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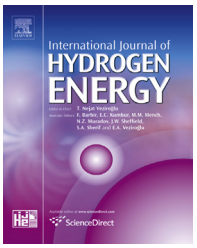

Comparison of conventional versus microwave heating for polyol synthesis of supported iridium based electrocatalyst for polymer electrolyte membrane water electrolysis

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ABSTRACT

Microwave irradiation heating is a simple and clean technique with many advantages over conventional heating. Microwave irradiation has been used to synthesize numerous organic and inorganic materials; however, it is rarely used to synthesize iridium based electrocatalysts for polymer electrolyte membrane (PEM) water electrolysis. In this work, an electrocatalyst consisting of a complex iridium oxide supported on antimony tin oxide (ATO) was synthesized using a polyol method with two different heating methods: conventional heating and microwave irradiation heating. With microwave heating the primary synthesis step could be completed in 1 min compared to more than 10 h for conventional heating. The morphological and electrochemical properties of the two catalysts were then compared using various characterization techniques. Their BET surface area, particle size/particle size distribution, and elemental compositions were measured using nitrogen physisorption, transmission electron microscopy (TEM), and scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX). Their electrochemical characteristics were studied using linear sweep and cyclic voltammetry in a three-electrode cell. Additionally, using the microwave irradiation heating method, the effect of various operating parameters such as pH, metal precursor concentration, temperature and the type of polyol on the morphology of the catalyst was studied. The results showed that the catalysts synthesized with both of the heating techniques have comparable physical and electrochemical properties. However, the clusters of iridium species in the conventional heating method were slightly smaller compared to those in the microwave irradiation heating method (2.30 ± 0.04 nm compared to 3.00 ± 0.03 nm).

Among the operating parameters tested, the pH of the synthesis solution and the type of polyol were two factors to influence the surface area of the iridium based species the most, each resulted in an increase of approximately 12%.

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Introduction

Energy is an important issue of 21st century, and hydrogen as an energy carrier, could be an important solution to the world energy problem [1]. Hydrogen can be burned in engines, turbines, or boilers to provide energy; it can also be converted to electricity directly in proton exchange membrane fuel cells (PEMFCs) [2]. High purity hydrogen can be produced efficiently and without environmental impact using polymer electrolyte membrane water electrolysis (PEMWE), if electricity coming from renewables such as wind, hydro and solar is used as the power source.

The minimum potential difference that is required to start water electrolysis at standard conditions is 1.23 V [3,4], but in practice the required voltage is higher due to overpotentials and ohmic resistance existing in the cell [5,6]. It is widely accepted that the oxygen evolution reaction (OER) electrode in PEMWE is the main source of overpotentials, energy loss, and electrode degradation problems; hence, it has been the focus of many studies [7–9]. Typically materials based on iridium and ruthenium have the lowest overpotentials for the OER reaction [9]. However, ruthenium has been shown to be less stable in acidic media [9–11]. Therefore, iridium is the most commonly used OER catalyst employed in PEM water electrolysers. Iridium is an expensive electrocatalyst and (like other noble metals) depositing it on a support material with high surface area is an effective way to increase its utilization [12]. Antimony tin oxide (ATO) is one of the most commonly used support materials for the iridium based electrocatalyst in PEM water electrolysers [13–18].

Several methods have been developed to synthesize supported and un-supported iridium based catalysts (e.g. iridium metal, hydroxide or oxides) in the form of powder for PEM water electrolysers. These methods include Hydrolysis [19,20], Sol–gel [21–23], Adams fusion [24–27], and polyol [17,28].

The polyol method is a relatively simple, effective, low cost, and high yield method, which was first described by Fievet et al. [29], in 1989 and is used to synthesize various materials including: PtRu [30], Pd [31,32], Pt [33], Ag [34], Sn [35], etc.

