



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Synthesis of polypyrrole (PPy) based porous N-doped carbon nanotubes (N-CNTs) as catalyst support for PEM fuel cells

Ayşenur Öztürk^a, Ayşe Bayrakçeken Yurtcan^{a,b,*}^a Chemical Engineering Department, Atatürk University, 25240, Erzurum, Turkey^b Nanoscience and Nanoengineering Department, Atatürk University, 25240, Erzurum, Turkey

ARTICLE INFO

Article history:

Received 15 December 2017

Received in revised form

15 May 2018

Accepted 17 May 2018

Available online xxx

Keywords:

Polypyrrole

Carbon nanotubes

FeCl₃

Activation

Catalyst support

PEM fuel cell

ABSTRACT

In this study, it was aimed to synthesize catalytically active, high surface area carbon nanotubes (CNTs) by means of nitrogen doping (N-doping). The synthesized nitrogen doped carbon nanotubes (N-CNTs) were used as Pt catalyst support in order to improve oxygen reduction reaction (ORR) kinetics at the cathode electrode in PEM fuel cell. Polypyrrole (PPy) was served as both carbon and nitrogen source and FeCl₃ solution was used as oxidizing agent in the synthesis procedure of N-CNTs. Chemical activation of the materials was made with potassium hydroxide (KOH) solution during 12 and 18 h time periods. It was considered that activation period is of great importance on the properties of the synthesized PPy based N-CNTs. 12 h activated N-CNTs gave higher surface area (1607.2 m²/g) and smaller micropore volume (0.355 cm³/g) in comparison to 18 h activated N-CNTs having smaller surface area (1170.7 m²/g) and higher micropore volume (0.383 cm³/g). PEM fuel cell performance results showed that 12 h activated N-CNTs are better catalyst supports than 18 h activated N-CNTs for Pt nanoparticle decoration.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The inclusion of heteroatoms to the structures of various materials especially to carbonaceous materials has been mostly highlighted in recent publications [1–6]. The reason why the researchers so focused on this topic is taking advantage of created defects by heteroatoms in the structure of the host material. These defects generally are the sources of new catalytic active sites especially for electrochemical reactions. For this reason, the electrochemical properties of main material will change positively in order to obtain better performance results. The possibility of increasing the catalytic

activity of materials without using expensive and scarce metals is an exciting point about the reaction kinetics. So far, nitrogen has been favored in the scope of heteroatom-doping studies. It is accepted that nitrogen doping to the material usually changes its structural and electrochemical properties. Nitrogen bond forms and concentration of nitrogen atoms within the carbon bulk structure generally manipulate the properties of the host material. Even more important point is that how the electronic properties of the carbonaceous material will change owing to new structural geometry associated with the inclusion of nitrogen atoms [7].

There are a lot of studies that mention about the positive effects of nitrogen doping to carbonaceous materials

* Corresponding author. Chemical Engineering Department, Atatürk University, 25240, Erzurum, Turkey.

E-mail address: ayse.bayrakceken@gmail.com (A.B. Yurtcan).

<https://doi.org/10.1016/j.ijhydene.2018.05.106>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

especially for oxygen reduction reaction (ORR). Preferentially, carbon nanotubes (CNTs) thematic studies were chosen as references because this work is also related to the synthesis of nitrogen doped carbon nanotubes (N-CNTs). Chen et al. [8] synthesized N-CNTs with chemical vapor deposition (CVD) by using pyridine, ethanol and ferrocene solutions. They evaluated the relation between the nitrogen content and ORR catalytic activity of the produced N-CNTs. The authors concluded that high ORR activity can be obtained by adjusting nitrogen amount higher in stock solution during the synthesis of N-CNTs. Li et al. [9] compared their synthesized product of multiwalled N-CNTs with commercial Pt/C and Ag/C catalysts in terms of catalytic activity and durability towards ORR by cyclic voltammetry (CV). They found that N-CNTs are capable to compete with Pt/C catalyst and better than Ag/C catalyst in alkaline environment. N-CNTs also maintained stability even though they were exposed to potential cycling for 3500 cycles in oxygen saturated electrolyte. Oh et al. [10] functionalized hydrophobic graphitized carbon nanotubes with polypyrrole in order to make CNTs hydrophilic without giving any damage to original structure of CNTs. As a catalyst support, polypyrrole coated CNTs provided uniform distribution of Pt particles over the surface and showed stable resistance to electrochemical carbon corrosion. 1.71 mA/cm² current density was obtained with the cell including PPy-coated CNTs supported Pt catalyst at 0.6 V cell potential.

