

Direct fabrication of Pt-supported porous carbon catalyst for fuel cell

Dong-Yun Zhang^{a,c*}, Guo Xiu Wang^{a,b}, Zi-Feng Ma^c, Konsta Konstantinov^{a,b}, Hua Kun Liu^a

^a *Institute for Superconducting and Electronic Material, University of Wollongong, NSW, 2522, Australia*

^b *ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW, 2522, Australia*

^c *Department of Chemical Engineering, Shanghai Jiaotong University, Shanghai, 200240, P.R.China email:dyz@uow.edu.au*

The homemade Pt/C electrocatalyst was prepared by direct Pt-embedded carbon xerogel method. It had typical polycrystalline phase and uniform Pt dispersion with mean particle size around 8nm. The CV curve of homemade Pt/C in 0.5M H₂SO₄ has an obviously peak appears around 0.54 V, which indicates higher catalytic activity of homemade Pt/C. It was further evidenced by ethanol electrooxidation. Subtracting the current produced by the basic H₂SO₄ electrolyte, the three typical current peaks of ethanol electrooxidation are all higher than that of commercial 20% Pt/C. It provides a much simple route to get the high electrocatalytic activity Pt/C electrocatalyst.

Introduction

Pt-based electrocatalysts are usually employed in proton exchange membrane fuel cells (PEMFC) and direct alcohol fuel cells (DAFC) as electrocatalysts in relatively low temperature. Conventional preparation techniques are based on wet impregnation and chemical reduction of the metal precursors, including impregnation-reduction [1], microemulsions [2], sonochemistry [3, 4], and microwave irradiation [5–7]. However, it is very tedious to prepare the Pt-supported carbon catalysts by those methods, because a very long time is required for the synthesis of carbon and post-fabrication steps such as surface modification of carbon and metal supporting are required. A new fabrication method has been reported for producing Pt-carbon catalysts directly by Pt-embedded template [8-9]. It provides a time saving route for the preparation of Pt catalysts supported on a mesoporous carbon.

In this work, Pt-supported porous carbon was directly prepared by carbon xerogel method. A platinum salt was dissolved in the aqueous solution of carbon xerogel precursor [10] and reduced by 5%H₂/Ar gas along with carbonization.

Preparation

A mixture solution of H₂PtCl₆ and ethylene diaminetetra acetic acid with mole ratio 1:1 was added in 0.29M resorcinol aqueous solution and ultrasonic dispersed. Then 0.57 M formaldehyde was slowly dropped and ultrasonic dispersed simultaneously. The

pH value was adjusted to be in the range of 6.5-7.4 by adding Na_2CO_3 solution. The mixture solution was put in an ampoule, sealed and heated in Muffle furnace for 5 days. The temperature was maintained at 85°C . Then samples were heated to 150°C under vacuum (103Pa) for 3 days.

After drying, the gels were pyrolyzed under Ar flow in a tubular furnace following sequential steps: (1) ramp at $1.7^\circ\text{C}/\text{min}$ to 150°C and hold for 15 min; (2) ramp at $5^\circ\text{C}/\text{min}$ to 400°C and hold for 60 min; (3) ramp at $5^\circ\text{C}/\text{min}$ to 800°C and hold for 120 min; (4) cool slowly to 350°C , convert to 5% H_2/Ar gas flow and hold for 120 min and (5) cool down to room temperature.

The electrocatalysts was characterized by BET (NOVATM1000 instrument), XRD (Philips PW1730 diffractometer with Cu Ka radiation), TEM (JEOL JEM 2010 system) and EDS (JEOL JSM-6460A scanning electron microscope with the energy dispersive spectrometer analysis). Electrochemical measurements were carried out by CHI 640. Samples were performed in a conventional three-electrode test cell consisting of glassy carbon (GC) with 3mm diameter as working electrode, Pt wire as the counter electrode and saturated $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode as the reference electrode. In the results, all the potential values were transformed to the values versus standard hydrogen electrode (SHE).

