

Synthesis of Graphene Supported Nanocatalyst and Its Electrocatalytic Performance for Methanol Oxidation

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Abstract: The improved Hummers method was used to prepare the graphene oxide. Then, using the precursor as the carrier and the triblock copolymer P123 as the reductant, the protective agent and the morphology control agent, the liquid phase co-reduction method and the continuous reduction method were respectively used to prepare the graphene oxide Three graphene-supported Pt Pd (Pt Pd / G) nanocatalysts were synthesized. The graphene oxide and the metal precursor were simultaneously reduced to achieve the in-situ loading effect. The morphology, structure and composition of Pt Pd / G nanocatalyst were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The results showed that both catalysts were nanodiesel structures. Hollow nanostructures were obtained by continuous reduction method. Electrochemical cyclic voltammetry and chronoamperometry showed that the Pt Pd / G nanocatalysts with the hollow structure were the most resistant to CO poisoning and the Pt Pd / G nanocomposite catalysts synthesized at 100 ° C had the best electrocatalytic oxidation Methanol performance, about 1.5 times the commercial Pt / C catalyst.

1. Introduction

Direct methanol fuel cell (DMFC) has high energy density, low operating temperature, green pollution-free, wide range of fuel sources and is easy to store. It is a promising green energy source and has drawn wide attention from all walks of life. Precious metal Pt is widely used and difficult to replace catalyst in DMFC at present, but its reserves are small and expensive, which leads to its large-scale application in fuel cell field is hindered. At the same time, pure Pt catalyst is easily poisoned by intermediate of alcohol oxidation While reducing the catalytic activity and stability 1. Therefore, reducing the amount of Pt while increasing its catalytic activity and stability is the only way to achieve the commercialization of DMFC.

Graphene is one of the most promising carrier materials for many fuel cell catalyst carriers due to its good electrical and thermal conductivity, high strength and good flexibility, large specific surface area and easy modification. The lattice spacing between Pt and Pd is very close. Pd can weaken the force of Pt-COad to enhance the poisoning resistance of the catalyst. The price of Pd is only about 1/4 of that of Pt. The addition of Pd can effectively reduce the amount of Pt Therefore, Pt Pd nanocatalysts are the hot topics of Pt-based fuel cell research. At present, scientists have done a lot of work on graphene-supported Pt-Pd nanocatalysts 27-29, in which a common method is to load graphene and a metal catalyst step by step, that is, to first reduce graphene oxide into a graphene carrier, The Pt Pd nanoparticles are reduced on graphene. The synthesis method has the disadvantages of complicated processes and high costs. Meanwhile, due to van der Waals forces, graphene oxide layers are easily accumulated during the reduction of graphene oxide into graphene, thereby greatly reducing the effective load area Resulting in subsequent Pt Pd nanoparticles can not be uniformly dispersed in the graphene, affecting the performance of the catalyst.

2. Experimental Preparation and Implementation

Potassium chloroplatinate (K₂PtCl₆, 99.9%), potassium chlorodipalladate (K₂PdCl₄, 99.99%), P123 and Nafion solution were all purchased from Sigma Aldrich; natural flake graphite The products were purchased from Zhongke Hengda Graphite Co., Ltd. Commercially available Pt / C

catalyst (20% (w)) was purchased from Alfa Aesar. The anhydrous methanol, concentrated H₂SO₄, NaNO₃, H₂O₂ and KMnO₄ were all analytically pure. Water is double distilled water. X-ray powder diffraction (XRD) testing was performed on FEI Te GNai-F30 using a Rigaku Ultima IV X-ray diffractometer, transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) using X-ray photoelectron spectroscopy (XPS), Thermogravimetric tests were performed on a STA 449 F5 Jupiter® thermogravimetric analyzer and the electrochemical test using the AUTOLAB (PGSTAT 12) electrochemical workstation.

The modified Hummers method 31 was used to prepare graphene oxide. The preparation method was as follows: 2.0 g of natural flake graphite and 1.0 g of NaNO₃ were added into 40 ml of concentrated sulfuric acid which had been precooled to 0 ° C. After stirring for 0.5 h, 6.0 g KMnO₄ at 40 ° C for 2 h, then slowly add 90 m L distilled water and react at 98 ° C for 0.5 h, then add 300 m L distilled water and 20 m L H₂O₂ to the mixture and stir for 0.5 h to The mixture turns bright yellow. Washed with 5% HCl and distilled water until the filtrate was neutral, filtered, washed and dried to obtain graphite oxide, which was then configured as 1.0 mg • m L⁻¹ graphite oxide dispersion for later use.

