Engineering International, Volume 1, No 2 (2013)

Electro-deposition Method for Platinum Nano-particles Synthesis

Md. Aminul Islam; & M. Saidul Islam

Department of Materials Science and Engineering, University of Rajshahi, Bangladesh

ABSTRACT

This review explores the recent development in the synthesis process of platinum nanoparticles by electro deposition method. Various developed supporting electrodes used in synthesis process of platinum nanoparticles have been discussed. It is possible to control the particle size by adjusting electrolysis parameters and to improve homogeneity of platinum particles by changing the composition of electrolytic solutions. Various electrolytic compositions also discuss briefly for single or mixed electrodes.

Keywords: Platinum nanoparticles; Electrodeposition; Cyclic voltammetry; Electrodes; Precursors; Application

INTRODUCTION

Electrochemical method for size-controlled synthesis of platinum nanoparticles in aqueous phase was developed as a novel method. Narrow size distributions of nano particles dispersed onto smooth, non-catalytic surfaces are great interest in various application especially in the catalytic activity of platinum (Pt) towards reactions of interest in fuel cell systems. Electrodeposition, a process where particle sizes distribution is highly controllable. Although when highly dispersed supports are used the electrocry stallization show less homogeneous distribution of deposit. This is the reason of predominating chemical deposition techniques in the area of nanoparticles fabrication, but Pt electrodeposits also attract attention. We will discuss about process, supporting materials, precursors etc used in electrochemical deposition technique. Classical electrodeposition techniques are applied during two recent decades mostly to predictable preparation of catalysts with certain and variable surface composition. Both potentiostatic and galvanostatic deposition modes are applied, including various pulse modes.

PROCESS

Electrochemical deposition (ED) of metal nanoparticles on supported material is generally performed in baths containing metal salts. The baths are either acidic or basic and use a three terminal potentiostat. Generally for electro deposition one needs a cathode where the metal nanopartisles are deposited, the counter electrode (anode) and Ag\AgCl or calomel forms the reference electrode. Electrodeposition process for nano particles synthesis is accomplished by scanning between a few range of voltages versus Ag/AgCl, at a suitable scan rate for suitable cycles in a electrolytic bath containing Pt salt. ED is widely used with different strategies/methodologies, such as cyclic voltammetry, potential step deposition and double-pulse.

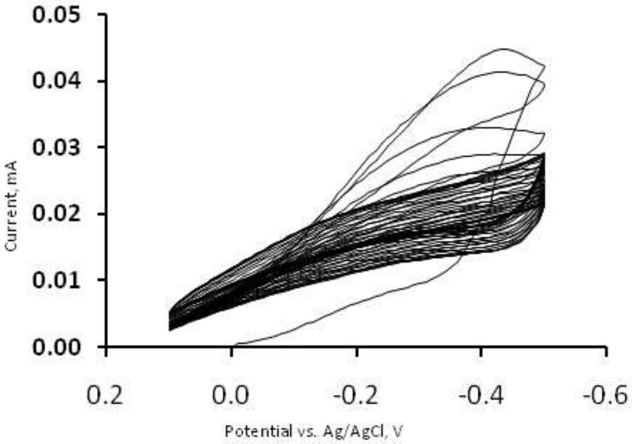

Fig. 1 Cyclic voltammograms for deposition of platinum nanoparticles on carbon fiber

Among these, potential step deposition (PSD) provides a tool to fine-tune the amount of metal deposited, the number of metallic sites and their size (Domı´nguez 2008). Using the electrochemical method for the reduction step, the reaction time and hence the growth of the particle can be controlled by the amount of current passed. The electrochemical reduction method, however, also depends on the connectivity and uniformity of the current conduction network of the porous matrix and the nucleation and growth processes are restricted to the charged interface, without three-dimensional homogeneity. In designing a structurally and dimensionally stable nanoparticle based electrode, it is very important to incorporate electro-catalytically active nanoparticles onto a suitable support. This can be accomplished by pasting or immobilizing chemically synthesized nanoparticles on catalyst supports or by electrodepositing the nanoparticles on the supports. Direct electrochemical reduction of platinum ions on a support is a relatively convenient way to fabricate nanoparticle based electrodes.

