



Pd/C CATALYSTS SYNTHESIZED BY MICROWAVE ASSISTED POLYOL METHOD FOR FORMIC ACID ELECTRO-OXIDATION

¹Özlem GÖKDOĞAN ŞAHİN

¹Selçuk University, Faculty of Engineering, Chemical Engineering Department, Campus, Konya, TURKEY
ozlem@selcuk.edu.tr

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ABSTRACT: Synthesis of carbon supported palladium particles based on a polyol process was investigated. The activity of Pd catalysts, synthesized by microwave assisted polyol method on carbon support, has been examined for formic acid electro-oxidation reaction. The catalysts were characterized with XRD to identify their nanostructure properties. The effect of catalyst preparation parameters on electrocatalytic performance of catalysts was examined. The electrocatalytic properties of Pd/C catalysts for the oxidation of formic acid were investigated by cyclic voltammetry (CV). The electrocatalytic activity of Pd/C synthesized at 30 s and 130 °C are higher than the other Pd/C catalysts synthesized at different temperature and reaction time. It is proposed that the longer reaction time and higher temperature increased the particle size.

Key Words: Formic acid electro-oxidation, Palladium catalysts, Polyol method, Preparation conditions, Fuel cells

Mikrodalga Destekli Poliöl Yöntemiyle Sentezlenen Pd/C Katalizörler için Formik Asit Elektro-Oksidasyonu

ÖZ: Karbon destekli paladyum parçacıklarının sentezi poliöl prosesi ile gerçekleştirildi. Mikrodalga destekli poliöl yöntemi ile sentezlenen Pd katalizörlerin formik asit elektrooksidasyon reaksiyonu için aktivitesi araştırıldı. Katalizör yapıları XRD ile karakterize edildi. Katalizör hazırlama parametrelerinin katalizörlerin elektrokatalitik performansına etkisi incelendi. Formik asitin oksidasyonu için Pd/C katalizörlerin elektrokatalitik özellikleri dönüşümlü voltametri (CV) ile incelendi. 30 s ve 130 °C'de sentezlenen Pd/C katalizörünün elektrokatalitik aktivitesinin, farklı sıcaklık ve reaksiyon zamanlarında sentezlenen diğer Pd /C katalizörlerinden daha yüksek olduğu bulundu. Artan reaksiyon süresinin ve sıcaklığın parçacık boyutunu arttırdığı düşünülmektedir.

Anahtar Kelimeler: Formik asit elektrooksidasyonu, Paladyum katalizörler, Hazırlama şartları, Poliöl metodu Yakıt hücreleri.

INTRODUCTION

The over-consumption of fossil fuels leads to environmental problems. Therefore, it is necessary to develop new power sources. As a high-efficiency energy conversion device, fuel cells have significant role in the energy utilization sector.

Hydrogen is often seen as an ideal fuel for fuel cells due to its ease of oxidation. However, the generation and storage of hydrogen is very difficult. Therefore, the use of liquid fuels such as methanol, ethanol or formic acid is an attractive way for the direct fuel cells.

Direct formic acid fuel cells (DFAFCs) have been investigated as potential power sources owing to their high theoretical energy density, fast oxidation kinetics, easy storage and low crossover effect through the nafion membrane (Zhu et al., 2004). Pt catalysts have been studied extensively for formic acid electro-oxidation. However the electro-oxidation of formic acid at the Pt catalyst is generally through the indirect pathway and Pt is easily poisoned by CO at lower potential. Therefore researches have been made to overcome the CO poisoning and improve the electrocatalytic activity of Pt (Mazumder et al., 2010). The use of bimetallic catalysts by alloying Pt with other metals is an effective way to solve the catalyst poisoning problem on formic acid electro-oxidation (Nethravathi et al., 2011). However CO could accumulate during long time operation and reduce the cell efficiency. In recent years, much attention has been focused on Pd based catalysts for formic acid oxidation. Pd-based catalysts are considered better catalysts for formic acid oxidation due to their high catalytic activity compared with Pt-based catalysts. The electro-oxidation of formic acid at the Pd catalysts is mainly through the direct pathway that means no formation of poisoning intermediates (Antolini, 2009). Moreover, Pd is more abundant and less expensive than Pt (Zhang et al., 2011).

