



Platinum nanophase electro catalysts and composite electrodes for hydrogen production

L.F. Petrik*, Z.G. Godongwana, E.I. Iwuoha

Department of Chemistry, University of the Western Cape, Bellville 7535, South Africa

ARTICLE INFO

Article history:

Received 27 March 2008

Received in revised form 2 June 2008

Accepted 28 June 2008

Available online 16 July 2008

Keywords:

Nanophase Pt

Electro catalyst

Ordered mesoporous carbon

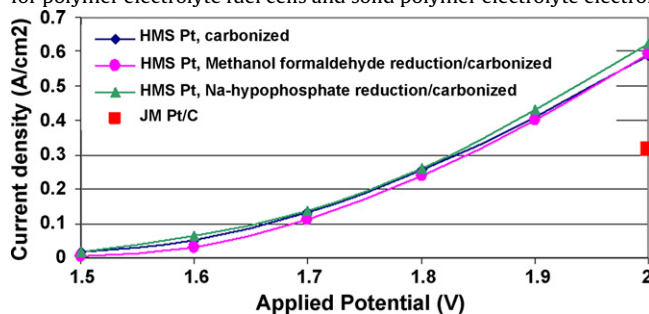
Composite electrode

Hydrogen production

Electrolysis of water

ABSTRACT

Nanophase Pt electro catalysts were prepared by impregnating a Pt salt containing solution upon a high surface area hexagonal mesoporous silica (HMS) matrix, which was then carbonized to varying degree by chemical vapour deposition of liquid petroleum gas (LPG). Thereafter the HMS Si matrix could be removed by chemical etching with NaOH to immediately form a Pt containing carbon analogue or ordered mesoporous carbon (OMC) with a porous structure similar to the parent HMS. Nanoparticles of Pt electro catalysts were thus successfully stabilized without agglomeration on both HMS and upon the porous HMS carbon analogue or OMC, which was graphitic in nature. The catalysts were electro active for the hydrogen evolution reaction and their activity compared favourable with an industry standard. Such nanophase Pt electro catalysts could be incorporated successfully in a composite electrode by sequential deposition, upon a suitable substrate and the catalysts in electrodes so formed proved to be stable and active under high-applied potential in high electrolyte environment for hydrogen production by electrolysis of water. This route to preparing a nanophase Pt OMC catalyst may be applicable to prepare active electro catalysts for polymer electrolyte fuel cells and solid polymer electrolyte electrolyzers.



© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical production of hydrogen is possible by water electrolysis. Water electrolysis is a non-polluting process, if high current densities can be obtained for a low energy input and particularly if performed in low electrolyte environments using renewable energy. With the strong emphasis upon waste reduction and reuse, the development of suitable high activity electro cata-

lysts that can be incorporated into composite electrodes for water electrolysis has a large commercialisation potential.

Composite electrode surfaces containing catalytic nanophases should result in high activity because of geometry, electro conductivity, high surface area, enhanced porosity and transport of reagents and products. Application of highly dispersed nanoscale active components may reduce the over potential of electro catalytic reactions such as water electrolysis resulting in overall increase in energy efficiency of the processes.

The greatest challenge at present is to find effective nanosynthesis procedures [1]. Nanoparticles of catalytically active metals may be deposited on inorganic supports, such as mesoporous materials [2–4] in order to prepare nano-composite materials suitable for electro catalysis. Enhancement of catalytic reactivity can be expected by matrix support of ultra fine particles.

Abbreviations: BET, Brünauer–Emmett–Teller method; CVD, chemical vapour deposition; LPG, liquid petroleum gas; OMC, ordered mesoporous carbon; HMS, hexagonal mesoporous silica; SEM-EDS, scanning electron microscopy–energy dispersive X-ray spectroscopy; XRD, X-ray diffraction.

* Corresponding author. Tel.: +27 21 9593304; fax: +27 21 9593878.

E-mail address: lpetrik@uwc.ac.za (L.F. Petrik).

Aggregation of the unstable highly dispersed nanophase state can be prevented due to the porous micro-texture and to interfacial interactions with the support.

In the surface coverage of a substrate with catalysts, the relatively low amount of active sites obtainable per unit area in a two dimensional plane has to date not resulted in sufficiently high catalytic activity for overcoming the barrier to producing cost competitive catalytic electrodes for hydrogen production or fuel cell applications. By use of porous three-dimensional supports, the highest number of active sites per unit volume may be obtained. Nanophases could be deposited on these high surface area three-dimensional mesoporous supports [5–9]. Metal salts may be impregnated in these inorganic silica-based porous materials for the preparation of supported metal nanoparticles. Inorganic hexagonal mesoporous silica (HMS) [10,11] and MCM-41 [12] materials have three-dimensional nanometer pores that are much larger (20–50 Å) than that typical for microporous zeolites (3–7 Å). Synthesis of Pt nanoparticles upon mesoporous materials may allow production of nanophase catalysts in a narrow nanoparticle size distribution, with a high stability. Recently, graphitic ordered mesoporous carbon (OMC) materials have been prepared using HMS as template via a chemical vapour deposition (CVD) route [13].

