RESEARCH ARTICLE

Formic Acid and Methanol Oxidation for Pt/C Catalyst Depending on Rotating Speed, Scan Rate and Concentration

M. Selim Çögenli^a, Ayşe Bayrakçeken Yurtcan^{a,b*}^aGraduate School of Science, Department of Nanoscience and Nanoengineering, Ataturk University, Erzurum 25240, Turkey^bFaculty of Engineering, Department of Chemical Engineering, Ataturk University, Erzurum 25240, Turkey

Abstract

The oxidation of small organic molecules on the catalyst under electrocatalytic conditions is important for the operation of liquid feed fuel cells. The basic reaction mechanisms toward the oxidation of methanol and formic acid continue to be a matter of debate under real operational conditions of electrochemical systems. The electrocatalytic activity of the commercial Pt/C catalyst was investigated in sulfuric acid/methanol and sulfuric acid/formic acid mixtures using electrochemical measurements. This work presents the variation of formic acid and methanol oxidation on the catalyst depending on hydrodynamic conditions using the rotating disk electrode. Cyclic voltammograms were obtained at different scan rates, rotating speeds and concentrations. As the rotating speed increases, the oxidation activity of formic acid and methanol decrease under voltammetric measurements. The peak currents of formic acid and methanol oxidation increased with the increase in the scan rate and concentration.

Keywords: Formic acid oxidation, Methanol oxidation, Cyclic voltammetry, Rotating speed, Scan rate

1. Introduction

Organic compounds such as formic acid and methanol have the simplest structure of all the possible organic fuels. Numerous publications exist in the literature with the intention of establishing the reaction mechanism and kinetics of the oxidation of formic acid and methanol molecules on platinum-based catalysts [1, 2]. The platinum catalyst is easily poisoned by intermediates from the oxidation of the organic fuels, thus significantly limiting the activity. The oxidation of formic acid is known to exhibit a dual path mechanism [3], where the direct oxidation to CO₂ occurs without formation of poisoning species such as CO. The indirect path occurs through formation of adsorbed CO, which blocks the direct oxidation and limits the activity of the catalyst. Strong evidence has been put forth that the oxidation of methanol can happen through different pathways: a serial pathway where this poisoning species is an intermediate in the oxidation, and parallel pathways where methanol is oxidized via short-lived intermediates to a stable oxidation product [4]. A multi-path mechanisms for methanol and formic acid oxidation shown in Figure 1 has been proposed to account for the data available in the literature [5, 6].

Cyclic voltammetry (CV) measurements are taken to determine the oxidations of methanol and formic acid. There are two well-defined peaks for methanol oxidation at the forward and backward scans were obtained for the catalysts (except some metals), the right peak and the left peak, which were produced by the forward and backward sweeps, respectively [7]. There are two peaks at forward scan and one peak at backward scan for formic acid oxidation. Second forward peak shows the oxidation of the poisoning intermediate while the first forward

peak shows the direct oxidation of formic acid. In addition to, on the backward scan, the reduction of the electrode surface provides active sites for the direct pathway to yield peak [3].

Figure 1. A schematic representation of the pathways for methanol and formic acid oxidation on platinum catalyst

The most common technique for investigating the catalytic activity of the catalysts for alcohol oxidation in both alkaline and acidic media is CV. In the CV measurements, the alkaline experiments are usually carried out with NaOH or KOH, whereas in acidic experiments H₂SO₄ or HClO₄ are used as the electrolytes [8]. In addition to the use of different electrolytes, the CV operating temperature, rotating speed, scan rate and electrolyte concentration are significant parameters that affects the formic acid and methanol oxidation [9].

*Corresponding Author: ayse.bayrakceken@gmail.com
(A. Bayrakçeken Yurtcan)

Received 13 Dec 2019 Revised 16 Dec 2019 Accepted 17 Dec 2019
Brilliant Engineering 2 (2020) 1-4
2687-5195 © 2019 ACA Publishing. All rights reserved.