The preparation method has great influence on the catalytic activities and properties of catalysts. At present palladium nanoparticles were synthesized using various methods such as polyol (Wang et al., 2015), electrochemical deposition (Sarto et al., 2014), chemical reduction (Shao et al., 2006) and hydrothermal (Guo et al., 2012) method. Among these methods, polyol synthesis is known very promising method for the preparation of metal catalysts. However, the polyol method with conventional heating needs a long preparation time. It has been known that using microwave heating provides selective, time and energy consuming synthesis (Harish et al., 2012; Husin et al., 2014).

In this study, the microwave assisted polyol method was used to synthesize the Pd nanoparticles supported on carbon black (Pd/C) catalysts for formic acid oxidation. A series of catalysts were synthesized to optimize the preparation conditions such as microwave heating time and temperature. The catalytic activities of prepared catalysts for formic acid oxidation were investigated by cyclic voltammetry.

EXPERIMENTAL

Preparation of catalysts

Pd/C catalysts were prepared by microwave- assisted polyol process in ethylene glycol 99.9%, J.T.Baker) with PdCl₂ (98%, Sigma-Aldrich). Carbon powder and 4.0 M HNO₃ (98% Sigma-Aldrich) was impregnated with aqueous solutions of Pd. 4 mL of 0.12 M KBr (99% Sigma-Aldrich) and appropriate amount of NaOH (Merck) was put into the above mixture to obtain a solution with a pH of 11 and then heated in a domestic microwave oven (Electrolux Ems model 21400W, 2450 MHz, 800 W). The temperature was measured by using an Infrared Thermometer Cole Palmer 800-323-4340.

Finally, the samples were filtered, washed and dried in a vacuum oven for 2 hours. The preparation conditions of different catalysts were shown in Table 1.

Table 1. Catalyst preparation conditions

No	Catalysts	Catalyst preparation conditions	
		Temperature (°C)	Time (s)
1	Pd/C	30	30
2	Pd/C	50	30
3	Pd/C	75	30
4	Pd/C	100	30
5	Pd/C	130	30
6	Pd/C	190	30
7	Pd/C	200	30
8	Pd/C	130	10
9	Pd/C	130	30
10	Pd/C	130	60

Preparation of catalyst modified electrodes

The bare glassy carbon electrode was polished carefully with alumina slurry and then washed with water. For the modification of electrode, 5 mg of catalyst was added into 1 mL of 0.5% Nafion solution to get catalyst mixture. Then, 3 mL of the mixture was pipetted onto the cleaned GCE. Finally, the modified electrode was dried under room temperature to evaporate the solvent.

Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode cell using a CHI 6043d electrochemical workstation at room temperature. A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The working electrode was a glassy carbon disk with a diameter of 3.0 mm. Cyclic voltammograms were recorded in 0.5 M H₂SO₄ solution on Pd/C catalysts at different preparation conditions. The formic acid oxidation reactions on the Pd/C catalysts were performed in 0.5 M H₂SO₄ + 1 M HCOOH. In all experiments, the electrolyte was previously saturated by nitrogen. To measure the activity of formic acid electrooxidation reaction, cyclic voltammograms were recorded between -0.25 V and 1.0 V vs. Ag/AgCl with a scan rate of 50 mV s⁻¹.

RESULTS and DISCUSSION

In this study, catalyst preparation is done by microwave assisted polyol synthesis method in microwave oven at different preparing conditions. The influence of heating temperature (30-200 °C) and time (10-60 s) on the particle size and the activity of the catalyst have been evaluated. The temperature and microwave heating time in oven has great influence on the catalysts structure and consequently on formic acid electro-oxidation activity.

The effect of heating temperature

First, the carbon supported Pd catalysts were kept in the microwave oven at different temperatures, keeping the heating time constant (30 s). This process was carried out to investigate the effect of the temperature on catalyst activity for formic acid electro-oxidation. For this aim Pd catalysts were synthesized in the microwave oven at seven different temperatures ranging from 30 to 200 °C.

The electrochemical characterization of Pd/C electrocatalysts prepared at different temperatures was evaluated by cyclic voltammetry in the 0.5 M H₂SO₄ solution. The cyclic voltammograms for formic acid electro-oxidation was recorded at a scan rate of 50 mV/s (Fig. 1a). Highest current value of hydrogen adsorption-desorption peaks was obtained for the Pd/C catalyst synthesized at 130 °C.

The cyclic voltammograms for formic acid electro-oxidation was also evaluated on Pd/C catalysts prepared with different temperatures in 0.5 M H₂SO₄+ 1.0 M HCOOH solution. As shown in Fig. 1b, the electro-oxidation peak currents increase with the temperature up to 130 °C. This result was attributed to the increase in the size of Pd nanoparticles with temperature. However, further increase in temperature resulted in the formation of particle aggregation.