Results

Fig.1 shows the XRD patterns of the homemade Pt/C and commercial 20%Pt/C electrocatalysts. The diffraction peaks at 40° , 46° , 68° and 81° are response to the Pt (111), (200), (220), and (311) planes, respectively, which represent the typical character of a polycrystalline Pt face centered cubic (fcc) phase. Apart from the four diffraction peaks of platinum, there appears diffraction peak at around 21° is due to the (020) plane of C60 structure. The (220) reflections of Pt are used to calculate the average particle size according to the Scherrer formula [23]. The particle size obtained from XRD pattern is 9.7nm, compared with the mean particle size about 8.02nm obtained from the TEM image. Furthermore, the Pt content of the prepared electrocatalyst given by the EDS result is 4.32 (wt%).

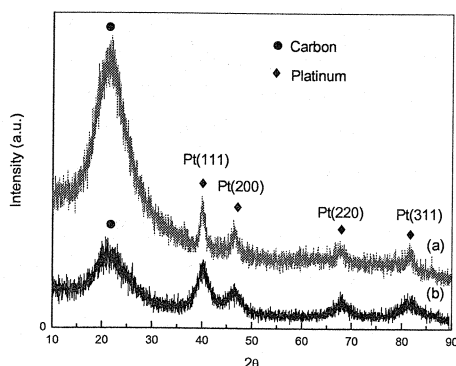


Fig.1 XRD patterns of (a) the homemade Pt/C and (b) commercial Pt/C electrocatalysts

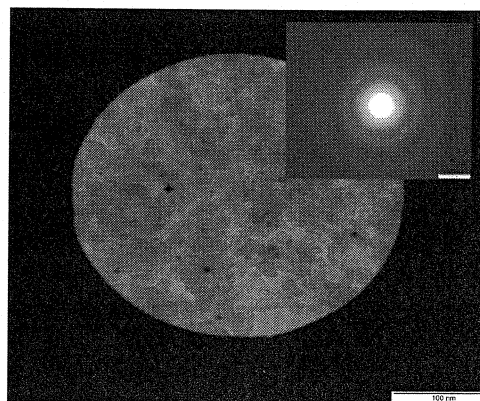


Fig.2 TEM image (insert: transmission electron diffraction pattern) of homemade Pt/C electrocatalysts

Fig. 2 is the TEM image of the homemade Pt/C electrocatalyst. It can be seen that the particles are dispersed uniformly with mean particle size around 8nm. However, the particles are distributed in a little broad range from 2-20nm. It is evidenced by the ring pattern of transmission electron diffraction (TED) in the insert of the Fig. 2. The rings are response to different phanes of polycrystalline Pt. The bright spots on the rings reflect to agglomerated particles with intensive X-ray diffraction.

The cyclic voltammograms of homemade Pt/C electrocatalyst in 0.5M H₂SO₄ with different scan rates are shown in Fig. 3. The current values were normalized per milligram of platinum. The CV curve of homemade Pt/C have no well-defined “double layer” region (0.25-0.35 V). Meanwhile, an obviously wide peak starts at 0.25 V and achieves a maximum current at 0.54 V. Similar performances of the low Pt loading electrode were reported by Ticianelli et al. [26] and Cha [27]. It was distributed to the relative faster diffusion rate to the reaction kinetic rate on the surface of Pt. Moreover, the peak disappeared with the increase of the scan rates [27]. In this case, all the curves have the same profile and the peak currents are increase with the increase of the scan rates. Thus, this peak is attributed to the adsorption of some species in H₂SO₄ aqueous solution. Furthermore, in the whole region, the current of homemade Pt/C is higher than that of commercial 20% Pt/C in 0.05V/s scan rate. Thus, it can be speculated that some homemade Pt/C electrocatalyst has higher mass catalytic activity. However, in the reverse scan direction, the potential of reduction peak of homemade Pt/C (0.45 V) is negative to that of commercial 20% Pt/C (0.55 V).

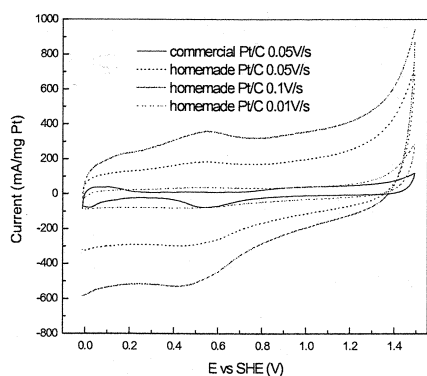


Fig. 3 Cyclic voltammograms of homemade Pt/C and commercial Pt/C electrocatalysts in 0.5M H₂SO₄ with different scan rates.