10 □ L Pt Pd / G ethanol dispersion (2.0 mg • m L⁻¹) on the polished glassy carbon electrode, after natural drying continue to drop 10 □ L of Nafion solution, after drying at room temperature work Electrode Pt Pd / G / GC. The theoretical loading of Pt on the electrode surface catalyst was 0.01 mg. Electrochemical performance test was carried out in a three-electrode system electrolytic cell. The auxiliary electrode was a platinum plate electrode and the reference electrode was a saturated calomel electrode (SCE). High purity nitrogen gas was removed for 15 min before electrochemical experiments to remove dissolved oxygen in the electrolyte. The CO dissolution test was performed in 0.1 mol • L⁻¹ H₂SO₄ solution. The cyclic voltammetry and chronoamperometry of methanol were carried out in 0.1 mol • L⁻¹ H₂SO₄ + 0.5 mol • L⁻¹ CH₃OH solution.

Take 10 m L graphite oxide dispersion in a three-necked flask, ultrasonic stripping 1 h get graphene oxide dispersion, add 1.0 g P123, stirred and sonicated to dissolve, magnetic stirring and control the temperature at 30 ° C, using a total of Reduction method, 10 m L K₂Pt Cl₆ solution (0.03 mol • L⁻¹) and 10 mL K₂PdCl₄ solution (0.03 mol • L⁻¹) were added dropwise to the three-necked flask with a constant pressure funnel at the same time. The reaction was carried out for 2 h, centrifuged and washed three times to obtain Pt Pd / G-1 and dispersed in anhydrous ethanol. The reaction temperature was kept at 100 ° C. and the other reaction conditions were kept unchanged. The sample was labeled Pt Pd / G-2 ; The same reaction temperature at 100 ° C, the amount of the reaction remained unchanged by continuous reduction method, that is, with a constant pressure funnel K₂Pd Cl₄ solution was slowly added dropwise after 2 h K₂Pt Cl₆ solution was added dropwise and the reaction was continued for 2 h , This method gives the sample labeled Pt Pd / G-3.

3. Results and discussion

The XRD patterns of graphene (G-100) prepared by reduction of graphite, graphite oxide (GO), P123 reduced at 30 ° C and G-100 obtained at 100 ° C were obtained. It is observed that the obvious diffraction peak appears at 26.3 °, which is the characteristic diffraction peak of the natural graphite (002) crystal plane, and the peak intensity is relatively large. After the strong oxidant, the graphite is oxidized to graphite oxide, and the characteristic diffraction peak of the (002) Shifted to the left, and the diffraction peak of the (002) plane of graphite oxide appeared at 11.1 °. The graphene oxide after the stripping was changed to graphene oxide. After reduction by P123 at 30 ° C and 100 ° C, G- 30 and G-100. Both of them show obvious peaks near 24.5 °, which is characteristic diffraction peak of (002) plane of graphene, which indicates that graphene oxide can be reduced by P123 to obtain reduced graphene oxide. Figure 1 (b) compares XRD patterns of Pt Pd / G-1, Pt Pd / G-2 and Pt Pd / G-3 with Pt Pd appearing around 39 °, 45 °, 66 °, 80 ° and 84 ° The diffraction peaks of (111), (200), (220), (311) and (222) crystal planes are proved to have a face-centered cubic structure. The broad peaks around 24 ° are diffraction peaks of (002) . Figure 1 (c) is a TEM image of graphite oxide. As can be seen from the figure, the prepared graphite oxide is a transparent sheet

structure, and at the same time can observe obvious wrinkle layers, which can provide larger load area. Low TEM image 2 (a1-c1) shows that the Pt Pd nanoparticles in the three kinds of Pt Pd / G are well dispersed and supported on the surface of the graphene. The inset in Fig. 2 (a1-c1) is a selective region electron diffraction (SAED) diagram, with four distinct diffraction rings corresponding internally to the four planes (111), (200) (220), (311), which corresponds to the first four distinct diffraction peaks in the XRD spectrum. The results showed that Pt Pd / G-1 and Pt Pd / G-2 with nanowire structures obtained by co-reduction method showed average diameters of 19 nm and 23 nm, respectively. The Pt Pd / G-2 synthesized by the continuous reduction method is an irregular-shaped hollow structure with an average particle diameter of 13 nm, and at the same time, particles of Pt Pd nano particles with smaller particle sizes can be observed. Figure 2 (a3-c3) can be more intuitive to see the fine structure of the three kinds of nano-catalysts: Pt Pd / G-1 (a3), Pt Pd / G-2 The darker outline of the nanostructures in Pt Pd / G-3 (c3) confirmed its hollow structure. The inset in Figure 2 (a3-c3) is an enlarged view of the white box area, with clear lattice fringes clearly visible, with lattice spacings around 0.23 nm, Face-centered cubic structure Pt Figure 1 (a) Graphite, graphite oxide (GO), graphene obtained by reduction of P123 at 30 ° C (G-30), graphene reduced by P123 at 100 ° C (B) XRD patterns of Pt Pd / G-1, Pt Pd / G-2 and Pt Pd / G-3; (c) lattice spacing of the (111) crystal plane Match.