Synthesis of Pt nanoparticles within the matrices of mesoporous materials such as HMS or ordered mesoporous carbon materials as supports may allow production of nanophase catalysts in a narrow nanoparticle size distribution, with a high stability, in a three-dimensional array without pore blocking. Nanophases thus may be handled in bulk, and optimally dispersed and stabilized upon the mesoporous support for the exposure of the maximum number of active sites to the reactant. Since Pt is electro active and simultaneously conductive, the close proximity of such particles to each other upon the support pore walls would in theory provide an electron pathway for the applied electrical charge even on a non-conducting inert support as well as provide the required bare metal sites in close proximity for the dissociation of the reactant, H₂O.

The aim of the study was to utilize the pore space of these ordered mesoporous materials as a high surface area support to stabilize uniformly sized, small and active nanoparticles of electro active metals. Prerequisites for such systems are complex. Firstly, the uniform, nano-sized pores of the mesoporous support matrix should act as a stable, constraining environment to prevent re-agglomeration of the highly dispersed, unstable, nanophase electro catalytic metals during water electrolysis for hydrogen production whilst also achieving the highest number of active sites per unit volume. The mesopores of the support should be large enough to accommodate Pt nanoparticles and yet enable diffusion of aqueous reactant through the porous matrix to the electro active metals encapsulated in the pore space, as well as allow product gas evolution. The composite catalysts should be electro catalytically active. Furthermore, it is not suitable to utilize these materials in powder form in electro driven reactions; therefore the composite electro catalyst would need to be stabilized upon a suitable conductive substrate in thin film format using binders in order to prepare a stable and durable thin film gas diffusion electrode whilst retaining sufficient electro activity. All these challenges were considered in this study.

2. Experimental

2.1. Synthesis and characterization of nanomaterials

HMS is not commercially available, therefore this material was synthesized and detemplated according to standard methods [10,11] and surface area characterization by N₂ BET was per-

formed upon the detemplated products obtained. The HMS was prepared at room temperature, using tetraethyorthosilicate as Si source and 1-dodecylamine as template. Pt was supported upon the mesoporous HMS by incipient wetness impregnation. 0.1545 M H₂PtCl₆·6H₂O (hexachloro platinumic acid) solution was prepared by adding exactly 12.45 ml deionised water to 1.00 g PtCl₆·6H₂O. 1 g of the HMS support was impregnated with 2 ml of 0.1545 M H₂PtCl₆·6H₂O hexachloro platinumic acid solution. Reduction of Pt salts to form Pt metal nanoparticles on microporous or mesoporous materials can be achieved by thermal reduction using H₂ or in this study by various previously developed chemical means [14], namely the use of a methanol/formaldehyde reduction method, reduction by NaH₂PO₂ and finally by carbonization with LPG. In the case of methanol/formaldehyde, the Pt seeding procedure was initiated by submerging the Pt impregnated sample in 2 ml of methanol/formaldehyde solution (20% deionised water, 27% methanol and 53% formaldehyde (37–40%)) for 60 min. The slurry was then dried in a hot-air oven at 100 °C for 60 min. The sample was removed from the oven, after which 6 ml of the methanol/formaldehyde solution was added and the formed slurry was left at room temperature (±32 °C for 24 h). Thereafter, the sample was heated again for 60 min at 100 °C, cooled, rinsed, filtered and dried. In the case of reduction by NaH₂PO₂ a solution of 0.48 g of sodium hypophosphite was made in 10 ml H₂O. 2.5 ml of this solution was added to 1.0 g of various Pt impregnated samples that had been impregnated by the incipient wetness technique. Samples were dispersed in the NaH₂PO₂ solution and then placed in a hot air oven at 50 °C for 4.5 h. As no significant reduction was observed, the oven temperature was increased to 100 °C overnight in sealed containers. Thereafter the samples were thoroughly rinsed and dried at 80 °C.

In specified cases, the pre-reduced or unreduced HMS Pt electro catalysts were carbonized for various times using a chemical vapour deposition method with low cost commercial grade LPG as feed prior to incorporation of the powder electro catalysts into catalytic inks. For all CVD experiments done, the LPG was sourced from Afrox (South Africa). The LPG is a mixture of propane, butane, propylene and contains small amounts of ethyl mercaptan for odorizing the gas. The carbonization procedure was as follows: ceramic boats, each containing 1 g of the Pt impregnated and reduced or unreduced HMS starting material was placed in a flow through quartz tube furnace. From a starting temperature of 50 °C and subsequent heating rate of 1.67 °C min⁻¹, the furnace was heated to a target temperature of 800 °C, under a constant flow of commercial grade liquefied petroleum gas (LPG). When the furnace reached the target temperature, the flow of LPG through the system was sustained from 15 up to 90 min. Thereafter, the LPG flow was stopped and the samples were allowed to cool to room temperature. After the carbonization process, a portion of each sample was treated with 50 ml of 1 M NaOH in solution at 75 °C under stirring in order to remove the HMS Si matrix. The resulting silica etched porous carbon analogue material was washed with ultra pure water and dried in an oven at 100 °C. Particle characterization of electro catalysts was performed using XRD, BET and TEM.

Carbonization was performed in order to investigate how long the CVD process should be and whether a carbon analogue of the parent HMS could be obtained by pore infiltration of the HMS with the carbon source followed by removal of the silica matrix. It was also of interest to ascertain whether different carbonization times would lead to improved electro conductivity or catalytic performance of Si containing samples because of an increase in the contact between the surface of the electro catalyst and the conductive carbon black phase added to the catalytic ink. This carbonization process could also replace the various metal reducing procedures described above.

Download English Version:

<https://daneshyari.com/en/article/1290188>

Download Persian Version:

<https://daneshyari.com/article/1290188>

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