Different nitrogen containing polymers are commonly used as nitrogen precursor during the synthesis of N-doped materials. Polypyrrole, polyaniline, polyacrylonitrile, acetonitrile, melamine, urea are mostly encountered precursor materials in this context [11–13]. Liu et al. [14] prepared N-CNTs by pyrolysis of functional tubular polypyrrole at different temperatures such as 700 °C, 800 °C and 900 °C under N₂ flow. It was stated that Pt catalyst supported with N-CNTs pyrolyzed at 800 °C is capable to compete with the commercial Pt/C catalyst in terms of ORR catalytic activity. Incorporation of transition metal species to the structure creates different binding forms of nitrogen (pyrrolic, pyridinic, graphitic, oxidized-N) that serve as catalytically active points located generally at edge plane sites [11]. For this reason, abundant iron and cobalt particles are the most commonly used transition metals in the synthesis of N-doped structures and/or non-precious ORR catalysts [15]. Iron particles promote CNT growth and stabilize nitrogen groups during CNT synthesis. Liu et al. [15] synthesized Fe–N-CNTs as non-precious catalyst for ORR by following sequent experimental steps: pyrolysis of ferric chloride and dicyandiamide, polymerization of pyrrole monomer and calcination at different temperatures (700 °C, 800 °C, 900 °C) under N₂ atmosphere. According to the rotating disk polarization curves, superiority of Fe–N-CNTs-PPy-800 CNTs (0.995 V; onset potential, 0.855 V; half wave potential) over commercial Pt/C (20%) catalyst (0.965 V; onset potential 0.835 V; half wave potential) was pointed out for ORR in alkaline media. Activity of any catalyst material can be evaluated depending on its onset potential and half wave potential (the potential measured at the half of diffusion current) [16].

Because of the fact that carbon supported Pt catalysts suffer from the degradation of support material during the long term operations in PEM fuel cell environment, the higher stability of CNTs make them as a promising Pt catalyst

support in PEM fuel cells. The catalytic properties of CNTs can also be modified positively in the light of above mentioned informations about N-doping. In this study, we aimed to synthesize both stable and catalytically active polypyrrole derived N-CNTs in order to be used as Pt catalyst support in PEM fuel cell. The produced N-CNTs differ from each other by chemical activation with KOH solution at different time periods. The activation durations were set as 12 h and 18 h in this step of the synthesis.

Materials and methods

Synthesis of N-doped carbon nanotubes (N-CNTs)

In this study, experimental procedure developed by Pan et al. [17] was followed in order to synthesize N-CNTs. Pyrrole (0.14 mol; reagent grade 98%, Aldrich), 50 mL FeCl₃ (0.2 mol; Iron (III) chloride crystal pure, Merck) aqueous solution, p-toluene sulfonic acid (0.2 mol; p-toluene sulfonic acid monohydrate 98%, Alfa Aesar) were used as main materials to start chemical oxidative polymerization of pyrrole. After polymerization, filtration and drying were carried out, the obtained powder was activated by KOH (potassium hydroxide pellets, Merck) aqueous solution (5 M) in a 50 °C water bath. In this study, activation time periods were extended to 12 h and 18 h as opposed to Pan et al. [17] which they maintained activation duration only 3.5 h. At the end of the activation time, suspension was cooled to room temperature. After then, filtration, washing and drying were implemented again. Activated powder was annealed at 900 °C by passing continuously N₂ gas through tube furnace during 2 h. The obtained powder was treated with (0.5 M) HCl (Hydrochloric acid, fuming 37%, Merck) aqueous solution in order to remove alkaline species and subsequently washed with distilled water until reaching nearly pH value of 7. After the last drying at 70 °C for 12 h, approximately 1600 mg N-CNTs were obtained as final product. In this study, separately synthesized two N-CNTs differ from each other by different activation durations such as 12 h and 18 h, respectively.

Platinum (Pt) catalyst loading on the synthesized N-CNTs

N-CNTs were synthesized in order to be used as Pt catalyst support in PEM fuel cell cathode electrode. Thus, H₂PtCl₆ (Chloroplatinic acid hydrate, ≥ 99.9%, Aldrich) salt was reduced in ethylene glycol by microwave irradiation in order to load these N-CNTs with Pt metal. Nores-Pondal et al. claimed that reduction in ethylene glycol by means of microwave irradiation provides obtaining a catalyst with high Pt utilization; which almost competes with commercial catalyst in terms of electrochemical activity [18]. 0.05 M H₂PtCl₆ solution and 100 mg related support material were mixed in 50 mL ethylene glycol (≥99.0%, Merck) for 30 min. Afterwards, the solution was held in a microwave oven at 800 W for 1 min in order to reduce Pt metal on support material. 20 % wt. Pt loading over each support was targeted. Subsequent to microwave irradiation exposure, the solution was cooled instantly, filtrated, washed with acetone (99.5%, BRP Chemistry) and distilled water for three times and then finally dried at 100 °C in a drying oven.

Download English Version:

<https://daneshyari.com/en/article/11011593>

Download Persian Version:

<https://daneshyari.com/article/11011593>

[Daneshyari.com](https://daneshyari.com)