<https://doi.org/10.36937/ben.2020.002.001>

In a CV experiment, scanning the potential in both directions provides with the opportunity to explore the electrochemical behavior of species generated at the electrode [10]. The potential scan rate sets the timescale of the experiment, e.g. with coupled homogeneous reactions, the value of scan rate will determine whether intermediates are formed or consumed and to what extent [11]. In a slow potential scan rate the diffusion layer will grow much farther from the electrode in comparison to a fast scan. The slow scan rate allows sufficient time for the products of the reduction of the reactant on the forward scan to participate in a chemical reaction whose products are not electroactive. The rotating disc electrode (RDE) is the classical hydrodynamic electroanalytical technique used to limit the diffusion layer thickness [11]. RDE is one of the major research tools in fuel cell technology [12]. The main advantage is an enhanced mass transfer of reactants to the electrode surfaces, so that evaluation of catalytic activity is carried out by measuring kinetic currents of electrocatalytic reactions [13].

The present study was carried out in order to determine the electrocatalytic efficiency of commercial Pt/C as an anodic electrocatalyst for formic acid and methanol electrooxidation reactions by changing the rotating speed and scan rate.

2. Experimental

Electrochemical activities of the commercial Tanaka Pt/C (67% wt.) catalyst were tested with a standard three electrode system controlled by an electrochemistry workstation at room temperature (Figure 2).

Figure 2. Schematic illustration of three electrodes system

The Ag/AgCl (3M) and the Pt wire electrodes were used as reference electrode (RE) and counter electrode (CE), respectively. The catalyst ink was deposited on a glassy carbon (GC) disk electrode which have 5 mm diameter used as working electrode (WE). The ink containing the catalyst (13.5 mg), ethanol (1 ml), Nafion solution (80 μ L and 20 wt%) were ultrasonicated for 20 min to obtain a well-dispersed ink. Then, 10 μ L of this ink was placed on a GC disk electrode and dried at room temperature.

Electrochemical oxidation of formic acid and methanol studies were performed in acidic media including 0.5, 1 and 5 M formic acid and 0.5, 1 and 5 M methanol in 0.5 M H_2SO_4 solution, respectively. Cyclic voltammograms of formic acid and methanol oxidation were recorded in the potential range of -0.2~1.2 V and at 5, 10, 20, 50, 100 mV/s scan rates under the proper rotating speeds (0, 200, 400, 800, 1600 rpm).

3. Results and Discussion

Further investigation is carried out to explore the electrochemical characterization of the Pt/C catalyst by measuring the CV response at 20 mV/s scan rate in N_2 saturated 0.5 M H_2SO_4 + 0.5 M formic acid solution, as shown in Figure 3. The voltammograms can be observed during anodic scan depending on rotating speed [13]. It can be seen that the anodic peak currents of formic acid oxidation decreased with the increase in the rotating speed whereas current increased for the

cathodic peak. If the current value of first anodic peak is high, the catalyst is more active for formic acid oxidation.

Figure 3. Formic acid oxidation CV curves at different rotating speeds

Figure 4 shows the CV curves at different rotating speeds for methanol oxidation of the Pt/C catalyst. CV curves of methanol oxidation was recorded at 20 mV/s scan rate in acidic media (0.5 M CH_3OH in 0.5 M H_2SO_4). Similar results to formic acid oxidation were seen that the peak currents of methanol oxidation decreased with the increase in the rotating speed. The decrease indicates that the reaction is not mass transport controlled and suggests increased diffusion of reactive species away from the electrode surface with the increase of the rotating speed [14]. Seland et al showed that the current density of methanol oxidation is decreasing as a function of rotating rate both in the positive-going scan and the negative-going scan [15]. The literature explanation for the sustained decrease in current with rotating rate is usually in terms of increased production of soluble intermediates [16, 17]. The idea is that removal of the soluble species prevents complete oxidation of the methanol.

Figure 4. Methanol oxidation CV curves at different rotating speeds

Figure 5 illustrates typical cyclic voltammograms of Pt/C catalyst in 0.5 M H_2SO_4 + 0.5 M $HCOOH$ solution at various potential scan rates in the range from 5 to 100 mV/s. A significant increase in the first anodic peak current of formic acid oxidation is observed with increasing the scan rate. Similar result was reported by Tian et al, in which they found the electrocatalytic enhancement of the modified catalyst over that of Pt/C was significantly reduced when the linear scan voltammograms were obtained at a scan rate of 10 mV/s [18].

