ATATÜRK ÜNİVERSİTESİ YAYINLARI
ATATURK UNIVERSITY PUBLICATIONS

NanoEra

Research Article

DOI: 10.5152/NanoEra.2023.1277591

Platinum/Vulcan XC-72R Electrocatalyst Doped with Melamine for Polymer Electrolyte Membrane Fuel Cells

Pınar ÇELİK
Ayşe BAYRAKÇEKEN YURTCAN

Atatürk University, Engineering Faculty, Chemical Engineering, Erzurum, Türkiye

ABSTRACT

Polymer electrolyte membrane fuel cells are the common type of fuel cells for stationary and portable applications. The main purpose of fuel cell research and development studies is to develop low-cost, high-performance, and durable materials. For this purpose, higher performance is targeted by reducing the cost of polymer electrolyte membrane fuel cell electrocatalysts. The use of carbon black in polymer electrolyte membrane fuel cells has been quite high in recent years. In this study, first platinum on carbon black electrocatalyst was synthesized via microwave irradiation method and then melamine as nitrogen source at a mass ratio of (1:1) for melamine:electrocatalyst was prepared. Examining the physicochemical and electrochemical characterizations of the electrocatalyst is very important for understanding their performance, durability, and material properties. Therefore, the synthesized electrocatalyst was characterized by using elemental analysis, inductively coupled plasma mass spectrometry and transmission electron microscope analysis. In addition, the fuel cell performance of the electrocatalyst was tested in a single fuel cell test hardware.

Keywords: PEMFC, electrocatalyst, nanoparticles, nitrogen doping, melamine

INTRODUCTION

Fuel cells are systems that convert chemical energy directly into electricity.[1] Fuel cells are divided into different groups according to the type of reactants used, electrolyte type, and operating temperatures.[2,3] Among the various fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) stand out with their features such as high power density,[4] low operating temperatures (60-80°C),[5] high reliability,[2] fast start-up times, [5,6] and zero/low emissions.[7] However, despite all these advantages, the main disadvantage of PEM fuel cells is their cost. In recent years, scientists have carried out different studies in order to commercialize PEM fuel cell technology and increase its performance.

The PEM fuel cells are composed of PEMs to provide proton conductivity and electrocatalysts for half-cell reactions.[8] One of the reasons for using platinum-based electrocatalysts in PEM fuel cells is their oxygen reduction reaction (ORR) activities and their relatively high stability in the acidic and oxidizing environment of the PEMFC cathode.[9] Due to the high cost of platinum (Pt), several studies were carried out in order to decrease the amount of Pt.[10] The electrocatalyst preparation method affects the pore size, surface area, morphology and physical properties of the synthesized electrocatalysts whereas the structure and composition of the support material and active catalytic component affects the chemical properties.[11] Commonly used carbon supports provide new active sites to increase the catalytic activity.[12] Pre-treatment of carbon materials can significantly increase their catalytic activity for ORR and change their electrochemical behavior.[13-15] One of these pre-treatments is the doping of carbon materials with heteroatoms such as nitrogen. Nitrogen doping on carbon support materials can be performed using the pyrolysis method.[16] In recent years, nitrogen-doped carbon materials have been widely used as support materials in fuel cell electrocatalysts for the homogeneous distribution of Pt nanoparticles. It was also suggested that nitrogen doping provides improvements for ORR in Pt/carbon (C)-based fuel cell electrocatalysts.[17] Nitrogen doping with melamine has positive effects on the performance of supercapacitors and energy storage devices.[18,19]

In the literature, mostly nitrogen doping is applied to the electrocatalyst support materials. In this study, our goal is to reduce the amount of platinum electrocatalyst and increase the performance of the fuel cell by doping the electrocatalyst other than the support material. First, the carbon black support material (Vulcan XC-72R, VXR) was decorated with Pt nanoparticles by microwave irradiation method and Pt/VXR electrocatalyst was obtained. Pt/VXR was mechanically mixed with melamine due to its high nitrogen content of 66.7%[20,21] at a mass ratio of 1:1 and after pyrolysis, the (Pt/VXR) + melamine-(1:1) electrocatalyst was obtained for PEMFC.

