Nano-Pt/C electrocatalysts: synthesis and activity for alcohol oxidation

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Received 12 December 2012
Accepted for publication 10 May 2013
Published 14 June 2013
Online at stacks.iop.org/ANSN/4/035008

Abstract
Nano-sized platinum electrocatalysts on a carbon support (Pt/C) have been synthesized by the polyol reduction method under microwave irradiation using ethylene glycol (EG) as the reductant and carbon vulcan XC-72R as the support material. The physical characteristics of the Pt/C materials were analyzed using transmission electron microscopy and Brunauer–Emmet–Teller nitrogen adsorption theory. The glycerol and EG electro-oxidation in alkaline media on the Pt/C catalysts was investigated with cyclic voltammetry and chronoamperometry. The particle size of Pt on carbon was about 3.0 nm. The catalytic activity for the alcohol electro-oxidation of Pt/C materials synthesized in various pH values (7.9–9.5) was found to be significantly higher than that of commercial Pt/C (Aldrich Sigma, 10 wt% Pt/activated carbon). The Pt/C catalyst synthesized in pH 9.5 showed the best electrochemical behavior. At all the synthesized Pt/C electrodes, compared with glycerol, the oxidation rate of EG was about ten times higher.

Keywords: alcohol oxidation, carbon support, electrocatalyst, nanoparticle, platinum

Classification number: 5.06

1. Introduction
Increasing energy demands, the depletion of fossil fuel resources and environmental pollution require research into alternative fuels as well as into energy conversion devices. Direct alcohol fuel cells (DAFCs), available for applications in portable and transport power supplies, are systems of anion-exchange fuel cells in which alcohol is used as the fuel for the anode. Platinum (Pt) is an effective electro-catalyst for hydrogen and methanol (MeOH) oxidation. However, the biggest challenge in the commercialization of this catalyst in DAFC technology is its high cost. The problem could be resolved by using nano-scale Pt, Pt alloys and/or Pt-free catalysts [1, 2]. Nanoparticle Pt based catalysts used for the alcohol oxidation reaction in the alkaline media of DAFCs may be synthesized by the conventional methods of borohydride reduction [3], ethylene glycol (EG) reduction [4], microwave irradiation [5] and sonolysis [6]. Using liquid fuels such as alcohol for the anode has some advantages compared to conventional hydrogen fuel, because of they are easy to handle, store and transport, and they have high mass energy density (6.1, 8.0, 5.2 and 5.0 kWh kg\(^{-1}\) for MeOH, ethanol (EtOH), EG and glycerol, respectively) [7]. Though they have inconsiderably lower energy density, glycerol and EG are less toxic than MeOH and their oxidation rate is higher than that of EtOH. EG is mainly produced through the oxidation of ethylene while glycerol is a by-product of biodiesel production by transesterification of vegetable oils or animal fats. The increasing demand for methyl esters as an alternative fuel for diesel engines has led to a decrease in the price of glycerol ($0.11 kg\(^{-1}\) for raw glycerol and $0.66 kg\(^{-1}\) for refined glycerol) [8].

Most research into DAFCs has focused on acidic media. In strongly acidic electrolytes, alcohol oxidation can easily be completed to CO\(_2\); however, if the rate is low, the performance of DAFCs is not good. It was reported [9] that
Figure 1. The CVs at the Pt electrode of 1.0 M glycerol in (a) HCl, (b) H₂SO₄, (c) HClO₄ and (d) KOH solutions, measured at 50 mV s⁻¹ and 25 °C.

Figure 2. Plots of: (a) \( i_{pa} \) versus [G], and (b) Ln(\( i_{pa} \)) vs 1/T, for glycerol oxidation in the 1.0 M KOH solution.

Figure 3. CVs at the Pt-based electrode measured at 50 mV s⁻¹ in the 1.0 M KOH solution containing 1.0 M of various alcohols, 25 °C.
the kinetics of the oxygen reduction reaction is more facile in a basic medium, so the alkaline media may improve DAFC performance.