Figure 5. Formic acid oxidation CV curves at different scan rates

The effect of varying the scan rate on the anodic and cathodic peak current of methanol oxidation was also studied (Figure 6). It can be seen that the anodic peak currents (at 0.7 V) of methanol oxidation increased with the increase in the scan rate. It shows that the oxidation of methanol is an irreversible charge transfer electrode process [19]. The higher forward peak current and backward peak current ratio for the methanol oxidation suggests more effective removal of the poisoning species on the catalyst surface, which implies that the methanol can be oxidized much more efficiently [20]. Figure 6 shows CVs recorded at varied scan rates from 5 mV/s to 100 mV/s. The new anodic peaks are observed at 0.5 V in the forward scan for high scan rates (50 and 100 mV/s). This change in voltammogram is attributed to the adsorption of CO reminiscent on the Pt surface at higher scan rates [21].

Figure 6. Methanol oxidation CV curves at different scan rates

Figure 7 shows the CVs for formic acid oxidation in solutions with different formic acid concentrations have been recorded at a scan rate of 20 mV/s. Formic acid oxidation starts at ca. $E > 0.3$ V, the current increased with high reactant concentration. The oxidation currents in the whole reaction potential region between 0.3 V to 1 V increased with an increase in HCOOH concentration [22]. More formic acid molecules present in the solution may lead to more interaction between the formic acid and the hydroxyl molecules which would in turn lead to a faster formic acid oxidation rate being observed [23].

Figure 7. Formic acid oxidation CV curves at different concentrations

Figure 8 shows the CVs at 20 mV/s of Pt/C in 0.5 M H_2SO_4 with different concentrations of methanol. The anodic and cathodic peak potentials of methanol electrooxidation shift to positive potentials and the current values of methanol electrooxidation increased with the increase in methanol concentration. It can be observed that there is a linear correlation between the peak currents and methanol concentration. The anodic and cathodic peak current rate of methanol oxidation on Pt/C catalyst decreased with increasing the methanol concentration. A lower ratio represents much CO molecules are adsorbed on the catalyst which indicates worse oxidation of methanol [24]. It can be assumed that the increment is due to the presence of a diffusion-controlled process that appears to play an important role at low concentrations [25]. These results confirm that the production of methanol radicals is directly related to the anodic oxidation potential and the concentration of methanol.

Figure 8. Methanol oxidation CV curves at different concentrations

4. Conclusions

We provide evidence that rotating speed, scan rate and concentration effects are particularly important for the formic acid and methanol oxidation. Measurements of the amounts of electrocatalytic poison formed from formic acid and methanol under various hydrodynamic conditions implies that a fast rotating speed does not allow a contact time long enough for formic acid and methanol to initiate their oxidation reactions. This implies fundamental differences in the mass transport dependence of the electrode kinetics during oxidation of these small organic molecules. Pt/C exhibited a significant activity toward formic acid and methanol oxidation with increasing the scan rate, but the CO adsorption for methanol oxidation was monitored with faster scan rate. Direct conversion of formic acid to CO_2 increased

with an increase in formic acid concentration. At high concentrations of methanol, the methanol molecules can quickly diffuse to the surface of Pt/C and can be electrocatalytically oxidized, but the CO molecules will poison the catalyst.

