydrogen in sc-CO₂, which promotes detachment of hydrogen bubbles from the cathode surface [1,12] and avoids the formation of deposit defects efficiently [10,11].

There are several articles published on electrodeposition involving sc-CO₂. For example, our previous study demonstrated the application of sc-CO₂ emulsion baths in fabrication of void-free micro-patterns of nickel with improved growth rate [13]. Shinoda et al. also reported that amount of the additive used in copper

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metallization of nano-scale holes could be reduced significantly by a sc-CO₂ suspension media [14]. In addition, several researches reported that lower surface roughness and smaller grain size of nickel [15] and copper [16] films can be obtained by means of the EP-SCE method in comparison with the case from normal aqueous solutions. Moreover, the pore size distribution of titanium dioxide was found to be more uniform through the electrodeposition with the sc-CO₂ emulsion method [17], and sc-CO₂ demonstrated the ability to control morphology and grain size of the TiO₂ films at the same time [18]. However, effects of the sc-CO₂ in the plating bath on electrochemical behavior of the electroplating system are still not fully clarified. The mechanism causing the effects of surface smoothing and grain refinement needs to be studied. These phenomena cannot be understood because of the lack of a reliable reference electrode for investigation of the electrochemical characteristics in the media containing sc-CO₂. Although Pt was often considered to be a dummy reference electrode for EP-SCE [16,19], Pt is still not a reliable reference electrode material to conduct electrochemical analysis. Therefore, developing a reliable reference to conduct electrochemical analysis in the aqueous sc-CO₂ emulsion media is very important.

Here, we propose a novel palladium hydride-coated titanium (PdH_x/Ti) electrode to be the reference electrode for the aqueous electrochemical systems containing sc-CO₂ emulsion solutions since hydrogen sorption into Pd can form palladium hydrides [20] with an equilibrium potential stable in the aqueous media [21,22]. In fact, due to the unique hydrogen sorption/desorption properties of Pd [20,23,24] and the stable/reliable potential of palladium hydride in aqueous electrolytes [25,26], palladium hydrides have been proposed to be a reference electrode in aqueous media for certain applications [25–27]. This work mainly focuses on the rest potential stability of the PdH_x/Ti electrode in both the Watts nickel bath under the ambient air pressure and the EP-SCE system. In addition, the PdH_x/Ti electrode has been demonstrated to be practically useful in the Watts nickel bath containing sc-CO₂ emulsion.

2. Experimental

Palladium was electroplated from a PdCl₂ solution onto titanium substrates (for the ambient condition: 10 × 10 mm² Ti plates and for the EP-SCE Watts nickel system: 4.0 cm long Ø0.5 mm wires). The titanium substrates were first degreased with soap and water, and etched in a 6 M HCl solution at 80 °C for 1 h. After the etching treatment, the Ti substrates were rinsed with deionized (DI) water, and vertically placed in a 100 mL jacket cell surrounded with a dimensionally stable anode (DSA, an (Ru–Ti)O₂-coated Ti electrode). All substrates were electroplated with Pd deposits with a constant current density (25 mA cm⁻²). The basic Pd electroplating bath, shown in Table 1, consists of 0.01 M palladium chloride (PdCl₂), 0.04 M sodium citrate, 0.3 g Lugalvan G35 (polyethyleneimine, PEI, Lugalvan G35, BASF), and 0.3 g Lugalvan P (poly-quaternary amine salt, Lugalvan P, BASF) [28]. pH of the plating bath was adjusted to be 10.5 with concentrated HNO₃

or NH₄OH. After the Pd deposition, these Pd-coated Ti (denoted as Pd/Ti) electrodes were repeatedly rinsed with DI water and finally dried in a vacuum oven at room temperature. The geometric exposure area of the Pd/Ti wire reference electrode in the EP-SCE Watts nickel bath is equal to ca. 0.3 cm² (i.e., exposed in the solution for 2 cm in length), which is enough for establishing the equilibrium potential of PdH_x/H⁺ in the medium studied. The other part of this Pd/Ti wire reference electrode was insulated with a PTFE film.

