

Electrochemically assisted organosol method for Pt-Sn nanoparticle synthesis and in situ deposition on graphite felt support: Extended reaction zone anodes for direct ethanol fuel cells

Derek R. Lycke, Előd L. Gyenge*

Department of Chemical and Biological Engineering, The University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1 Z3

Received 26 September 2006; received in revised form 30 November 2006; accepted 30 November 2006

Available online 3 January 2007

Abstract

Two electrochemically assisted variants of the Bönnerman organosol method were developed for Pt-Sn nanoparticle synthesis and in situ deposition on graphite felt electrodes (e.g. thickness up to 2 mm). Tetraoctylammonium triethylhydroborate $N(C_8H_{17})_4BH(C_2H_5)_3$ was employed as colloid stabilizer and reductant dissolved in tetrahydrofuran (THF). The role of the electric field at a low deposition current density of 1.25 mA cm^{-2} was mainly electrophoretic causing the migration and adsorption of $N(C_8H_{17})_4BH(C_2H_5)_3$ on the graphite felt surface where it reduced the $PtCl_2-SnCl_2$ mixture. Faradaic electrodeposition was detected mostly for Sn. Typical Pt-Sn loadings were between 0.4 and 0.9 mg cm^{-2} depending on the type of pre-deposition exposure of the graphite felt: surfactant-adsorption and metal-adsorption variant, respectively. The catalyst surface area and Pt:Sn surface area ratio was determined by anodic stripping of an underpotential deposited Cu monolayer. The two deposition variants gave different catalyst surfaces: total area 233 and $76 \text{ cm}^2 \text{ mg}^{-1}$, with Pt:Sn surface area ratio of $3.5:1$ and $7.7:1$ for surfactant and metal adsorption, respectively. Regarding electrocatalysis of ethanol oxidation, voltammetry and chronopotentiometry studies corroborated by direct ethanol fuel cell experiments using $0.5 \text{ M H}_2\text{SO}_4$ as electrolyte, showed that due to a combination of higher catalyst load and Pt:Sn surface ratio, the graphite felt anodes prepared by the metal-adsorption variant gave better performance. The catalyzed graphite felt provided an extended reaction zone for ethanol electrooxidation and it gave higher catalyst mass specific peak power outputs compared to literature data obtained using gas diffusion anodes with carbon black supported Pt-Sn nanoparticles.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Nanoparticles; Three-dimensional electrodes; Direct ethanol fuel cells

1. Introduction

The synthesis of nano-size metal particles (or colloidal metals) can be traced back to the classic experiments of Faraday regarding the generation of colloidal Au by reduction of $[AuCl_4]^-$ with sodium citrate [1]. Due to their importance in catalysis and other areas of science and engineering (biomedical, electronics, etc.) diverse methods have been developed to produce nano-size metals and alloys. The goal has been to synthesize particles in a narrow size distribution range in order to address the often-encountered particle size sensitivity of catalytic/electrocatalytic reactions and to develop application specific metal compositions. To achieve monodis-

persity several modes of particle growth inhibition could be employed separately or in combination: steric hindrance (e.g., solvent-stabilized ethylene glycol and polyol methods [2–4], microemulsion [5–9], surfactant assisted organosol [10–12] and templating methods [13,14]), electrostatic repulsion due to double layer formation on the particle surface by ion adsorption (e.g., sodium citrate reduction of $[AuCl_4]^-$ [1,15]) and/or fast nucleation coupled with diffusion limited growth in pulsed electrodeposition techniques [16–19].

In addition to the particle size and catalyst composition, the type, structure and chemical functionality of the catalyst support can have a major effect on the rate and selectivity of catalytic reactions (e.g., nanoporous molecular sieves acting as supports [20]). For electrocatalysis of fuel cell reactions on the other hand, the choice of catalyst support thus far has been largely limited to carbon particles (i.e. carbon black) such as Vulcan XC-72 and Ketjen Black. Hence, the majority of nanoparticle

* Corresponding author. Tel.: +1 604 822 3217; fax: +1 604 822 6003.
E-mail address: egyenge@chml.ubc.ca (E.L. Gyenge).

catalyst preparation techniques for fuel cell applications were developed for carbon particle supports [21]. There is, however, emerging interest in the use of nanoporous carbon, nanotubes and nanocoils as catalyst supports with promising results for methanol electro-oxidation [22–24]. The slurry composed of supported catalyst, ionomer (e.g. Nafion®) in liquid form and possibly a hydrophobic agent, is utilized to form the catalyst layer (thickness typically between 5 and 50 μm) of the membrane-gas diffusion electrode assembly.

Interestingly, for the electrocatalysis of alcohol oxidation – aiming at direct alcohol fuel cell anodes – whether the carbon black support plays a beneficial role can still be considered somewhat controversial in the literature. There are only a few studies devoted to a comparison between carbon black supported and unsupported catalysts looking exclusively at the case of methanol electrooxidation.