In this work we prepared nano-sized Pt catalysts on a carbon support (Pt/C) by a reduction method using EG as the reducing agent under microwave irradiation in reaction solutions of various pH. The physical properties of the synthesized Pt/C were determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemical behavior of glycerol and EG at the synthesized catalysts was characterized using the methods of cyclic voltammetry (CV) and chronoamperometry (CA).

2. Experimental set-up

2.1. Catalyst synthesis

Vulcan XC-72R carbon powder (Cabot, USA) was treated by soaking in 1.0 M HNO₃ solution at room temperature for 10 h, followed by ultrasonic irradiation for 15 min. The mixture was then filtered and washed several times with deionized water DI (18.2 MΩ cm). The acid-treated carbon powder was dried at 70 °C overnight, and then soaked in 1.0 M NaOH solution for 1 h. After being filtered and washed, the base-treated carbon powder was dried at 70 °C overnight and heated at 200 °C for 2 h. The carbon supported Pt catalysts (Pt/C) at 20 wt% were prepared using the microwave polyol process. A solution of 210 µL aqueous H₂PtCl₆ (Sigma Aldrich, 8%) and 25 ml of EG (Merck, 99.5%) in a 100 ml beaker was ultrasonically homogenized for 5 min. Then, the pretreated vulcan XC-72R carbon powder was added, followed by ultrasonication for 15 min. The mixture was stirred under microwave heating for 3 min at 600 W and the pH was controlled using 0.5 M NaOH/EG solution to obtain pHs of 7.9, 8.8 and 9.5. The product was filtered, washed with DI water and finally dried in an oven at 120 °C for 2 h. The synthesized catalysts are denoted as 20Pt/C-7.9, 20Pt/C-8.8 and 20Pt/C-9.5 according to the pH of the preparation solution.

XRD was carried out using a PANalytical X’Pert MPD diffractometer with Cu Kα radiation, with 0.05° step and 8 s
per step counting times to minimize noise. The morphology of the catalysts was characterized by TEM using a JEOL JEM 1400 microscope at 120 kV. The Brunauer–Emmett–Teller (BET) specific surface area ($S_{\text{BET}}$) was determined by nitrogen adsorption measurements (QuantaChrome Autosorb 1C), removing the gas at 200 °C over 2 h.

2.2. Electrode preparation

2.5 mg of Pt/C catalyst was added to 1.0 ml of EtOH solution and 25 µl of polytetrafluoroethylene (PTFE) (Sigma Aldrich, 65%). The mixture (ink) was dispersed sonically over 1 h. A volume of 75 µl of ink was dropped on the supported electrode of glassy carbon (12.56 mm²), and then the working electrode (WE) was dried at room temperature for 1 h.

2.3. Electrochemical measurements

The catalytic behavior of the synthesized nano-Pt/C for glycerol and EG electro-oxidation was studied by CV and CA using a potentiostat/galvanostat PGSTAT320N (Metrohm, AG). The electrochemical measurements were performed in a three-electrode cell with the WEs being smooth Pt (12.56 mm²) or a glassy carbon foil covered by Pt/C films. A Pt wire of geometric area of about 1.41 cm² was used as the counter electrode and a Ag/AgCl/3.0 M KCl was used as the reference electrode (0.21 V versus SHE). The electrolyte was 1.0 M alcohol in 0.5 M KOH (Merck) solution. All measurements were carried out at 25 °C in nitrogen (99.999%) atmosphere. The electrochemical behavior of the synthesized catalysts was compared with commercial Pt/C powder (Sigma Aldrich, loading 10 wt% Pt on active carbon) (10Pt_Com).

3. Results and discussion

3.1. Alcohol oxidation on the smooth Pt electrode

Figure 1 shows the CVs of the smooth Pt electrode in a solution of 1.0 M glycerol (Fisher, AG) with various electrolytes (0.5 M HCl, 0.5 MH2SO4, 0.5 M HClO4, and 1.0 M KOH) and a with potential scan rate of 50 mV s⁻¹.

