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Improvement of Electrochemical Activity of Pt/MWCNT Catalyst for Proton Exchange Membrane Fuel Cell

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ABSTRACT: In last years, the carbon nanotubes have been studied as an advanced metal catalyst support for proton exchange membrane fuel cell. This study focuses on the sonochemical treatment of multi walled carbon nanotubes (MWCNTs) as a platinum supporting material for proton exchange membrane fuel cell (PEMFC) by mixture of sulfuric acid and nitric acid and mixture of sulfuric acid and hydrogen peroxide. X-ray diffraction (XRD) and Infrared (IR) spectroscopy were used to characterize the surface of sonochemically treated MWCNT and nanostructured electrocatalyst Pt/MWCNT. According to the experimental results of this work, the surface of MWCNT can be more successfully functionalized with hydroxyl and carboxyl groups after sonochemical treatment by mixture of sulfuric acid and nitric acid. The particle size of prepared Pt - electrocatalyst on MWCNT was determined 3.4 nm by XRD.

Keywords: Proton Exchange Membrane Fuel Cell, Multi Walled Carbon Nano Tubes

Introduction

Carbon nanotubes (CNT) have attracted much attention due to their extraordinary electrical, mechanical and structural properties [1]. In recent years, there has been increasing interest in carbon nanotubes as heterogeneous catalyst support. Studies have shown that metal nanoparticles supported on carbon nanotubes may provide much improved catalytic activity [2].

Recently, carbon nanotubes have been proposed as promising support materials for fuel cell catalyst due to their unique characteristics, including high aspect ratio, high electron conductivity, and enhanced mass transport capability [3]. The catalytic activity of the Pt based catalysts is strongly dependent on the composition, structure,

morphology, particle size, alloying degree [4, 5] and catalyst supports [6, 7].

In many of these applications, CNTs have to be surface functionalized [8]. Among various surface functionalization techniques, oxidation is probably the most widely studied. Oxidation of CNTs has been used to remove amorphous carbon for purification purposes [9] and to open CNT ends for metal nanoparticle insertion [10]. Early treatment techniques have involved gas-phase oxidation in air and oxidative plasmas but these techniques have led to an over-oxidation of CNTs, often severely damaging the CNTs and removing the amorphous carbon in addition.

Liquid-phase oxidation involves acidic etching with nitric and/or sulfuric acids. Compared to gas-phase oxidation, this

method is mild and slow, and can provide a high yield of oxidized CNTs. For an amorphous carbon removal and end opening, oxidation damage to the surface of the CNTs is not desired [11].

Noble metals, such as Pt, Ru or Pt-Ru alloys, supported on carbon materials with high surface area are important electrochemical catalysts for PEM fuel cells. It is well known that the catalytic activities highly depend on the size and dispersion of the supported metal nanoparticles as well as the particle interactions with the support substrates [12].

Carbon black, the most common catalytic support, has good electronic conductivity, high surface area, promising electrochemical performance and stability in acidic environments [13]. However, the main reason for using CNTs as support is to reduce Pt loading through increasing the catalyst utilization and improving the catalyst activity.

Experimental

For the experiment MWCNT was taken and its surface was sonochemically treated with sulfuric and nitric acid. After the surface treatment, the MWCNT was washed with ethanol a few times. Finally, the slurry was dried in a drying oven at 70°C during overnight. After drying it was mixed with 100 ml ethylene glycol and the carbon suspension was placed in a three-necked flask. H₂PtCl₆·6H₂O dissolved in ethylene glycol was dropped gradually to the suspension of MWCNTs. The mixture was stirred for 12 hours in additionally. After that, the mixed solution was adjusted with 1M NaOH until the pH reached 12, and stirred again for 1 hour. Before the mixture was heated, a few drop of 5% nafion117 (Sigma-Aldrich) solution was added to adjusted mixture. The mixture was heated at 160°C for 3h. Prepared catalyst was washed with ethanol and then dried overnight at the temperature of 80°C. The treated catalyst support was characterized by IR method and prepared catalyst was characterized by XRD method.

Results and Discussion

Whether the functional groups were formed or not formed on the surface of multi

walled carbon nanotube before and after chemical treatment was determined by infrared spectroscopy.

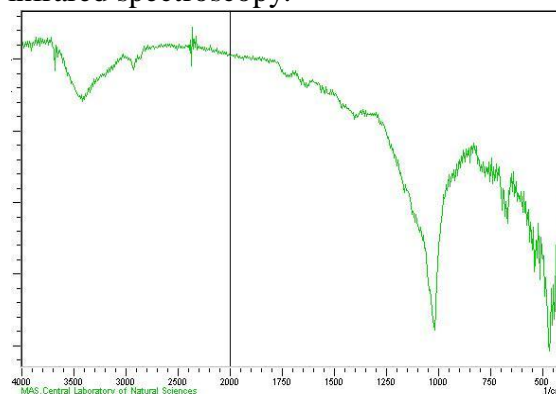


Fig 1. IR spectrum of MWCNT before the chemical treatment

In figure 1 it is shown IR spectrum of untreated MWCNT. Before chemical treatment the lines of 3223.05 and 3305.99 in IR spectrum are for NH₂ and OH groups. C-O bonds appeared in range of 1000-1250 cm⁻¹. Below 1000 aromatic compounds are coming. The carbon nanotube has many aromatic rings with -OH, -NH₂ groups that is shown a multiple structure of compounds.

