Preparation and Characterization of Pd/TiO$_2$-Graphene Catalyst with Enhanced Electrocatalytic Activity in Direct Methanol Fuel Cell

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Introduction
Direct methanol fuel cells (DMFCs) have been identified as promising energy converters for a variety of portable applications. Pt/C catalyst is most widely used for the oxygen reduction reaction (ORR) in DMFCs. However, Pt/C catalyst has many problems, including the high cost and insufficient durability because that the crossover of methanol from the anode to the cathode leads to a "mixed potential" effect on the cathode side, decreasing the fuel efficiency. Therefore, looking for a cheap, good resistance to methanol and Pt-free catalyst is of great significance. Pd and Pt have very similar properties. Meanwhile, Pd has the lower reactivity for the adsorption and oxidation of methanol, which is of great importance for the improved methanol tolerance in the DMFCs.

The most widely used catalytic support is the amorphous carbon. However, carbon as the catalytic support can be corroded leading to the loss of the noble metal and the electrochemical activity. Many methods have been reported to solve these problems, including using carbide 10) or metal oxides 11) as catalytic supports. Among them, TiO$_2$ has a high stability in acidic and alkaline solutions. In addition, the interaction between TiO$_2$ and Pd is conducive to the first step in the electron transfer of O$_2$ and weakens the adsorption of atomic oxygen on Pd in comparison with Pt supported on carbon. But TiO$_2$ is a semiconductor, restricting its electrocatalytic performance. So another material is necessary to be added to improve the electronic conductivity.

Graphene (G) is a two-dimensional single-layer sheet of graphite with p-electrons fully delocalized on the graphite plane. Recently, G has been regarded as an excellent catalytic support material because of its superior electrical conductivity and high specific surface area. However, because of its high specific surface area, carbon corrosion has further exacerbated. Therefore, the load of G surfaces with stabilized TiO$_2$ can effectively solve this problem, while improving the conductivity of TiO$_2$.

In this paper, Pd nanoparticles supported on TiO$_2$ modified G (Pd/TiO$_2$-G) catalysts were prepared and employed as a cathode catalyst for DMFCs. These catalysts exhibited a significantly enhanced ORR electrocatalytic activity and stability in the presence of methanol compared with the conventional Pt catalysts supported on the carbon black.

Experiment
Firstly, 40 mg graphite oxide was dispersed in 40 mL ethylene glycol (EG) by ultrasound treatment for 1 h to obtain graphene oxide (GO). Additionally, various mass ratios of TiO$_2$ which came from the hydrolysis of titanium tetraisopropoxide (TTIP) were added to obtain TiO$_2$(x)-GO supports, where x = 0%, 10%, 20%, and 30% represented the mass ratio of TiO$_2$ to GO. Then, Pd/TiO$_2$(x)-GO were synthesized by EG reduction method. The Pd loading on the TiO$_2$-GO support in all samples was controlled to be 20 wt.%. Stoichiometric amounts of PdCl$_2$ as Pd precursor were dispersed in EG solution of TiO$_2$-GO, and then taken in a 125 mL round-bottom flask equipped with a N$_2$ in/outlet. The resulting suspension was heated at 130°C for 3 h under constant stirring. 36 μL N$_2$H$_4$·H$_2$O (98 wt.%) was added and maintained at 95°C for 1 h to reduce GO to G. Finally, the resulting product was dried by lyophilization drying which could prevent irreversible aggregation of G during drying process.

Results and discussion
The morphology of the Pd/TiO$_2$(20%)-G is elucidated by HRTEM analysis in Figure 1. The Pd nanoparticles with a uniform size of 3 nm are fairly well monodispersed. The interplanar spacing of the particle lattice is 0.224 nm, which agrees well with the (111) lattice spacing of the face-centered cubic Pd. Besides, no particle lattice related to TiO$_2$ phases can be observed from Figure 1. It might be that the TiO$_2$ was amorphous in Pd/TiO$_2$-G catalysts.

![Figure 1. HRTEM images of Pd/TiO$_2$(20%)-G.](image)

Figure 1 shows the cyclic voltammograms of the Pd/TiO$_2$ (20%)-G catalyst in N$_2$-purged 0.1 M HClO$_4$ solution. Figure 2b displays the ORR polarization curves of Pd/TiO$_2$ (20%)-G in O$_2$-saturated 0.1 M HClO$_4$ solution obtained at different rotation rates. The obtained experimental number of electron (n$_{exp}$) at the diffusion limiting potential of 0.3 V, 0.35 V, and 0.4 V is found to be 3.97. The methanol tolerance of the Pd/TiO$_2$(20%)-G catalyst is shown in Figure 2c. In the presence of methanol, the ORR activity of Pd/TiO$_2$(20%)-G decreases slightly by 0.05 V. After the accelerating aging test (Figure 2d), the half wave potential and the limiting current are almost unchanged, meaning Pd/TiO$_2$(20%)-G has an enhanced long-term durability.

![Figure 2. (a) Cycle voltammograms of Pd/TiO$_2$(20%)-G in 0.1 M HClO$_4$ solution, (b) ORR polarization curves of Pd/TiO$_2$(20%)-G at different rotation rates for the ORR in O$_2$-saturated 0.1 M HClO$_4$, (c) ORR polarization curves of Pd/TiO$_2$(20%)-G in O$_2$-saturated 0.1 M HClO$_4$ with and without 1 M CH$_3$OH, and (d) ORR polarization curves of Pd/TiO$_2$(20%)-G before and after 1000 potential sweeps between 0.6 and 1.2 V.](image)

References

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