Received: April 5, 2023

Accepted: May 15, 2023

Publication Date: 23.06.2023

Corresponding author:
Ayşe BAYRAKÇEKEN YURTCAN
E-mail: abayrakceken@atauni.edu.tr

Cite this article as: Çelik P, Bayrakçeken Yurtcan A. Platinum/vulcan XC-72R electrocatalyst doped with melamine for polymer electrolyte membrane fuel cells. *NanoEra* 2023;3(1):16-19.

EXPERIMENTAL

Synthesis of Nitrogen-Doped Electrocatalyst

In the synthesis of nitrogen-doped electrocatalyst, first Pt nanoparticles were deposited on carbon black (Vulcan XC-72R, VXR) support material by microwave irradiation method. The nominal amount of Pt targeted on the support material is 20%. After the Pt reduction process on the support material, it was washed and then dried for 12 hours at 100°C. After drying, Pt/VXR electrocatalyst and melamine were mixed mechanically with a mass ratio of 1:1 and then pyrolyzed for 2 hours at 900°C in a nitrogen gas environment. The synthesized electrocatalyst was used at the cathode side and commercial Pt/C electrocatalyst (Tanaka, 67%) was used at the anode side. The anode, cathode, and the membrane were hot pressed to prepare the membrane electrode assembly (MEA).

Characterizations

It is expected that the electrocatalysts prepared for use in the PEM fuel cell will have features such as high activity, high selectivity, and stability. It is very important to understand the physicochemical and electrochemical characterizations of the structures of the electrocatalysts in order to achieve these properties. In this study, the structures of the synthesized electrocatalysts were investigated using physicochemical and electrochemical characterization techniques.

The LECO CHNS 628 model Elemental Analyzer was used to quantitatively determine the amount of nitrogen in the synthesized electrocatalyst. Inductively coupled plasma-mass spectrometry (ICP-MS) Agilent 7800 device was used to determine the amount of Pt over the support material, while Hitachi HighTech HT7700 device was used for transmission electron microscope (TEM) analysis. Finally, the prepared electrocatalyst was turned into MEA and its performance was tested under atmospheric pressure in a fuel cell station (HenatechTM, 600 W).

RESULTS AND DISCUSSION

Elemental Analysis Result

The nitrogen amount of the electrocatalyst was analyzed by using elemental analysis. Element analysis data are given in Table 1. According to this process, the nitrogen amount of (Pt/VXR) + melamine-(1:1) electrocatalyst is obtained as 2.67%. From the results obtained, it is seen that the nitrogen doping process with the pyrolysis method is successful. The nitrogen amount change will significantly affect the activity of the electrocatalyst.[22]

Inductively Coupled Plasma-Mass Spectrometer Analysis Result

Inductively coupled plasma-mass spectrometer analysis was performed to obtain information about the Pt loading amount in the synthesized Pt/VXR + melamine-(1:1) electrocatalyst. The targeted nominal amount of Pt on the support material in the prepared electrocatalyst is 20%. The ICP-MS result is given in Table 2. According to this table, the loaded Pt (% by mass) amounts were obtained as 13.9% which was lower than the nominal value.

Transmission Electron Microscope Result

The Pt nanoparticle distribution over carbon support material and particle size of Pt nanoparticles in the synthesized electrocatalyst were analyzed by TEM analysis. The TEM image of the electrocatalyst at 50 nm and the particle size histogram plot are given in Figure 1. Particle sizes were calculated from TEM images by using the ImageJ program. It was seen that the sizes of Pt nanoparticles loaded on the carbon support have an average of 7 nm.