The electrochemical synthesis of Pt nanoparticles on the surface of carbon nanotubes (CNTs) is a common phenomenon. Carbon support is used because of its absence of catalytic activity and for its good electronic conductivity properties allowing the electrochemical preparation of metallic nanoparticles. The complexes of Pt (IV), precursors were converted to Pt nanoparticles.

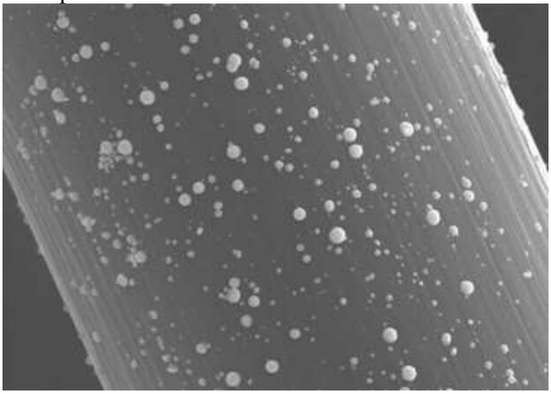

Fig. 2 SEM micrographs of platinum nanoparticles deposited on carbon fiber by cyclic voltammetry

Carbon materials are of special interest due to their outstanding properties, such as their tune able shape, size and porosity, chemical stability, corrosion resistance, low cost, good thermal resistance and electrical conductivity.

There are some reports in the literature on the preparation of supported platinum nanopartilces by electrodeposition method. Furthermore, Carbon nanotubes (CNTs), a novel carbon material discovered by Iijima in 1991, are very promising for a variety of applications. CNTs consist of either one (single-walled carbon nanotubes: SWNTs) or more (multi-walled carbon nanotubes: MWNTs graphene layers wrapped into cylinders. The properties of CNTs vary depending on the diameter and wrapping angle of the graphene cylinders, and the experimental results have confirmed that CNTs have special mechanical, electronic and magnetic properties. Generally, MWNTs have larger diameters and better electrical conductivity compared to SWNTs (Li J 2002). They can be used as simple conducting wires to build single nano electrodes, 2-D, or 3-D nanoelectrode ensembles. Their high surface area with the property of fast electron transfer rate was found to be very useful in application for higher performance and miniaturization of nanosensors and biosensors. Jian-Shan Ye and et,al. have been reported the electrodeposition of Pt nanoparticles at MWNTs and compared to Pt dispersed at flat Glassy carbon(GC) electrodes, the Pt nanoparticles-MWNTs nanocomposites, Pt nanoparticles at MWNTs was displayed better performance towards the methanol Oxidation. However, investigation has been studied that single-walled carbon nanotubes/polyaniline composite was used to support materials of Pt nanoparticles for HCHO fuel cell. It is insufficient for HCHO sensing study. The electrosynthesis of Pt/PAN/MWCNTs nanocomposite has been achieved so far for HCHO sensing and Guan-Ping Jin & et al have been suggested a simple approach for electrosynthesis of platinum nanoparticles on polyaniline-coat multi-walled carbon nanotubes film. How ever other novel carbon-support materials such as graphite nanofibers (GNFs), carbon nanohorns (Yoshitake 2002), and carbon nanocoils provide alternate candidates of carbon support for fuel cell applications. Bessel et al. and Steigerwalt et al. used GNFs as supports for Pt and Pt–Ru alloy electrocatalysts. They have observed better activity for methanol oxidation. The high electronic conductivity of GNF and the specific crystallographic orientation of the metal particles resulting from well-ordered GNF support are believed to be the factors for the observed enhanced electro-catalytic activity. In heterogeneous catalysis, one of the important tasks is the determination of the number of active sites in the catalyst. For a given catalyst, the number of active sites present is responsible for the observed catalytic activity. A considerable amount of research has been devoted toward understanding the number of active sites and the role played by the carrier of the supported catalysts. The most efficient utilization of any supported catalyst depends on the percentage of exposed or the dispersion of the active component on the surface of the carrier material.

