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Graphene-carbon nanotube composite aerogel with Ru@Pt nanoparticle as a porous electrode for direct methanol microfluidic fuel cell[☆]

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HIGHLIGHTS

- Ru@Pt nanoparticles on graphene aerogel as a porous anode for MFC is proposed.
- CNT enhanced the reaction rate by increasing conductivity in the anode.
- The MFC could achieve 30.2 mW/cm^2 or 18.7 mW/mg Ru@Pt with 1 M MeOH in 3 M KOH.
- Ru@Pt GA electrode outperformed similar works in the literature.

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ABSTRACT

A Ru@Pt core–shell nanoparticles decorated graphene-carbon nanotube composite was produced as a porous anode for a flow-through direct methanol microfluidic fuel cell (MFC). The composite was characterized by TEM and SEM, which reveals that the size of the nanoparticles is less than 5 nm and the pore size of the porous electrode is less than 10 µm. TEM image showed that the nanoparticles were evenly distributed in the carbon substrate without agglomeration. The carbon nanotubes (CNT) increased the composite conductivity by connecting the graphene oxide nanosheets together. An orthogonal flow air-breathing microfluidic fuel cell combining the advantages of co-flow and counter flow MFC was designed to compare the electrode performances and a maximum specific power of 13.1 mW/mg catalyst was achieved with 1 M methanol in 1 M KOH as supporting electrolyte, which outperformed most others' works in the literature.

1. Introduction

Microfluidic fuel cell (MFC) was first introduced by Ferrigno in 2002 [1], with the distinct advantage of eliminating the membrane between anode and cathode. As a result, all the problems associated with the membrane in Proton Exchange Membrane Fuel Cell (PEMFC) or Anion Exchange Membrane Fuel Cells (AEMFC) can be resolved. For example, the water management problem could be handled easily by the two flowing electrolyte streams and the membrane degradation problem was avoided as well as the cost of the fuel cell could be lowered by discarding the membrane [2]. The co-laminar flow of the anolyte and catholyte provided great operation flexibility of fuel and oxidant in terms of types of fuels, pH of supporting electrolyte, reactant concentration and flow rate. These unique properties facilitated the MFCs to achieve high cell voltage and high current density due to the improved reaction rate. As a result, the maximum power density of MFC could be comparable or even higher than that of traditional fuel cells.

Despite of the advantages stated above, the cost of fuel cell needs to be further reduced to encourage the popularity of industrial application. The main cost of the fuel cell comes from the high loading of precious catalysts which provide a pathway with lower activation energy for fuel oxidation and oxygen reduction reaction. Moreover, those expensive metal catalysts suffer from the problem of unsatisfactory stability. Different fuels require different catalysts to increase the reaction rate. In general, noble metals like platinum (Pt), gold (Au), and Palladium (Pd) are the most active catalysts for common organic fuels like methanol, ethanol, glucose, etc. These noble metal catalysts are supported on carbon black and are coated on carbon papers with binders, forming a 2-D electrode as the reaction is taken place on a 2-D plane between the electrode and the electrolyte. From our previous finding [3], a 3-D porous electrode with high surface area for catalyst loading which allows electrolyte to flow-through could achieve much higher cell performance compared with the 2-D electrode with the same catalysts loading. The as produced 3-D electrode provided a surface

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area of more than 300 m^2/g which could allow high catalyst loading without agglomeration. As a result, the non-agglomerated catalyst would have higher surface area exposed to the reactants. It was obvious that loading the catalysts on a 3-D porous electrode could reduce the fuel cell cost significantly.

Methanol, a stable and safe fuel for transportation, has a reasonable energy density. It could be fed into direct methanol fuel cells (DMFC) as a fuel. A well-known catalyst for methanol oxidation reaction (MOR) in the anode is platinum. However, MOR involves complicated oxidation steps and platinum alone could not oxidize methanol completely. Some intermediates like carbon monoxide, will be formed during the MOR reaction, which is poisonous to platinum. As a result, the fuel cell performance would be degraded after operating for a certain period. To remedy this deficiency, platinum was combined with other metals, for example copper [4–6], nickel [7], palladium [8] and ruthenium [9,10] to form a more stable and anti-poisoning catalyst. Among these metals, the combination of Ru with Pt could improve the MOR significantly by the synergistic effect of the bimetallic structure [11,12].

It was reported that there would be Ru dissolution during the cell operation [12] and the stability of PtRu catalyst could be reduced. However, the Ru rich core and Pt rich shell (Ru@Pt) structure could alleviate this problem due to the fact that less Ru was directly exposed. As a result, it is expected that the Ru@Pt nanoparticles decorated on a porous electrode for flow-through microfluidic fuel cell could achieve a much better cell performance. Besides galvanic displacement between Pt ions and Ru metal [13], the polyol reduction method was the most popular and well-studied method for the synthesis of the Ru@Pt nanoparticles. Alayoglu et al. [11] reduced the $Ru(acac)_3$ to Ru metal with PVP as a stabilizer in glycol and coated the Ru nanoparticles with a Pt shell by subsequent reduction of $PtCl_2$ to metallic Pt. Due to the fact that glycol could also serve as a stabilizer, Muthuswamy et al. [14] synthesized the Ru@Pt by tuning the pH in the ethylene glycol without surfactant or stabilizer successfully and found that MOR activity was closely related to the shell composition. Microwave assisted polyol method could speed up the reduction of the Ru ions to be the Ru core in ethylene glycol as reported by Hu et al. [15]. Not only ethylene glycol, ethanol could also reduce Ru and Pt ions at elevated temperature. Hsieh et al. [12] synthesized the ordered bilayer Ru@Pt nanoparticles in ethanol with annealed Ru core for CO tolerant fuel cells. To the best of our knowledge, Ru@Pt on graphene aerogel has not been reported while only a few groups had produced PtRu alloy nanoparticles decorated on 2-D graphene [9,16] and 3-D graphene [10] for MOR in fuel cell. Therefore, a graphene-carbon nanotube composite decorated with Ru@Pt core-shell nanoparticles as a flow-through anode for microfluidic DMFC is the focus of the present study.