Polymer Electrolyte Membrane Fuel Cell Test Results

(Pt/VXR) + melamine-(1:1) electrocatalyst was tested in a PEM fuel cell test station using a single fuel cell hardware. The polarization curve for the corresponding electrocatalyst is given in Figure 2. It is more appropriate to evaluate the performance of

Table 1. Elemental Analysis Result

	Elements, %			
Electrocatalyst	C (%)	H (%)	N (%)	S (%)
(Pt/VXR) + melamine-(1:1)	78.46	1.2	2.67	0.43

Pt/VXR, platinum/Vulcan XC-72R.

Table 2. ICP-MS Result

Electrocatalyst	Pyrolysis Temperature (°C)	Pt (% by Weight)
(Pt/VXR) + melamine (1:1)	900	13.9

ICP-MS, inductively coupled plasma-mass spectrometry; Pt/VXR, platinum/Vulcan XC-72R.

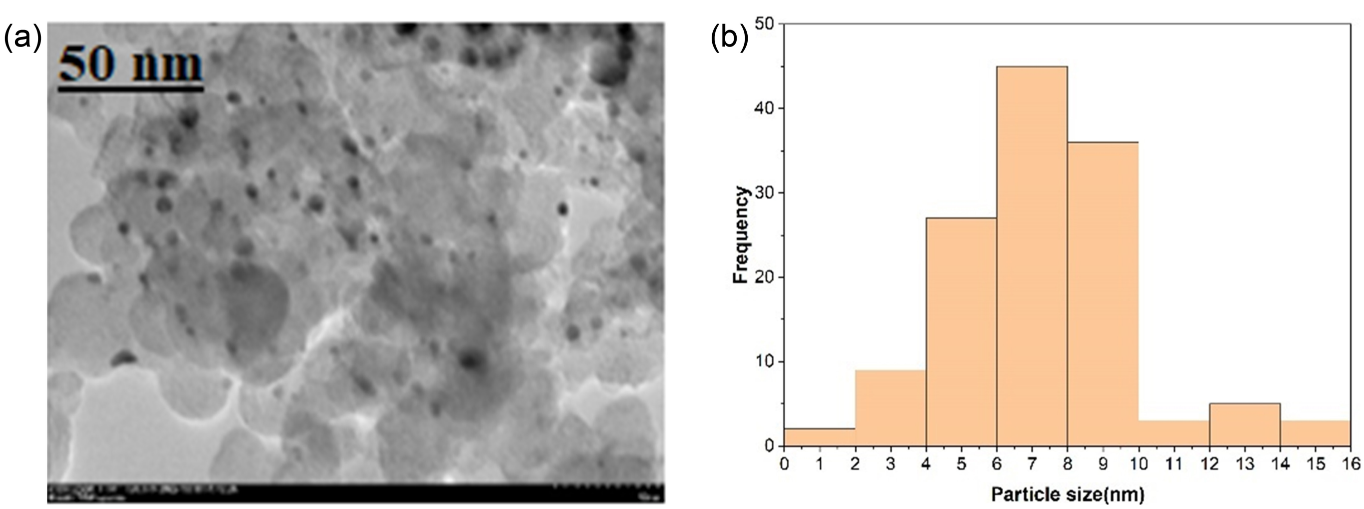

Figure 1. (Pt/VXR) + melamine-(1:1) electrocatalyst (A) TEM image at 50 nm; (B) particle size histogram. Pt/VXR, platinum/Vulcan XC-72R; TEM, transmission electron microscope.