For the electrochemical characterization of PdH_x/Ti in ambient aqueous electrolytes, the electrochemical analyses were performed with an electrochemical analyzer system, CHI 724 d (CH Instruments, USA). All electrochemical analyses were carried out in a three-compartment cell. An Hg/Hg₂SO₄ electrode (saturated K₂SO₄, 0.64 V versus a standard hydrogen electrode (SHE) at 25 °C) was utilized as the reference electrode and a piece of platinum gauze with an exposed area equal to 4 cm² served as the counter electrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from surface of the substrates, was used to minimize errors due to *iR* drop in the electrolytes. For the purpose of convenient comparisons with the literature results, a calculated reversible hydrogen electrode (RHE) was employed as the reference electrode for the electrochemical behavior of oxide formation/reduction and hydrogen sorption/desorption on Pd/Ti. The calculated RHE was estimated from the pH value of electrolytes and confirmed from the onset potential of hydrogen evolution on a Pt wire electrode (4 cm²) since pH values measured by pH meters in concentrated acidic and basic solutions may significantly deviate from the true values. For testing the PdH_x/Ti reference electrode in the EP-SCE system, the electrochemical analyses were performed with an electrochemical analyzer system, Solartron SI1287. The chamber used here was a stainless steel 316 vessel (PEEK coating on the inner wall) with a total inner volume of 50 mL, kept in a temperature-controlled air bath. There were holes at the chamber cap for CO₂ flow and electric-wiring. Through the holes, plastic-coated platinum wires were used to position the substrates and connection with an electrochemical analyzer system. A magnetic agitator with a cross-shaped magnetic stirrer bar was placed within the reaction chamber.

There are two testing solutions in this work, shown in Table 2. One testing solution is an additive-free Watts nickel bath containing 1 M NiSO₄·6H₂O, 0.2 M NiCl₂·6H₂O, and 0.5 M H₃BO₃. Another solution is a simulated Watts nickel bath containing 1 M Na₂SO₄, 0.4 M NaCl, and 0.5 M H₃BO₃ in order to avoid the Ni deposition during the testing. pH of the above two solutions was 3.3. For the tests in the normal aqueous electrolytes, the PdH_x/Ti reference electrode was obtained after Pd/Ti has been polarized at –0.4 V (vs. RHE, under the three-electrode mode) for 5 min in 0.5 M H₂SO₄. This PdH_x/Ti electrode was rinsed with DI water for 5 seconds and then was dipped into the testing electrolytes for being employed as the reference electrode under a three-electrode mode where graphite or copper plates of 10 × 10 mm² is served as the working electrode and the platinum gauze is the counter electrode. The bath temperature of normal aqueous electrolytes was controlled at the specified values by a water thermostat (Haake) with an accuracy of 0.1 °C. For the EP-SCE Watts nickel system, polyoxyethylenelauryl ether (C₁₂H₂₅(OCH₂CH₂)₁₅OH), a non-ionic surfactant, was added into the additive-free Watts bath at

Table 1
Composition of the Pd electroplating bath and electroplating conditions.

Basic Pd plating bath	
PdCl ₂	0.01 M
Sodium Citrate	0.04 M
Lugalvan G35	0.3 g
Lugalvan P	0.3 g
Current density	25 mA cm ⁻²
Temperature	25 °C
pH	10.5

Table 2
Composition of the additive-free Watts nickel and the Watts nickel-like baths.

Watts nickel bath		Watts nickel-like bath	
NiSO ₄ ·6H ₂ O	1 M	Na ₂ SO ₄	1 M
NiCl ₂ ·6H ₂ O	0.2 M	NaCl	0.4 M
H ₃ BO ₃	0.5 M	H ₃ BO ₃	0.5 M
pH	3.3	pH	3.3

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