In figures 1(a) and (b), no oxidation peak of glycerol is observed in the whole potential window from 0 to 1.20 V in the HCl and H2SO4 media. Water oxidation occurs at potentials higher than 1.20 V. Meanwhile HClO4 and, especially, KOH, facilitate glycerol oxidation: oxidation peaks of glycerol were present in both the forward and backward scans for these solutions. However the behavior of glycerol in these media is different. In HClO4 solution (figure 1(c)), both oxidation peaks occur at the positive potentials and the anodic oxidation peak current density of the forward scan ($i_{pa}$) was smaller than that of the backward scan ($i_{pb}$). On the contrary, in KOH, both the forward and backward oxidation peaks are observed at negative potentials and $i_{pa}$ was about five times higher than $i_{pb}$ (figure 1(d)). The forward and backward curves in HClO4 show $i_{pa}$ of 1.5 and $i_{pb}$ of 2.2 mA cm⁻² at the peak potentials of 0.65 and 0.45 V, respectively. These parameters for the KOH solution were 32 and 7 mA cm⁻², and -0.15 and -0.25 V, respectively. This may be explained as follows: the anodic peak in the forward scan is due to the oxidation of freshly chemisorbed glycerol molecules [10] and that on the reverse scan is primarily associated with the removal of carbonaceous species which are not completely oxidized in the forward scan. Thus, the forward peak may be used as a measure to characterize the glycerol oxidation reaction (GOR), and its parameters ($i_{pa}$ and $E_{pa}$) were chosen afterwards to evaluate the catalytic activity of the synthesized materials for the GOR. Thus $E_{pa}$ in KOH is much more negative compared with the acidic solutions. This fact indicates that the alkali media facilitate the GOR on the Pt surface better than acidic media.

The phenomenon that the oxidation, but not the reduction, peak occurred in the backward scan reveals the irreversibility of the multi-step electro-oxidation of glycerol under the studied experimental conditions. We suggest that the backward oxidation peak characterizes the secondary oxidation of the intermediates—the products of the primary oxidation occurred at the forward scan. From the recorded CVs, we observed the negative shift of the backward oxidation peak potentials compared with the forward ones at about 100 mV (in KOH) and 200 mV (in HClO4), which leads to the suggestion that the secondary oxidation of intermediate.
by-products occurs more easily than the primary oxidation of glycerol. The lower peak current of the secondary oxidation may be due to its low rate and/or the low concentration of intermediates.

The influence of glycerol concentration ([G]) and temperature on the GOR at the Pt electrode was studied in the [G] range of 0.1–2.5 M and temperatures from 25 to 55 °C. The relationship between \(i_{pa}\) and [G] is presented in figure 2(a), from which we can see that the highest current was obtained with the 1.0–2.0 mol l\(^{-1}\) glycerol solutions. Therefore the 1.0 M concentration of glycerol was chosen as the condition for the experiments for evaluating the catalytic activity of the synthesized materials.

The activation energy (\(E_a\)) of the GOR was calculated from the slope of the \(\ln(i_{pa})\) versus \(1/T\) plot as shown in figure 2(b). An \(E_a\) of 18.407 kJ mol\(^{-1}\) was found for the GOR in the 1.0 M KOH solution.

The CVs in figure 3 were obtained from measurements in 1.0 M KOH with added EG, glycerol, EtOH and MeOH at 50 mV s\(^{-1}\). Table 1 shows that the \(i_{pa}\) of the electrochemical oxidation of these alcohols on the smooth Pt electrode in the KOH solution decreased in the order EG > glycerol > MeOH > EtOH.

3.2. Characterization of the Pt/C catalysts

Figures 4(a–c) show the TEM images and particle size distributions of the 20Pt/C-7.9, 20Pt/C-8.8 and 20Pt/C-9.5 catalysts, respectively. The TEM images clearly show that the Pt nanoparticles were precipitated on the surface of the carbon. The sizes of the Pt particles synthesized at 7.9–9.5 pH were distributed from 2.0 to 6.0 nm (figure 4). More than 50% of the 20Pt/C-7.9 particles were larger than 3.0 nm (figure 4(a)). An increase in pH leads to a little smaller and more uniformly sized Pt particles on carbon (table 2).

The XRD pattern for the 20Pt/C-7.9 catalyst shown in figure 5 exhibits diffraction peaks of (111), (200) and (220) at 2\(\theta\) values of 39.9°, 46.55° and 67.85°, respectively. These peaks characterized the face-centered cubic structure of the synthesized Pt nanomaterials.