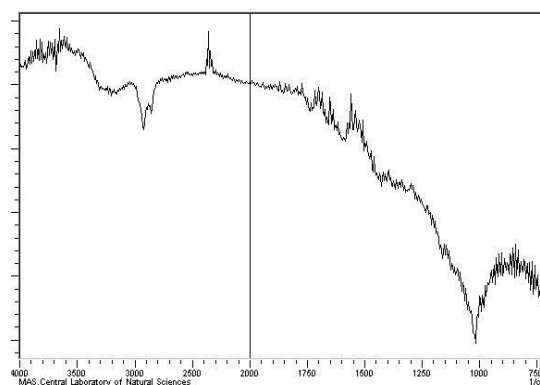


Figure 2. After treatment of Multi walled carbon nanotube with sulfuric acid and hydrogen peroxide by IR spectroscopy

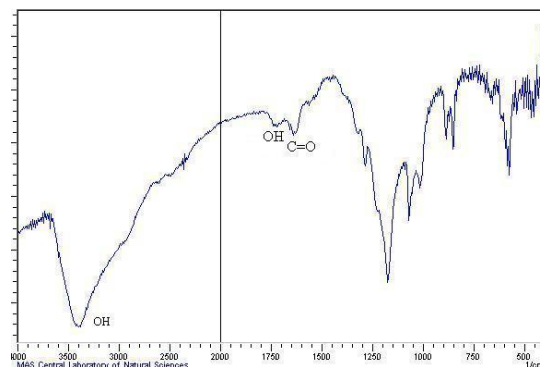


Figure 3. After treatment of Multi walled carbon nanotube with sulfuric and nitric acid by IR spectroscopy

It is shown in Figure 2, IR spectrum of multi walled carbon nanotube after sonochemical treatment with sulfuric acid and hydrogen peroxide mixture. The formation of hydroxyl group was here not so strong.

The sonochemical treatment of MWCNT with sulfuric and nitric acid was shown in figure 3. The peaks coming in range of $1700-1500\text{cm}^{-1}$ show that obviously after sonochemical treatment hydroxyl, carbonyl and carboxyl groups were formed.

The broad peak of $3500-3000\text{cm}^{-1}$ shows obviously after sonochemical treatment hydroxyl groups were formed and the treatment with sulfuric and nitric acid is more effective than the treatment with mixture of sulfuric acid and hydrogen peroxide. This can be also confirmed by XRD result. In figure 4 it is shown that after treatment with sulfuric and nitric acid the peaks of amorphous carbons are disappeared which occur in range of $2\theta=64^\circ$ and $2\theta=77.5^\circ$. After the treatment with sulfuric acid and hydrogen peroxide the peaks of amorphous carbon not completely disappeared so that the treatment with sulfuric and nitric acid gives better result than the treatment with sulfuric acid and hydrogen peroxide. For further experiment which is the preparation of electrocatalyst of Pt/MWCNT sulfuric and nitric acid treated MWCNT was used as a catalyst support.

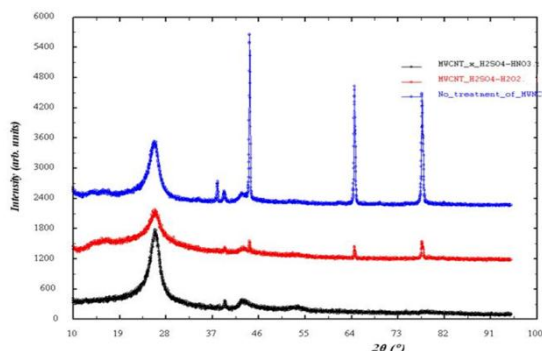


Figure 4. X-ray diffraction patterns of untreated MWCNT (1) and treated MWCNT with sulfuric acid/hydrogen peroxide (2) and sulfuric acid/nitric acid (3)

The prepared electrocatalyst of Pt/MWCNT was characterized by XRD. The XRD patterns in Figure 5 show the Pt loading of the catalyst.

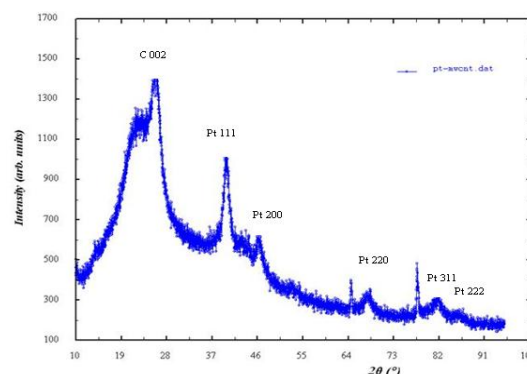


Fig 5. X-ray diffraction patterns of Pt/MWCNT catalysts

The patterns clearly show the five characteristic peaks of face centered cubic crystalline Pt namely the $2\theta=39.7^\circ$ [111], 46.2° [200], 67.4° [220], 81.2° [311] and 91.2° [222]. The first broad peak is associated with the multi-walled carbon nanotube as support material and on the XRD is not demonstrated the amorphous carbon. The average particle size of Pt was calculated by following equation (1).

$$S = \frac{360\lambda}{\pi^2 \gamma} = \frac{360 \cdot 1.54}{3.14^2 \cdot 1.654} = 3.4 \text{ nm} \quad (1)$$

Conclusions

Multi walled carbon nanotube was used as a support material for fuel cell catalysts. Its surface modification was carried out by sonochemical treatment with sulfuric and nitric acid also sulfuric acid and hydrogen peroxide. The surface was characterized by IR- spectroscopy and XRD. According to the experimental results of this work, the surface of MWCNT can be more successfully functionalized with hydroxyl and carboxyl groups after sonochemical treatment by mixture of sulfuric acid and nitric acid. Synthesized catalyst of Pt/MWCNT has the Pt particle size of 3.4 nm determined by XRD which is a relatively good result for electrocatalyst of PEMFC.

Acknowledgments

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