FUNCTIONALIZATION OF CNF

However, since the surface of carbon nanotube is rather inert, to explore a feasible technique to activate the surfaces of CNTs is an essential prerequisite to deposit noble metal nanoparticles on CNTs.

The general process of functionalization of CNF is as follows:

The CNF is treated with mixed acid aqueous solution of HNO3 and H2SO4 in 1:3 ratios under magnetic stirrer for 3 h. It is then washed with water and evaporated to dryness.

Without surface modification, most of the carbon nanomaterials lack sufficient binding sites for anchoring precursor metal ions or metal nanoparticles, which usually lead to poor dispersion and the aggregation of metal nanoparticles, especially at high loading conditions. To introduce more binding sites and surface anchoring groups, an acid oxidation process was very frequently adopted to treat carbon nanomaterials in a mixed acid aqueous solution, which introduces surface bound polar hydroxyl and carboxylic acid groups for subsequent anchoring and reductive conversion of precursor metal ions to metal nanoparticles (Yu RQ 1998).

An improved technique was later developed and involved refluxing carbon nanotubes in nitric and sulfuric acids to create surface functional groups, such as carboxylic(-COOH), carbonyl(-CO), and hydroxylic(-COH). The treated carbon nanotubes were then used for nanoparticles deposition by reducing metal precursors in ethylene glycol solution.

Chemical functionalization of carbon nanotubes with organic molecules is a widely used way to anchor noble metal nanoparticles to the surface of MWNTs. Many recent literatures have reported that aryl diazonium salts could react efficiently with individual carbon nanotube to form aryl-functionalized carbon nanotubes. Organic thiol derivatives, on the other hand, are generally well known to interact strongly with platinum surfaces. Jin Shi, Xin-Sheng Li and et al has been described a new method to electro-deposit platinum nanoparticles on the surface of multi-walled carbon nanotubes (MWNTs) functionalized with 4-mercaptobenzene.

Electrochemical experiments were performed in a three-electrode system. The MWNT paste electrode was used as working electrode.

A platinum sheet (geometric surface area = 1 cm^2) and a saturated calomel electrode (SCE) were used as the counter and reference electrodes. Pt nanoparticles were electro-deposited on the functionalized MWNTs in 1 mM K_2PtCl_6+0.1 M K_2SO_4 aqueous solutions. Guo and Li reported a so called three-step process to deposit Pt nanoparticles on carbon nanotubes (CNTs), involving electrochemical treatment of CNTs, electrochemical oxidation of Pt (II) complex to Pt (IV) complex, and the transformation of Pt (IV) complex to Pt nanoparticles on the surface of CNTs. The deposition of Pt nanoparticles within a CNT–Nafion composite for a wide range of sensing applications has been reported in the literature.

OTHER SUPPORTING MATERIALS

Conducting polymers are useful supports for the immobilization of dispersed noble metal catalysts, due to the prevention of particle agglomeration. The porous structure and high surface area of many conducting polymers have led to their use as supporting materials in the development of new electro-catalytic materials. Due to the relative high electric conductivity of some polymers it is possible to transfer electrons through polymer chains, between the electrode and dispersed metal particles, where the electro-catalytic reaction occurs.

Incorporation of Pt particles into conducting polymer coated electrode also increases the electrocatalytic activity of Pt particles for the electrooxidation of organic fuels by decreasing the poisoning phenomena, which is caused by high dispersion of Pt particles in polymer matrix and the synergistic effects of conducting polymer and metal particles. The used polymers are polyaniline, polypyrrole, and polythiophene.