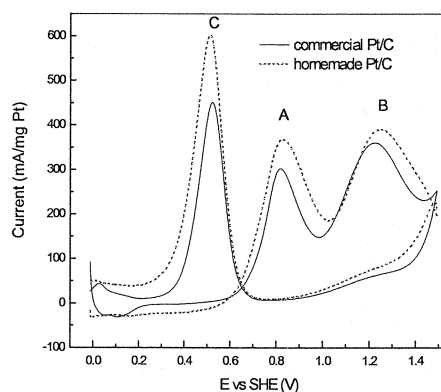


Fig. 4 Cyclic voltammograms of homemade Pt/C and commercial 20% Pt/C electrocatalysts in 0.5 M H₂SO₄ with 0.5 M ethanol, scan rate: 0.05 V/s

The performances of homemade Pt/C electrocatalyst and commercial 20% Pt/C in ethanol electro-oxidation are shown in Fig. 4. The currents are subtracted by the basic currents in 0.5M H₂SO₄, which exactly reflect the property of ethanol electrooxidation. It can be clearly seen that in the investigated potential range, there are three typical oxidation peaks (marked as A, B and C) in both cases of homemade Pt/C and commercial 20% Pt/C. From the current density point of view, homemade Pt/C presents higher catalytic activity to ethanol electro-oxidation in comparison with commercial 20% Pt/C. The low Pt loading catalysts shown higher catalytic activity than high Pt loading

catalysts, because of the smaller particles and higher surface area with lower the Pt loading on carbon [26]. However, in this case, the mean particle size of Pt is larger than that of commercial 20% Pt/C. Thus, the high catalytic activity is speculated to attribute to the high roughness of Pt surface, which produced during the carbon gelation and carbonization. Compare the BET results listed in table. 1, the special surface area of homemadePt/C is higher than that of pure carbon prepared by the same method. However, the surface area of commercial 20% Pt/C is lower than that of Vulcan XC72 which is used as the supported. It indicates that additive Pt increased the surface area and pore volume, meanwhile, the surface area of Pt was enhanced by carbon gelation and carbonization process.

Table 1 BET results of pure carbon and Pt/C catalysts

Catalysts	Surface area (m ² /g)	Average pore diameter (nm)	Maximum Pore diameter (nm)
Homemade carbon	518.3070	25.996	30.739
Vulcan 72	277.2376	25.186	30.787
Homemade Pt/C	562.9745	25.898	30.836
Commercial Pt/C	153.6480	24.896	30.934

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References

- [1] I.S. Armadi, Z.L. Wang, T.C. Green, A. Henglein and M.A. El-Sayed, *Science*, 272 1924 (1996).
- [2] Z.L. Liu, J.Y. Lee, M. Han, W.X. Chen and L.M. Gan, *J. Mater. Chem.*, 12, 2453 (2002).
- [3] K. Okitsu, A. Yue, S. Tanabe and H. Matsumoto, *Chem. Mater.*, 12, 3006 (2000).
- [4] T. Fujimoto, S. Teraushi, H. Umehara, I. Kojima, W. Henderson, *Chem. Mater.*, 13, 1057 (2001).
- [5] W.X. Tu, H.F. Liu, *Chem. Mater.*, 12, 564 (2000).
- [6] S. Komarneni, D.S. Li, B. Newalkar, H. Katsuki, A.S. Bhalla, *Langmuir*, 18, 5959 (2002).
- [7] Z.L. Liu, J.Y. Lee, W.X. Chen, M. Han, L.M. Gan, *Langmuir*, 20, 181 (2004).
- [8] L. Zhang, B. Cheng, E.T. Samulski, *Chemical Physics Letters*, 398, 505 (2004).
- [9] P. Kim, J.B. Joo, W. Kim, H. Kim, I.K. Song, J. Y, *Carbon*, 43, 2397 (2005).
- [10] N. Job, R. Pirard, J. Marien, J.-P. Pirard, *Carbon*, 42, 619 (2004).
- [11] V. Radmiloviæ, H. A. Gasteiger, P.N. Ross, *J. Catal.*, 154, 98 (1995).
- [12] E.A. Ticianelli, C.R. Derouin, S. Srinivasan, *J. Electroanal. Chem.*, 251, 275 (1988)
- [13] Q.X. Cha, *Chemical Electrical Sources Theory* (Uni. of Wuhan Press, Wuhan, 2005) P 6.