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Microwave-assisted Synthesis of Fuel Cell Catalyst

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Abstract

In this paper microwave-assisted synthesis of a special catalyst, namely, Pt/C catalyst comprised of nanoparticles is discussed. Owing to its unique characteristics, the catalyst is very beneficial to the performance of proton exchange membrane fuel cells (PEMFCs). As mentioned in the article, Pt nanoparticles once integrated with Carbon, provide better catalytic activity/stability. Such integration has been achieved successfully by microwave heating. The relevant experimental works of some researchers are briefly reviewed in the end.

1) Introduction

1-1) Background of Microwave Synthesis

First published reports on the application of microwave synthesis were at 1986 by the group of Gedge and Giguere/Majetich [1]. Nowadays, most of the documents published on this concept are about microwave assisted organic synthesis (MAOS) [2, 3]. In most of the reports microwave heating has been applied to reduce reaction times, increase product yields and enhance product purities by reducing unwanted side reactions compared to conventional heating methods. Due to short reaction time associated with microwave synthesis it could be ideal for reaction scouting and optimization of reaction conditions. Inasmuch as, new experiments can be conducted in a short time.

1-2) Pt/C Catalyst to Upgrade Fuel Cells

Over past twenty years proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have been under research for their effective energy conversion and high efficiency for the application of power resources for electric devices [4, 5]. One of the most efficient metal catalysts for fuel cells is Platinum. The main problem for commercialization of fuel cells is the high cost of membrane electrode assembly (MEA) especially Pt which is the only catalyst active for hydrogen oxidation, methanol oxidation and oxygen reduction in low temperature [6]. There have been two solutions suggested for reducing the application of Pt in fuel cells: Replacing Pt with alternative non-noble catalysts, reduction of Pt loading by exploiting non-precious supports [7, 8]. In this regard, the interaction of Pt and carbon as a support has attracted the attention of many researchers. Carbon as catalyst support, improves growth, structure and dispersion of Pt particles which in turn betters catalytic

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properties and stability of electrocatalysts [9, 10]. In the following sections advantages of microwave-assisted synthesis of the aforementioned catalyst and studies by different researchers on this practice are discussed.

2) Application of Microwave Heating in Synthesis of Pt/C Catalyst

The three main factors in metal catalytic activity are namely: particle shape, size and the particle size distribution [11]. Many efforts have been made to replace conventional methods of catalyst preparation based on wet impregnation and the chemical reduction of metal precursors which do not satisfy ideal shape and size conditions. Eventually alternative methods based on microemulsions [12], sonochemistry [13, 14] and microwave irradiation [15-18] which are meant to produce colloids and clusters in nanoscale and with greater uniformity.

Microwave heating has the benefits of being fast, simple, uniform and energy-efficient. Lately, the use of microwave synthesis has been extensively enhanced to prepare high purity nanoparticles with narrow particle size distributions.

2-1) Experimental Works

Chen et al. [19] have executed a simple microwave procedure for preparing Pt metal nanoparticles supported on Carbon. The prepared Pt/Carbon nanocomposites containing 10, 15 and 20 wt% of Pt successfully by microwave irradiation (see Fig. 1). They demonstrated a uniform dispersion of spherical Pt nanoparticles of 3.5-4.0 nm in diameter and with a narrow particle size distribution on the Carbon surface by TEM imaging. Their tests showed more electrochemical activity of Pt/Carbon catalysts in room temperature oxidation of liquid methanol than commercially available catalysts.

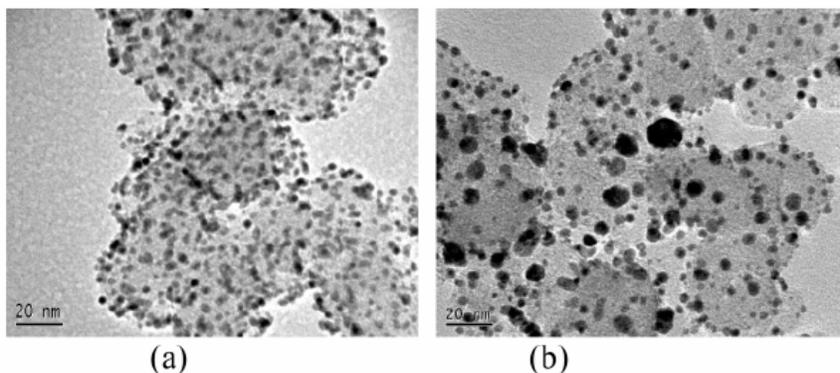


Figure 1) TEM images of (a) microwave-synthesized Pt nanoparticles supported on Vulcan Carbon XC-72 and (b) commercially available E-TEK Pt/C catalyst (nominal Pt loading 20 wt%) [19]

Hsieh et al. [20] synthesized bimetallic Pt-Zn catalyst with high and stable electrochemical activity toward Sulfuric acid and methanol oxidation by microwave assisted polyol(MP) method (see Fig. 2). They used catalytic chemical vapor deposition (CVD) method to directly grow multi-layered Carbon nanotubes. They examined catalytic activities of supported Pt-Zn catalysts toward acid electrolyte and methanol oxidation by cyclic voltammetry test with potential cycling. Experimental results confirmed that two-stage MP synthesis enables the improvement of electrochemical activity, antipoisoning effect, and

long-term durability of the binary catalyst. They attributed the improvement of the bifunctional mechanism of binary catalysts to Zn content serving as a promoting center for the generation of Zn–OH species, and more Pt sites are thus available for methanol oxidation. Accordingly, their Pt–Zn/CNT catalyst, prepared by the MP approach, displays a potential candidate for fuel cell application due to its easy fabrication (6 min), low cost, and without any additional reduction process.