A polyol is an alcohol with two or more OH groups that serve as both solvent and reducing agent for a metal precursor in polyol synthesis. The most common polyol used in this method is ethylene glycol (EG); however, other kinds of polyols have been tried as well [36]. At medium temperatures (150–200 °C), the OH groups in the polyol molecule interact with the metal precursor salts and oxidize to aldehyde, glycolic acid and oxalic acid groups [30]. Electrons released during the oxidation process are consumed to instantaneously reduce the dissolved metal precursor cations and to form metal nanoparticles. The polyol synthesis has multiple advantages. First of all, the polyols can be considered as water equivalent and show solubility of compounds similar to water [37]. A variety of simple and low cost metal salts (such as halides, nitrates, sulfates) can be used as the starting metal precursor. Secondly polyols are excellent reducing agents, and they allow reduction of noble metal precursors without the need for any additional reducing agents [30,38]. Since their boiling temperature is high, they allow synthesis of materials at higher temperatures in the range of 200–320 °C without the necessity of high pressure vessels. If the polyol method is performed in high temperature, crystalline nanomaterials is possible directly from the liquid phase without requiring any further post synthesis calcination [37]. Additionally, in this method a stabilizer is not required as, glycolic acid, obtained from the oxidation of polyol (e.g. ethylene glycol), can be adsorbed on the surface and act as a surfactant for the metal particles [30]. The polyols also have a strong dipole and adsorb microwave energy efficiently, and this allows polyol synthesis to be performed efficiently using microwave irradiation heating, as opposed to "conventional" heating (e.g. using a heating plate). Microwave heating has a number of advantages over the conventional heating system. The microwave heating is a selective, fast, homogenous (without temperature gradient) and more efficient heating method compared to the conventional convective and conduction methods [39]. This method can reduce the time of the reaction from hours to minutes, it is more compact and safer under high pressure and temperature conditions, reduces the unwanted side-reactions, and increases reproducibly. Also it appears to be more environmentally friendly compared to the conventional method, and it has emerged as a tool in green chemistry [40,41]. Some of the catalysts synthesized with the microwave irradiation polyol method include: Pd/C [31], Pt/C [42,43], Ru/C and PtRu/C [43] for methanol electro-oxidation, Pt/C [44] and Pt/CNTs [45] for PEM fuel cell technology, copper nano-crystal [46], gold nanorods and nanowires [47], and nanowire shaped silver [48] for different areas of physics and chemistry. However, despite all the advantages the polyol method has to offer, only a few publications have reported its use for OER electrocatalyst synthesis involving Ir and IrRu catalysts [17,49].

The physical properties of the materials synthesized by the polyol method are effected by specific preparation parameters for both the conventional and microwave heating methods. Chieng and Loo [36] have shown that particle sizes of synthesized ZnO nanoparticles increases from 19.62 nm to 68.57 nm with changing the polyol type from ethylene glycol to tetraethylene glycol. Temperature and concentration have also been shown to influence the morphology of metal catalysts such as Au, Pt, Pd, and Ru [38,50]. Bock et al. [30] found that the Pt and Ru nanocatalyst particle size increased from 0.7 nm to 4 nm as the pH of the suspension was decreased from 11.1 to 7.2. Tsuji et al. showed that they could control the diameter and length of gold nanorods and nanowires by changing the concentration of metal precursor ($HAuCl_4$) in the microwave irradiation method [47]. Moreover, Knupp et al. [51] found that adjusting the water content in ethylene glycol during synthesis of Pt/CNT (carbon nanotubes), efficiently control the Pt particle size and size distribution.

In this work, iridium based species supported on ATO are synthesized using polyol method with two heating methods: conventional heating and microwave irradiation heating. The physical and electrochemical properties of the synthesized catalysts were then studied and compared using multiple physical and electrochemical characterization techniques. Additionally, the influence of operating parameters such as: temperature, solution pH, precursor metal concentration and glycol chain length, on the surface area of the iridium based

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