Dendrimers are good candidates for preparing metal nanoparticles because they can act as structurally and well-defined templates and robust stabilizers. In recent years, well-defined, almost monodisperse PtNPs have been synthesized using poly (amidoamine), PAMAM, dendrimers as a template. . Polyamidoamine (PAMAM) dendrimers, in particular, have been used as nanoreactors with effective nanoparticle stabilization. In general, PAMAM dendrimers are of interest as templates to prepare metal nanoparticles because they yield nanoparticles with quite uniform composition and structure. In addition, encapsulated nanoparticles surfaces are accessible to substrates so that catalytic reactions can be carried out. PAMAM dendrimer encapsulated Pt nanoparticles and PtPd bimetallic nanoaparticles are electrocatalytically active for oxygen reduction. Also dendrimer-encapsulated platinum nanoparticles supported on carbon fiber and nitrogendoped CNT as electrodes for oxygen reduction.

PRECURSORS

The range of precursors became much wider during two recent decades. The common precursor used in platinum nanoparticles synthesis is H_2PtCl_6. The precursor is usually dissolved in an aqueous or organic liquid phase. In situations of mixed metal nanoparticles the different reactivities of two types of precursors, e.g. $RuCl_3$ and H_2PtCl_6 are usually used. Sometimes {Pt $(NH_3)_2$ $(NO_2)_2$, $Ru_3(CO)_{12}$, $RuNO(NO_3)$} (William, 2002), {$Na_6Pt(SO_3)_4$, $Na_6Ru(SO_3)_4$}, {$PtCl_2$ and $RuCl_3$} etc. various complex precursors are also used.

Various complexing agents have been also used to improve the quality of the deposits.

S.M.S.I. Dulal and et al have been used 1 mM aqueous solution of hydrogen hexachloroplatinate and Tri-sodium citrate (TSC) as a complexing agent and its concentration was 1 mM in all baths. Tri-sodium citrate was chosen because it was non-toxic and had brightening, leveling and buffering actions. Moreover, citrate electrolyte has recently been used for precision electrode position.

New platinum and ruthenium complexes with inorganic and organic ligands were proposed as the precursors. Bimetallic Pt–Ru particles were prepared by co-deposition from two precursors, $Pt(dba)_2$ and Ru $(COD)(COT)_4$(*) dissolved in tetrahydrofuran (various ratios) (Dulal 1999).

The original technique of Pt–Ru electrodeposition on carbon support was worked out. The mixture of Nafion solution, Vulcan XC-72, and the appropriate amounts of H_2PtCl_6 and $RuCl_3$ were applied over a coarse glassy carbon disc, and pulse galvanostatic deposition was started (assisted by special homemade device providing homogeneity of deposition). Subsequent and simultaneous deposition of Pt and Ru on HOPG is reported in comparative study.

APPLICATIONS

The future shortage of fossil fuels drives the search for alternative, renewable sources of energy. The nanostructured elongated platinum and Pt + other metallic materials have already established a niche in renewable energy related technologies including: cathodes for batteries, catalyst and membrane components for fuel cells, supports for light-adsorbing centers in dye-sensitized solar cells, together with hydrogen sensing and storage systems. Some of the promising applications are listed below:

(a) Hydrogen Storage and Sensing.
(b) Cathode materials for fuel cells, battery or others.
(c) Electro analysis.
(d) Electrodes for electrochemical biosensors:
    (i) Free Hydrogen Peroxide Biosensor

(ii) Nonenzymatic Glucose Sensing

CONCLUSION

Electrochemical deposition (ED) is an efficient method for the preparation of metal particles, Electro-deposition has also been used to deposit PtNPs on electrode surfaces; here, the particle sizes are possibly larger than 10 nm and have wide particle size distribution

ACKNOWLEDGEMENTS

We would like to acknowledge the referees whose valuable remarks were extremely helpful.

*[Abbreviations: dba—dibenzylidene acetone; COD—1,5-cyclooctadiene; COT—1,3,5-cyclooctatriene.]

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