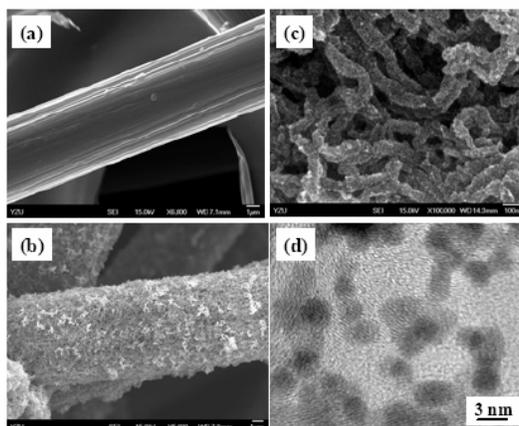


Figure 2) FE-SEM micrographs for (a) pure CP, (b) CNT/CP, and (c) Pt-Zn catalysts-supported CNTs. (d) HR-TEM image for Pt-Zn catalysts-supported CNTs.

Bensebaa et al. [21] reported preparation and characterization of a novel catalyst material consisting of alloyed Pt-Ru nanoparticles dispersed in a polypyrrole di(2-ethylhexyl) sulfosuccinate (or PPyDEHS) matrix using the microwave synthesis approach. They used a published literature procedure for the preparation of PPy-DEHS which guaranteed good electronic conductivity and solubility in alcohols [22–29]. Thin films containing Pt-Ru nanoparticles embedded in a PPyDEHS matrix were fabricated and tested for direct methanol fuel cell (DMFC) catalytic activity. They concluded that presence of anion dopants may provide a good pathway for protonic species, improving the capabilities of this new material for DMFC applications. They also concluded that the structure and morphology of the new material may also help lessen the effect of methanol crossover by decreasing the required methanol pressure.

Song et al. [30] with the aim of achieving a high loaded Pt/C catalyst, which is desirable for fuel cell in order to make the system compact, obtained highly dispersed high loading Pt/C up to 50% by a pulse-microwave assisted polyol method (PMP), in which the metal reduction was accomplished in 2 min in the presence of ethylene glycol (EG). They adopted pulse-microwave procedure in order to avoid the agglomeration of the metal particles at high temperatures. This was due to the fact that continuous microwave can easily cause a quite rapid heating rate for carbon materials. In their process, EG acts not only as dispersant and reducing agent, but also as the microwave additive due to the fact that the dielectric constant (41.4 at 25 °C) and dielectric loss for ethylene glycol are high and as a consequence, rapid heating takes place under the microwave radiation. The support, Carbon (Vulcan XC-72R, Cabot Corp.) is also a microwave-sensitive material, which is believed to play an important role in the acceleration of the metal reduction.

Wikander et al. [31] reported spherical crystalline Pt nanoparticles, with diameters of 1.6–2.6 nm, synthesized using the phase transfer method with alkylamines, C_nNH_2 , as stabilizing agents. Zhou et al.

[32] prepared highly dispersed Pt nanoparticles using a microwave synthesis procedure by adjusting the amount of mesoporous Carbon. The prepared Pt catalysts exhibited high catalytic activity for hydrogen electro-oxidation. The average size of Pt particles increased slightly (4.0–5.0 nm) when the amount of CTAB added to the synthesis solution was increased. In Shao's review [33], Pt based catalysts with nitrogen-doped carbon as a support exhibited enhanced catalytic activity and durability toward oxygen reduction and methanol oxidation, which can be attributed to the high dispersion of Pt nanoparticles and the modified interaction between Pt nanoparticles and the nitrogen atom in the support.

Liu et al. [34] synthesized Pt/C catalyst using $Pt(phen)_2^{+2}$ complex as a precursor and 1,10-phenanthroline as the chelating agent. They reduced Pt-complex by microwave synthesis. They concluded that the short impregnation time avoids slow reaction kinetics during the preparation, resulting in the formation of ultrafine Pt nanoparticles with a narrow size distribution supported on carbon. They found that a stoichiometric amount of the chelating agent added to the synthesis solution improved the particle size distribution of Pt nanoparticles in carbon black supports. They also found out that the electrochemical performance of the Pt/C catalyst in PEMFC was better than that of a commercial catalyst with the same Pt loading.

3) Conclusion

The role of microwave heating in synthesis of Pt/C catalyst was investigated in this paper. The aforesaid catalyst is used in proton exchange membrane fuel cells (PEMFCs). As discussed, the quality of synthesis of Pt metal nanoparticles (supported on Carbon) is highly important and affects the performance of PEMFCs. Microwave heating, being fast, simple, uniform and energy-efficient, has been chosen by many researchers for preparation of such particles. In this way, ultrafine Pt nanoparticles with a narrow size distribution supported on carbon have been resulted. Another exemplary case in which microwave was applied concerns microwave-assisted polyol synthesis of Pt–Zn electrocatalysts on carbon nanotube electrodes for methanol oxidation which proved to be quite successful/effective. All in all, it can be deduced that microwave-assisted synthesis brings about enhanced activities for catalysts of various purposes and gives them extraordinary superiorities compared to their commercial counterparts.

4) References

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