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## Multi-component electrocatalyst for low-temperature fuel cells synthesized via sonochemical reactions

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#### ABSTRACT

This review presents recent advances in multi-component electrocatalysts for low-temperature fuel cells (FCs) synthesized via sonochemical reactions. As a feasible approach to develop novel electrocatalysts that can overcome the many problems of the prevailing Pt electrocatalysts, Pt- or Pd-based alloy and core-shell M@Pt nanoparticles (NPs) have been pursued. Synthesizing NPs with desirable properties often turn out to be challenging. Sonochemistry generates extreme conditions via acoustic cavitation, which have been utilized in the syntheses of various Pt and Pd NPs and Pt- and Pd-based alloy NPs. Especially, it has been reported that several M@Pt core-shell NPs can be synthesized by sonochemistry, which is hard to achieve by other methods. The principles of sonochemistry are presented with examples. Also alloy NPs and core-shell NPs synthesized by sonochemistry and those by other methods are compared.

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#### 1. Introduction

Low-temperature FCs are promising environment-friendly energy conversion systems with high energy density and efficiency to be used as components of electronic devices for stationary and portable applications [1–5]. Depending on the type of fuel and electrolyte, low-temperature FCs are divided into proton exchange membrane FCs (PEMFCs), alkaline FCs, phosphoric acid FCs, and molten carbonate FCs [6,7]. All FCs consist of an anode, a cathode, and electrolyte, each of which needs to be fully investigated for the enhancement of FC performance. In the PEMFCs, effort is concentrated on the overpotential reduction of the oxygen reduction reaction (ORR) at a cathode to overcome the sluggish kinetics of the PEMFCs operation [8,9]. In addition, methanol or formic acid oxidation reactions (MOR or FAOR) at an anode have received attention because their storage is easier and safer than hydrogen [10,11].

Because Pt is a highly efficient catalytic element for low-temperature reactions, Pt nanoparticles (NPs) supported on porous carbon have been most widely used as the electrocatalyst in PEMFCs [10,12]. However, there are a number of important problems in using Pt as the catalyst material in real applications. Its

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high cost and limited amount in the earth crust are outstanding economical challenges. As for the catalytic performance, there are a number of important scientific and technical issues to be addressed. CO poisoning, the inactivation of catalysts due to strongly bound CO or other intermediates formed during the oxidation of small organic molecules, is a notorious problem of Pt catalyst [13,14]. Pt catalyst typically shows rather large overpotential of ~0.4 V in ORR which is a serious source of potential loss of low-temperature FCs [15,16].

Ultimately, the most desirable solution to all of these problems will be to find Pt-free electrocatalysts with catalytic properties comparable to or better than Pt. A number of different kinds of material have been suggested and studied as candidates [17-19]. However, this direction of research appears to have a very long way to go. A more feasible approach is to form alloy NPs based on Pt and a second element (M). Alloy formation can be an efficient way to reduce the amount of Pt to be used in the catalyst, partly addressing the issues of cost and resources of Pt. More importantly, it has been demonstrated that, by incorporating the right element by the right amount into the Pt lattice, the electronic structure of Pt can be tuned to result in significant reduction of the over-potential and the CO-poisoning problems [20,21]. The most commonly accepted theoretical model to explain the effects of alloying on the electronic structure of Pt is the d-band center theory proposed by Nørskov [22]. According to this model, the M atom in the Pt lattice decreases the Pt-Pt distance as well as interacts electronically



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with Pt. The net result is the lowering of the center of Pt d-band, weakening the binding energy to ad-atoms, which effectively lowers the activation energy of the overall catalytic reaction. Many Pt– M binary alloy NPs have been synthesized and studied as electrocatalysts. A number of elements (M = Co, Ni, Fe, Cu, Cr, Ti, V, Sn, Pd, Au, Ag, Ru, Ir, Rh and Sn) have been identified to enhance the electrocatalytic properties of Pt [10,12,14,16,23–31].

Although Pd is considered to be inferior to Pt as an electrocatalyst, especially for ORR in acidic media, it is an attractive alternative to Pt because it is cheaper than Pt and has some properties that can overcome the problems of Pt. For instance, the notorious CO-poisoning problem on Pt is not as serious with Pd [32,33]. Furthermore, it has been shown that alteration of the electronic structure of Pd, mostly through alloy formation, can improve the electrocatalytic properties of Pd, sometimes comparable to those of Pt. For instance, unlike Pt-based NPs, Pd–M alloy NPs have been reported to show high activity for small molecule oxidation reaction in alkaline media [34]. For these reasons Pd–M alloy NPs also have attracted attention.