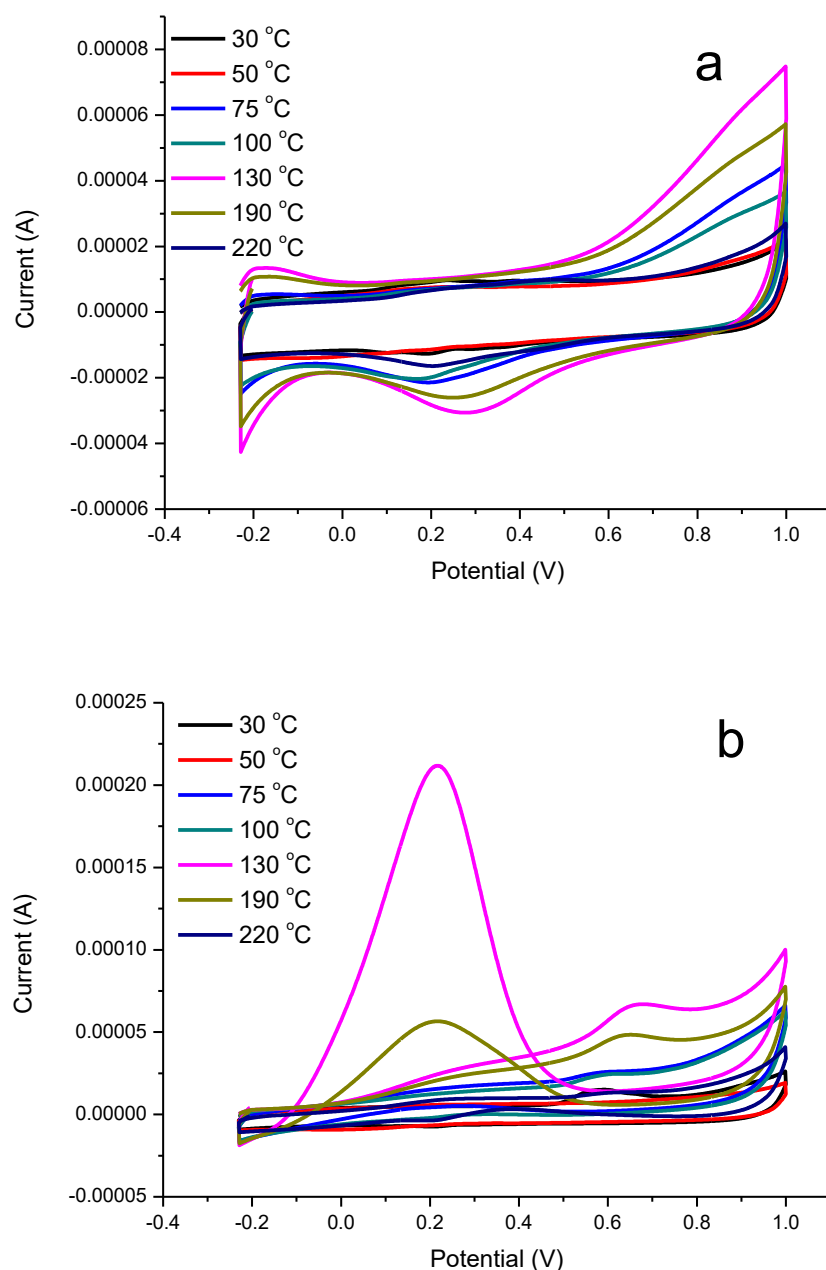


Figure 1. Cyclic voltammograms on Pd/C with different microwave heating temperature in an N₂-saturated solution of 0.5 M H₂SO₄ (a), 0.5 M H₂SO₄+1.0 M HCOOH (b). Scanning rate: 50 mV/s

The effect of heating time

Another important parameter affect the catalyst preparation is microwave heating time. After the optimum catalyst preparation temperature was determined, carbon supported Pd catalysts were

prepared at different heating times. Thus, three different catalysts were synthesized at a temperature of 130 °C for 10, 30 and 60 s.

XRD pattern of these catalysts were shown in Fig. 2. XRD pattern of these catalysts exhibits a diffraction peak at around 20° value, related to the (002) reflection of the structure of hexagonal carbon (JCPDS card no 75-1621). Furthermore, XRD pattern of these catalysts have (111), (200), (220), and (311) planes, revealing that this catalyst Pd face-centered cubic (fcc) structure (JCPDS card no 46-1043). According to the XRD data, the catalysts prepared with the increasing time has been getting narrower that is attributed to the increase in the size of the particles with time.