References

- [1] E. Herrero, J. Feliu, Understanding formic acid oxidation mechanism on platinum single crystal electrodes, *Curr Opin Electrochem*, 9 (2018) 145-150.
- [2] R.W. McCabe, D.F. McCready, Kinetics and Reaction Pathways of Methanol Oxidation on Platinum, *J Phys Chem-Us*, 90 (1986) 1428-1435.
- [3] M.S. Cogenli, A. Bayrakceken Yurtcan, Graphene aerogel supported platinum nanoparticles for formic acid electro-oxidation, *Mater Res Express*, 5 (2018).
- [4] S. Sauerbrei, M.A. Nascimento, M. Eiswirth, H. Varela, Mechanism and model of the oscillatory electro-oxidation of methanol, *J Chem Phys*, 132 (2010).
- [5] Y.X. Chen, M. Heinen, Z. Jusys, R.J. Behm, Kinetics and mechanism of the electrooxidation of formic acid - Spectroelectrochemical studies in a flow cell, *Angew Chem Int Edit*, 45 (2006) 981-985.
- [6] D. Cao, G.Q. Lu, A. Wieckowski, S.A. Wasileski, M. Neurock, Mechanisms of methanol decomposition on platinum: A combined experimental and ab initio approach, *J Phys Chem B*, 109 (2005) 11622-11633.
- [7] M.S. Cogenli, A.B. Yurtcan, Catalytic activity, stability and impedance behavior of PtRu/C, PtPd/C and PtSn/C bimetallic catalysts toward methanol and formic acid oxidation, *Int J Hydrogen Energ*, 43 (2018) 10698-10709.
- [8] E. Antolini, E.R. Gonzalez, Alkaline direct alcohol fuel cells, *J Power Sources*, 195 (2010) 3431-3450.
- [9] M.S. Cogenli, A.B. Yurtcan, Carbon-Based Nanomaterials for Alcohol Oxidation, *Mater Res Found*, 49 (2019) 1-78.
- [10] Allen J. Bard and Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, *Russ J Electrochem+*, 38 (2002) 1364-1365.
- [11] G. Denuault, M. Sosna, K.-J. Williams, Classical Experiments, in: *Handbook of Electrochemistry*, 2007, pp. 431-469.
- [12] S.J. Lee, S.I. Pyun, S.K. Lee, S.J.L. Kang, Fundamentals of Rotating Disc and Ring-Disc Electrode Techniques and their Applications to Study of the Oxygen Reduction Mechanism at Pt/C Electrode for Fuel Cells, *Isr J Chem*, 48 (2008) 215-228.
- [13] D. Shin, Y.R. Kim, M. Choi, C.K. Rhee, Formic Acid Oxidation Depending on Rotating Speed of Smooth Pt Disk Electrode, *J Electrochem Sci Te*, 5 (2014) 82-86.
- [14] V.K. Puthiyapura, W.F. Lin, A.E. Russell, D.J.L. Brett, C. Hardacre, Effect of Mass Transport on the Electrochemical Oxidation of Alcohols Over Electrodeposited Film and Carbon-Supported Pt Electrodes, *Top Catal*, 61 (2018) 240-253.
- [15] F. Seland, R. Tunold, D.A. Harrington, Activating and deactivating mass transport effects in methanol and formic acid oxidation on platinum electrodes, *Electrochim Acta*, 55 (2010) 3384-3391.
- [16] S.L. Gojkovic, Mass transfer effect in electrochemical oxidation of methanol at platinum electrocatalysts, *J Electroanal Chem*, 573 (2004) 271-276.
- [17] H.S. Wang, C. Wingender, H. Baltruschat, M. Lopez, M.T. Reetz, Methanol oxidation on Pt, PtRu, and colloidal Pt electrocatalysts: a DEMS study of product formation, *J Electroanal Chem*, 509 (2001) 163-169.
- [18] Q.F. Tian, Z.W. Zhu, B. Fu, Y. Li, Kinetic Study of Formic Acid Electrochemical Oxidation on Supported Pd Based Electrocatalysts, *J Electrochem Soc*, 165 (2018) F1075-F1083.
- [19] Z. Yavari, M. Noroozifar, M. Khorasani-Motlagh, The improvement of methanol oxidation using nano-electrocatalysts, *J Exp Nanosci*, 11 (2016) 798-815.
- [20] A.T.E. Vilian, M. Rajkumar, S.M. Chen, C.C. Hu, K.M. Boopathi, C.W. Chu, High electrocatalytic performance of platinum and manganese dioxide nanoparticle decorated reduced graphene oxide sheets for methanol electro-oxidation, *Rsc Adv*, 4 (2014) 41387-41397.
- [21] V.S. Joshi, D.C. Poudyal, A.K. Satpati, K.R. Patil, S.K. Haram, Methanol oxidation reaction on Pt based electrocatalysts modified ultramicroelectrode (UME): Novel electrochemical method for monitoring rate of CO adsorption, *Electrochim Acta*, 286 (2018) 287-295.
- [22] J. Xu, D.F. Yuan, F. Yang, D. Mei, Z.B. Zhang, Y.X. Chen, On the mechanism of the direct pathway for formic acid oxidation at a Pt(111) electrode, *Phys Chem Chem Phys*, 15 (2013) 4367-4376.
- [23] E. Erasmus, J.O. Claassen, W.A. van der Westhuizen, Catalytic wet peroxide oxidation of formic acid in wastewater with naturally-occurring iron ore, *Water Sa*, 42 (2016) 442-448.
- [24] M.S. Çögenli, A. Bayrakceken Yurtcan, Heteroatom doped 3D graphene aerogel supported catalysts for formic acid and methanol oxidation, *Int J Hydrogen Energ*, (2019).
- [25] J.B. Raoof, R. Ojani, S.R. Hosseini, An Electrochemical Investigation of Methanol Oxidation on Nickel Hydroxide Nanoparticles, *S Afr J Chem-S-Afr T*, 66 (2013) 47-53.