The BET surface areas (\(S_{BET}\)) of 20Pt/C-7.9, 20Pt/C-8.8 and 20Pt/C-9.5 were evaluated as 138.7, 172.2 and 189.7 m\(^2\) g\(^{-1}\), respectively (table 2).

3.3. Electrochemical surface area

The real electrochemical surface area (ECA) of the catalytic electrode was determined by a charge value of hydrogen reaction on Pt/C in 0.5 M HClO\(_4\). ECA is calculated with the following formula [11]:

\[
ECA = \frac{Q_{H}}{Q_{M}}.
\]

where \(Q_{H}\) (\(\mu\)C) is the charge associated with the integral of the peak area in the hydrogen desorption region (−0.16 to 0 V). \(Q_{M}\) is the charge density associated with the monolayer adsorption of hydrogen (210 \(\mu\)C cm\(^{-2}\)) [12,13]. Figure 6 shows the CVs of the 20Pt/C-7.9, 20Pt/C-8.8, 20Pt/C-9.5, and 10Pt/com electrodes in the potential range between −0.2 and 1.0 V at a 10 mV s\(^{-1}\) scan rate.

The real ECA was also determined by the Coulombic charge corresponding to the oxide reduction peak [14] at a negative potential of 0.567 V versus Ag/AgCl. The peaks of the oxide formation are observed at a forward potential of about 0.45 V (figure 6). The calculated ECA of 20Pt/C-7.9,
Figure 8. (a) CVs of 20Pt/C-7.9 in 1.0 M KOH + 1.0 M glycerol, (b) plots of correlation between ln $i_{pa}$ and temperature for the GOR on various Pt/C electrodes.

Figure 9. Plots of $i_{pa}$ from a continuous scan in a solution of 1.0 M KOH + (a) 1.0 M glycerol; (b) 1.0 M EG on various nano-Pt/C electrodes at 50 mV s$^{-1}$.

Figure 10. CA curves at −0.20 V of 1.0 M KOH with 1.0 M glycerol (a) and with 1.0 M EG (b) on Pt/C electrodes.

3.4. The kinetics of alcohol electro-oxidation at the nano-sized Pt/C catalysts

The electrocatalytic activity of the carbon supported Pt for the GOR and the ethylene GOR (EGOR) were evaluated using CV measurements in the 1.0 M KOH solution containing 1.0 M glycerol and 1.0 M EG at 25 °C. Figure 7 shows the CVs of the 20Pt/C-7.9, 20Pt/C-8.8, 20Pt/C-9.5 and 10Pt_com electrodes at a 50 mV s$^{-1}$ scan rate.

For the GOR, in comparison with 10Pt_com, the $i_{pa}$ of 20Pt/C-7.9, 20Pt/C-8.8 and 20Pt/C-9.5 were higher by about...
three (2.8), four (4.1) and seven (7.1) times, respectively (figure 7(a) and table 3). For the EGOR the same order was observed with a higher effect: the corresponding values are 10.4, 16.2 and 27.7 times. Thus, in the studied conditions, 20Pt/C-9.5 was the best electrocatalyst for alcohol oxidation. The rate of alcohol oxidation at the Pt/C electrodes increased in the order pH 7.9 < pH 8.8 < pH 9.5.

Figure 7 shows the onset potential values of the GOR and EGOR of about −0.5 V (versus Ag/AgCl), which means that both reactions occur at the studied electrode with the same ease. However, the oxidation peak potential \( E_{pa} \) of the EGOR was much more positive than that of the GOR (table 3). As we know, the peak potential values depend on the onset potential itself, and also on the ratio of the diffusion coefficient of the reactants (\( D_{EG} \), \( D_{G} \)) to that of the oxidation products (\( D_{ox,product} \)). Indeed, in water solutions, \( D_{EG} \) was reported to be higher than \( D_{G} \) [16], which leads to some higher oxidation peak potential of the EGOR. However, the contribution of the diffusion coefficient of the oxidation products is still unknown (to get more positive \( E_{pa} \) values of the EGOR over the GOR, the diffusion coefficient of the EGOR products should be smaller than \( D_{ox,product} \) for the GOR).