Even though incorporating M into the Pt or Pd lattice has proven to be an effective way to enhance the electrocatalytic properties, the high chemical reactivity of M atoms leaves the problem of instability. In this regard, core-shell NPs with Pt or Pd on the shell are considered to be more desirable. In core-shell NPs, the benefits of alloying can be preserved and, at the same time, the reactive M atoms can be protected from the harsh environment of FC operation [35]. Later on, studies of core-shell NPs as electrocatalysts have created further issues on how to optimize the performance through controlling the various features of the core-shell structure. For instance, the size and shape of a coreshell NP and its shell thickness can affect the electrocatalytic performance and durability profoundly [36,37]. Since these parameters are dependent on the nature of M, the study on core-shell NPs requires methods to synthesize them with ranges of such aspects. However, to the best of our knowledge, not a single method can cover the whole range of the various parameters. In fact, the examples of core-shell NPs in the literature are rather spotty making observations on the trend according to any parameter almost impossible. More generalized synthetic methods that can cover inaccessible ranges by the existing methods are deeply in need.

In the present review, we will introduce sonochemical methods as a viable means to synthesize various NPs of Pt or Pd and their alloys. Sonochemical reaction techniques in the synthesis of nanomaterials have been introduced in the 1980s by Suslick's group [38]. They have published a number of excellent review papers since then [39,40]. Their foci have been more on the general introduction and on the action of ultrasound to matters; materials of particular interests in FCs field are not the major focus. Pollet has written two review papers of the uses of ultrasound as a synthesis tool for FC materials [7,41]. In the more recent paper, he gave a comprehensive account on various aspects of ultrasound including principles, theories, and many practical issues such as ultrasound equipments and their characteristics. The other review in 2010 is focused on the materials in FCs. Most of the literature works on electrocatalysts published until 2010 are summarized in this paper. A number of alloy and core-shell NPs are discussed along with the majority of single element NPs. During the past a few years, a number of new alloy and core-shell NPs based on Pt and Pd have been synthesized by sonochemistry and studied for their electrocatalytic properties. As will be seen later, these examples have improved material qualities, which are in part possible only through sonochemistry. In light of the importance of finding more dependable electrocatalysts in the present status of FC researches, we believe that sonochemistry can find uses more frequently in the future.

#### 2. Characteristics of sonochemistry

The sonochemical phenomenon in liquid was first reported by R. W. Wood and A. L. Loomis in 1927 [42]. They observed sonic waves travelling through liquid, and at the same time, found that the dispersion of sound in water generates bubbles with a loud noise. Following this discovery, advances in sonochemistry were accelerated with the introduction of cheaper and more reliable generators of high-intensity ultrasound in the 1980s [38]. Fundamental experiments have been carried out using these sonicators to investigate the chemical and physical properties of ultrasound. Nowadays, ultrasound generators with various features to meet diverse purposes and uses are commercially available. Bath- and horn-type sonicators are most commonly used for sonochemical reactions. In general, the frequency of an ultrasonic horn sonicator is 20 kHz or 40 kHz, and that of a bath sonicator is 40 kHz [7,39]. Because of the insufficient intensity of ultrasonic cleaning baths, the majority of sonochemical reactions have been conducted by ultrasonic horn-type sonicators.

During the irradiation of ultrasound in liquid, the repetitive expansion and compression of acoustic wave creates bubbles which grow in size. Finally, the collapse of overgrown bubbles releases highly accumulated ultrasonic energy; this acoustic cavitation provides hot spots with unusual characteristics, including temperatures of  $\sim$ 5000 K, pressures of  $\sim$ 1000 atm, and a fast cooling rate of  $10^9$  K s<sup>-1</sup> [40]. Early studies of sonochemistry have been systematically conducted by Suslick's and other research groups [39,40]. When solid material is immersed or dispersed in liquid, the solid is subjected to the similar conditions of temperature and pressure as the liquid. In addition, liquid jets generated via ultrasound can damage the heated surface of the solid. The collision between solid-state particles can affect their reactivity, surface morphology, and composition. By taking advantage of these properties of ultrasound, sonochemistry has been widely utilized in materials chemistry, organic chemistry, environmental chemistry, and biomedical uses [43,44].

The types of sonochemical reactions can be divided into homogeneous sonochemistry of a single liquid, heterogeneous sonochemistry of liquid–solid or liquid–liquid, and sonocatalysis [45]. Pure solid or solid–gas systems have not been studied by sonochemistry because the sonochemical phenomena is generated via acoustic cavitation in liquid. Among these sonochemical reactions, the heterogeneous sonochemistry of liquid–solid systems has been studied in relation with nanoscience, because nanomaterials can be formed or fabricated through sonochemical reactions of mixtures of solid-state precursors and liquid-state solvents. Depending on the type of solvents and the volatility of precursors, various nanomaterials have been synthesized including noble metals, metal oxides, metal carbides and metal sulfides [32,46–48].

#### 2.1. Physical effects of ultrasound in nanomaterials preparation

Ultrasound irradiation in a liquid medium generates several physical effects which have been utilized to induce physical and chemical changes of materials. During acoustic cavitation, highintensity ultrasound generates liquid jets and shock waves in the media. Rapid mass transfer and thermal heating take place. Interparticle collisions are an additional physical effect leading to the agglomeration of metal particles or the fragmentation of brittle materials, which can affect particle size, surface composition, and morphology [40]. These physical effects have been utilized for mechanical exfoliation of layered materials, emulsification, and introducing defects on surfaces for surface modification.

The use of ultrasound enhances the intercalation of molecules or atoms inside layered-structure materials such as graphite, boron Download English Version:

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