Microfluidic fuel cell could be classified into two major categories, which was the co-laminar flow and counter flow configurations depending on the electrolyte flow direction across the electrode. As Shown in Fig. 1(a), co-laminar flow MFC was the conventional MFC with 2-D electrodes adopted the face-to-face configuration in two parallel flowing electrolyte streams. In this arrangement, the anode-to-cathode distance was small and uniform across the electrode, the ionic resistance between the anode and cathode was minimal and as a result, the MFC performance of co-laminar flow MFC was better than the counter flow MFC as shown in Fig. 1(c). However, the MOR could only be taken place on a 2-D plane and most of the methanol would be flushed away. By the introduction of a 3-D porous electrode, which forced the whole anolyte stream to flow through the anode, the current and power output could be increased due to more reaction sites available on the electrode. However, it was no longer suitable for the 3-D electrode to adopt the co-laminar flow design since the flow-through anode itself was a resistance to the flowing electrolyte stream. The anolyte would flow to the catholyte stream rather than flow-through the porous anode and the co-laminar flow would be distorted and cause severe fuel crossover as shown in Fig. 1(b). The fuel crossover could result in a poor power output since the potential in cathode decreased by a mixed potential of ORR and MOR. To ensure all the anolyte to flow-through the anode, a counter flow MFC as shown in Fig. 1(c) could provide the most stable flow since all the anolyte shall flow-through the porous anode before meeting the catholyte. So that the interface between anolyte and catholyte could be well maintained. However, the counter flow structure suffered from low cell performance due to the increased ionic resistance. To design a high performance MFC, the merits of both counter flow and co-flow MFC shall be held while avoiding their corresponding drawbacks. As a consequence, a novel orthogonal flow microfluidic fuel cell will also be designed to better utilize the above-mentioned composite 3D anode in this study.

2. Experimental

2.1. Materials

Ruthenium chloride ($RuCl_3$, 42%Ru basis), potassium hexachloroplatinate (K_2PtCl_6, 99.9%) and graphitized carbon nanotube (CNT, > 99%) were purchased from Shanghai Aladdin Bio-Chem Technology. Ethylene glycol (EG, > 99.5%), potassium hydroxide (KOH, > 85%) and Potassium permanganate ($KMnO_4$, > 99.0%) were purchased from Sigma-Aldrich. Sodium hydroxide (NaOH, 96%) was purchased from Uni-Chem. The air breathing cathode was obtained from Shanghai Hesen using JM Pt/C catalyst (2 mg Pt/cm^2). All the chemicals employed were analytical grade and used as received without any further purification and all aqueous solutions were prepared by 18.2 MΩ Deionized water (DI water, Barnstead, NANOpure Diamond™).

2.2. Preparation of low defect graphene oxide

The low defect graphene oxide (LDGO) was prepared by a Modified Hummer's Method at room temperature. The synthesis procedure was

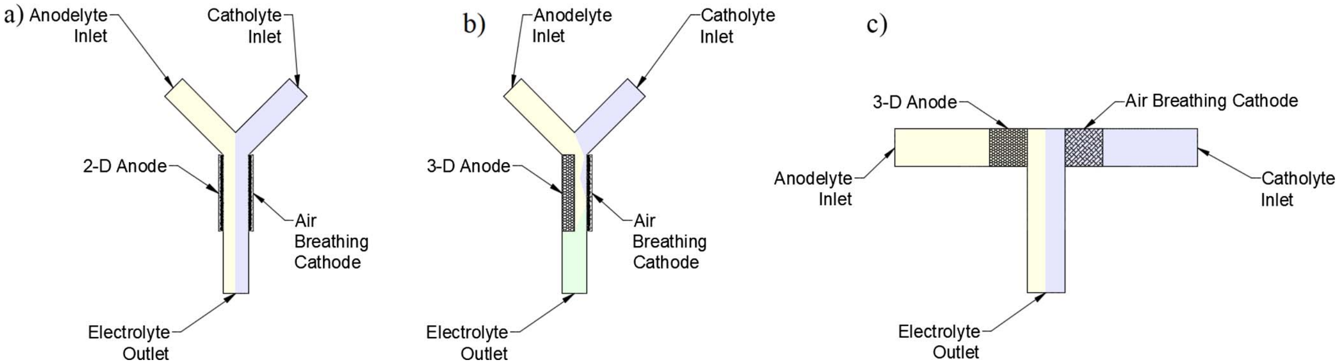

Fig. 1. (a) A typical Y-shape MFC with 2-D electrodes maintaining the co-laminar flow of electrolyte in the microchannel. (b) A Y-shape MFC with 3-D anode would disturb the co-laminar flow in the microchannel which cause serious fuel crossover. (c) A counter flow MFC with 3-D anode could well maintain the co-laminar flow.