Smotkin and co-workers reported up to three-times higher mass specific activities for the supported Pt-Ru (1:1) versus the unsupported catalyst for liquid-feed methanol electrooxidation at temperatures between 50 and 90 °C [25]. Based on this finding using carbon black supports allows the reduction of the precious metal catalyst load. However, the same authors observed a higher methanol crossover to the cathode in the cells equipped with the thinner supported catalyst layer [25]. For methanol electrooxidation in the temperature range of 90–130 °C on the other hand, Arico et al. found the unsupported Pt-Ru (1:1) catalyst with 15 wt% Nafion® yielded about 30% higher maximum power density, up to 260 mW cm^{-2} at 130 °C, compared to the supported catalyst with identical Nafion® loading [26].

The interface established between the carbon support micro and mesoporous structure and Nafion® micelles will impact the ionic conductivity of the catalyst layer [27], and moreover, in conjunction with the electrocatalyst particle size and dispersion [28,29] it will determine the effective electrochemically active surface area and the catalyst utilization efficiency.

Another aspect of the carbon black supported catalyst layer in direct alcohol fuel cell anodes relates to possible CO_2 entrapment in the micro and mesopores causing adverse effects such as an increase of the anodic diffusion overpotential and a decrease of the effective ionic conductivity.

There are very few investigations aimed at developing anode structures different than the carbon-supported gas diffusion electrode for direct alcohol fuel cells. In the case of the direct methanol fuel cell (DMFC) Scott and co-workers used Ti mesh as catalyst support and anode matrix [30], while Gyenge and co-workers recently proposed graphite felt and reticulated vitreous carbon as catalyst supports acting as three-dimensional, extended reaction zone, anodes [31,32]. In addition to different interaction effects between the electrocatalyst and porous three-dimensional support, the extended reaction zone ($\sim 200\text{--}1000 \mu\text{m}$) could also minimize the fuel crossover to the cathode by oxidizing the fuel at active sites situated farther from the membrane. The compressed graphite felt anode with electrodeposited Pt–Ru–Mo nanoparticles gave a DMFC power density of 210 mW cm^{-2} at 80 °C in 1 M CH_3OH –0.5 M H_2SO_4 liquid feed electrolyte [33].

The goals of the present investigation were two-fold. First, to develop a new method for nanoparticle synthesis and in situ deposition onto graphite felt electrodes. Second, to investigate the suitability of such electrodes as anodes for direct ethanol fuel cells by employing both fundamental electrochemical methods (e.g. cyclic voltammetry, chronopotentiometry) and fuel cell experiments.

It must be noted that functionalizing three-dimensional carbon matrices by nanoparticle electrocatalyst deposition could be beneficial for the applicability of these electrodes in other areas of applied electrochemistry as well, such as CO_2 reduction, electrosynthesis and electrochemical removal of organic contaminants from waste waters. The various applications of the graphite felt electrode together with certain physico-chemical properties such as electronic conductivity, was discussed by Oloman et al. [34].

The high theoretical energy density of ethanol (6.3 kWh l^{-1}) coupled with the possibility of ethanol generation from renewable agricultural resources and biomass could make direct ethanol fuel cells advantageous low-emission power sources. However, the sluggish kinetics and the complex mechanism of ethanol electrooxidation leading to acetaldehyde (2e^- oxidation) and/or acetic acid (4e^- oxidation) as the major reaction products instead of CO_2 (12e^- oxidation) compromise the fuel cell performance [35–37]. The group of Lamy and Léger showed that Pt catalyst formulations with Sn as a co-catalyst are superior to Pt or other binary compositions such as Pt-Ru [38–40]. The beneficial role of Sn for ethanol electrooxidation seems to be related also to the catalysis of the acetaldehyde intermediate oxidation to CO_2 , in addition to CO oxidation enhancement [40]. Therefore, the focus in the present work was Pt-Sn nanoparticle catalyst synthesis and deposition on graphite felt.

2. Experimental methods

2.1. The graphite felt substrate

All the nanoparticle deposition experiment reported here, were conducted using uncompressed graphite felt (Carborundum Co.) as catalyst support (Fig. 1) with ca. 2 mm thickness, porosity of 0.95, mean fiber diameter of ca. 20 μm and electronic conductivity of 10 S m^{-1} . In the fuel cell the graphite felt anode is under compression thus, the porosity decreases and the electronic conductivity increases according to ref. [34]:

$$\sigma = \sigma_0 + 2800 \left(1 - \frac{\varepsilon}{\varepsilon_0} \right)^{1.55} \quad (1)$$

where ε and ε_0 are the compressed and uncompressed porosities, σ and σ_0 are the compressed and uncompressed transverse electronic conductivities of the graphite felt matrix (S m^{-1}).

2.2. Pt-Sn catalyst preparation by the Bönne man organosol method

The modified version developed by Götz and Wendt [41] for the Bönne man organosol method [10–12,42] was used to prepare

Download English Version:

<https://daneshyari.com/en/article/195914>

Download Persian Version:

<https://daneshyari.com/article/195914>

[Daneshyari.com](https://daneshyari.com)