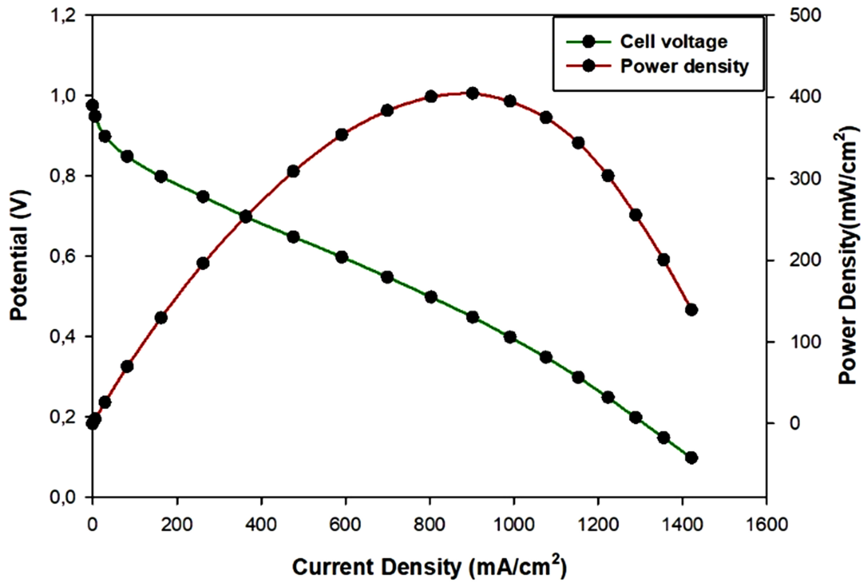

Figure 2. PEM fuel cell polarization curve. PEM, polymer electrolyte membrane.

Table 3. Current and Power Density Values at 0.6 V for (Pt/VXR) + Melamine-(1:1) Electrocatalyst

	@ 0.6 V	
Electrocatalyst	*i* (mA/cm2)	*P* (W/cm2)
Pt/VXR + melamine-(1:1)	591.3	353.6
Pt/VXR	513.2	306.9

Pt/VXR, platinum/Vulcan XC-72R.

the electrocatalyst layer at 0.6 V, as it generally strikes a balance between fuel cell efficiency and practical power output.[23] For this reason, the current and power density values corresponding to the PEM fuel cell performance of the electrocatalyst prepared using Pt/VXR and melamine at a mass ratio of 0.6 V (1:1) and the Pt/VXR values prepared without adding melamine in order to make comparisons are summarized in Table 3. According to the graph in Figure 2, the measured values of (Pt/VXR) + melamine-(1:1) electrocatalyst at 0.6 V were obtained as 591.3 mA/cm^2 current density and 353.6 mW/cm^2 power density which was higher than the melamine-free electrocatalyst.

CONCLUSIONS

According to the elemental analysis results, nitrogen doping with the pyrolysis process was successful, but the Pt loading on the support material was lower than the nominal value. In TEM analysis, it was observed that Pt nanoparticles showed a homogeneous distribution on the electrocatalyst surface. The PEM fuel cell performance test shows a current density of 591.3 mA/cm^2 and a power density of 353.6 mW/cm^2 for the (Pt/VXR) + melamine-(1:1) electrocatalyst based on values measured at 0.6 V. The melamine-free Pt/VXR catalyst synthesized under the same conditions (with the same Pt loading rate and pretreatment) showed a current density of 513.2 mA/cm^2 and a power density of 306.9 mW/cm^2, according to the values measured at 0.6 V. (Pt/VXR) + melamine-(1:1) catalyst showed better fuel cell performance than melamine-free Pt/VXR catalyst. According to the results obtained from the fuel cell performances, it can be said that nitrogen doping of the electrocatalyst seems to be a promising way.

Peer-review: Externally peer-reviewed.

Author Contributions: Concept – P.Ç., A.B.Y.; Design – A.B.Y.; Supervision – A.B.Y.; Resources – P.Ç., Materials – P.Ç., A.B.Y.; Data collection and/or Processing – P.Ç.; Analysis and/or interpretation – P.Ç., A.B.Y.; Literature research – P.Ç.; Writing manuscript – P.Ç., A.B.Y.; Critical review – P.Ç., A.B.Y.

Acknowledgments: The authors thank the East Anatolia High Technology Application and Research Center (DAYTAM) for the ICP-MS and TEM characterizations of the synthesized electrocatalyst and the Atatürk University Science Faculty Chemistry Department for elemental analysis.

Declaration of Interests: The authors declare that they have no competing interest.

Funding: The authors declared that this study has received no financial support.

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