The nanodial structures of Pt Pd / G-1 and Pt Pd / G-2 were prepared under one-step co-reduction conditions. It was found that triblock copolymer P123 consisted of hydrophilic PEO and hydrophobic PPO with Reducing PEO fragments can reduce Pd precursors at room temperature but not Pt precursors, both of which can be reduced at high temperatures. The special structure and selective reduction of Pt and Pd at low temperatures enable P123 As a good topography control agent 18,32. Under the condition of continuous reduction at 100 ° C, the Pd precursor is first completely reduced to Pd and then added to the Pt precursor. Since the reduction potential of Pt is higher than the reduction potential of Pd, the Pd element can undergo a potential substitution reaction with the Pt precursor, So as to obtain a hollow structure 33. In the TEM image, we can find that some of the smaller nanoparticles that do not form a hollow structure may be due to the reduction of part of the Pt precursor directly by P123, and some grow on the surface of the Pd nanoparticle to form Pt Pd core-shell structure. To this end, we try to use continuous reduction method at 30 ° C in an attempt to avoid direct reduction of Pt precursors at high temperatures, but repeated tests show that the synthesized materials exhibit poor electrocatalytic oxidation of methanol under acidic conditions, However, it has some catalytic activity under alkaline conditions. Therefore, we speculate that during the continuous reduction process at low temperature, it may be due to the interaction between graphene and Pt precursor that the nucleated Pd can not react with the Pt precursor Displacement reaction. The three kinds of Pt Pd / G are all precursors of graphene oxide and metal precursors during the synthesis process. The previous studies showed that graphene oxide had defects in the reduction process of P123. The reduced Pt and Pd precursors Experience preferred nucleation and growth defects in order to achieve the effect of in situ load, which makes the metal particles and graphene stronger force will not easily fall off, but also makes the metal particles loaded on the graphene More uniform.

Chronoamperometry is an important means to evaluate the electrocatalytic oxidation of methanol to methanol. The chronoamperometry curves of four catalysts at 0.6 V potentials in 0.1 mol • L⁻¹ H₂SO₄ + 0.5 mol • L⁻¹ CH₃OH solution . It can be observed that the catalyst will generate a larger initial current in the initial stage of the test, then the speed decreases and tends to be stable. This is due to the step-by-step overpotential momentarily produced when the potential reaches the set constant potential of 0.6 V during the chrono-current test, resulting in a significantly larger transient current which decays rapidly over time, indicating In addition, when the electrode potential changes instantaneously, it takes a certain amount of power to charge the electric double layer. Due to the large electric double layer of graphene, the relative commercial Pt / C, the starting current is significantly higher than Pt / C. The combined effect of the two results in a much higher initial current density of Pt Pd / G in the J-t curve than the theoretical value. The stability of the current density from descending order: Pt Pd / G-2 □ Pt Pd / G-3 □ Pt / C □ Pt Pd / G-1, and sulfuric acid

in methanol solution positive sweep peak current density Trend consistent. The results of chronoamperometry and cyclic voltammetry show that Pt Pd / G-2 has higher catalytic activity and stability to methanol oxidation.

4. Conclusion

Three kinds of Pt Pd / G nanocatalysts were prepared by liquid co-reduction method and continuous reduction method. The precursor of the graphene oxide was reduced synchronously with the metal precursor to achieve the in-situ loading of graphene. XRD, TEM and XPS characterization analysis showed that graphene oxide was reduced to graphene. Pt Pd / G-1 and Pt Pd / G-2 catalysts obtained by the co-reduction method were obtained by the continuous reduction method Pt Pd / G-3 hollow structure. Electrochemical tests showed that Pt Pd / G-3 possesses good resistance to CO poisoning and Pt Pd / G-2 electrocatalytic oxidation of methanol.

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