From table 3 we can see that \( i_{pa} \) of the EGOR was about ten times higher than that of the GOR. Thus, in alkaline media, nano-sized Pt/C materials perform better as catalyst for the EGOR than for the GOR.

Figure 8(a) shows the CV of the GOR on 20Pt/C-7.9 in 1.0 M KOH containing 1.0 M glycerol at a temperature of 15–65 °C. The higher temperature improved the catalytic behavior of the Pt/C catalysts. When the temperature increased from 15 to 65 °C, the \( i_{pa} \) of the GOR on 20Pt/C-7.9 increased about ten times. A similar effect was observed at 20Pt/C-8.8, 20Pt/C-9.5. The current density of the negative oxidation peaks also increased at higher temperatures. Figure 8(b) shows the significant decrease of \( \ln i_{pa} \) with inverse temperature (1/\( T \)) for the studied electrodes. The \( E_{ox} \) calculated from the \( \ln i_{pa} – 1/T \) slope is showed in table 3, which also implies that 20Pt/C-9.5 with the lowest \( E_{ox} \) was the best catalyst for the GOR among the studied materials.

To evaluate the stability of the synthesized nano-Pt/C catalysts for multi-cycle oxidation, voltammograms were recorded in 1.0 M KOH containing 1.0 M glycerol or EG solutions from −0.8 to 0.8 V for 30 cycles. In figure 9(a), the \( i_{pa} \) of the GOR increases slightly from the first to 30th scan at 20Pt/C-7.9, 20Pt/C-8.8, 20Pt/C-9.5; while the \( i_{pa} \) of the GOR on 10Pt/C-com decreases. In figure 9(b), the \( i_{pa} \) of the EGOR remains unchangeable over 30 cycles. These results indicate that the catalytic activity for the GOR and EGOR of all the synthesized materials was stable over 30 cycles. The slight increase in \( i_{pa} \) for the GOR may be due to some activation of the materials during the reverse scans.

3.5. CA measurements

Figure 10 shows the CAs of 20Pt/C-7.9, 20Pt/C-8.8, 20Pt/C-9.5 and 10Pt/C-com in 1.0 M KOH containing 1.0 M glycerol and EG at a set-up potential of −0.20 V for 3600 s. It can be seen that the current density decreased rapidly for about the first 100 s. As we know, at the beginning the current density in CA measurements decreases sharply with time (i proportional to \( t^{-1/2} \)). The decreasing rate with time may characterize the poisoning of the electrodes by the products of the GOR and EGOR, such as \( \text{C}_2\text{H}_4\text{O}_{ads} \), \( \text{C}_2\text{H}_6\text{O}_{ads} \), etc [17]. At following times, the currents decayed slowly and the Pt/C catalysts for alcohol oxidation gradually achieved steady state and in all of the cases the current densities of the synthesized electrodes for the EGOR were higher than for the GOR by about three times. This fact once again emphasizes the better catalytic performance of the synthesized materials for the EGOR. The results also show that synthesized catalysts were better than the commercial 10Pt/C-com, and among those studied, 20Pt/C-9.5 was the best catalyst for the GOR and EGOR.

4. Conclusions

Nano-sized Pt/C electrocatalysts were prepared using an EG reduction method under microwave irradiation in alkaline environments. The synthesized Pt/C materials show better catalytic activity and a more stable steady for the GOR and EGOR in alkaline media than the equivalent commercial material. A higher pH of the reaction solution improves the performance of the Pt/C catalysts.

The electrode made from Pt/C material synthesized at a pH of 9.5 has the highest ECA of 30.77 m² g⁻¹ and shows the best alcohol electrode-oxidation catalysis. In alkaline media, the catalytic activity of the synthesized Pt/C nanomaterials for the EGOR is better than that for the GOR.

Acknowledgments

This work was supported by Vietnam Ministry of Science and Technology through a grant for the NCCB-DHUD.2011/G11 project. The authors thank professor Elisabeth Djurado, Grenoble Institute of Technology, France, for the XRD analysis.

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