The cyclic voltammograms (Fig. 3) for formic acid electro-oxidation was also recorded for Pd/C catalysts prepared with different heating time. The highest formic acid electrooxidation current has been obtained for 30 s heating time.

The above results indicated that the size of the palladium particles increases with time .Further increase in microwave heating time resulted agglomeration of palladium particles. When the particles are too small, crystallinity is not suitable for adsorption of formic acid on the Pd surface. If the particles are large, electrochemical active surface will decrease. The Pd/C catalysts synthesized at 30 s heating time has better catalytic performance for formic acid oxidation than the other synthesized palladium catalysts.

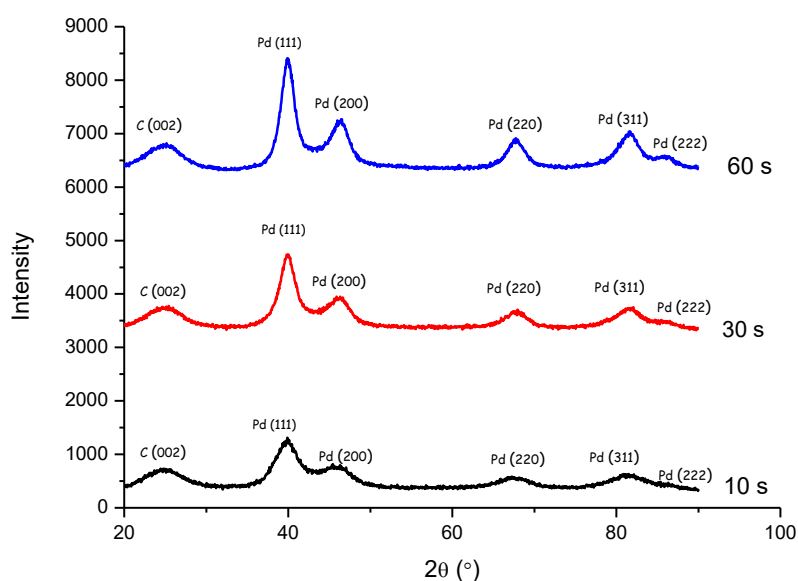


Figure 2. XRD patterns of catalysts prepared different heating time.

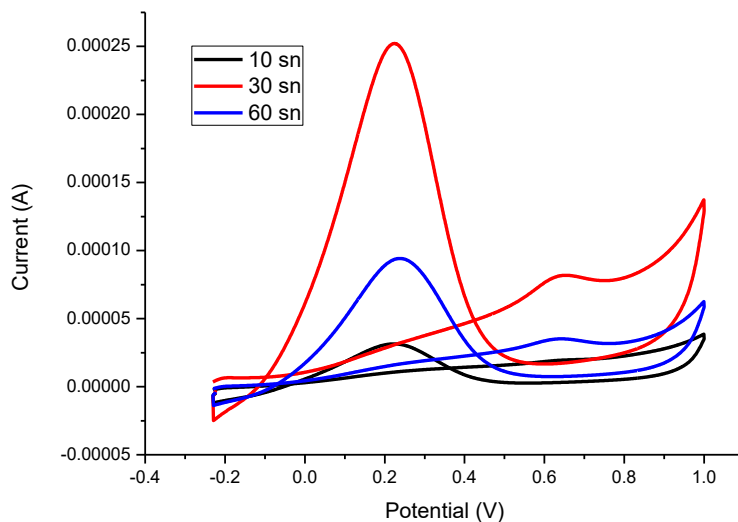


Figure 3. Cyclic voltammograms on Pd/C with different microwave heating time in an N₂-saturated solution of 0.5 M H₂SO₄+1.0 M HCOOH. Scanning rate: 50 mV/s

CONCLUSION

In summary different size of carbon supported Pd catalysts were prepared by microwave assisted polyol method and characterized by XRD technique. The electrocatalytic properties of the synthesized materials were investigated with cyclic voltammetric technique. Study on the electro-oxidation of formic acid on the catalysts showed that Pd/C catalysts prepared with 30 s microwave heating time at 130 °C temperature has much higher catalytic activity than the other Pd/C catalysts prepared at different preparation conditions. The longer microwave heating time and higher reaction temperature increased the size of palladium nanoparticles.

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