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Stability study of ultra-low Pt thin film on TiO_2–C core–shell structure and TiO_2 encapsulated in carbon nanospheres as cathode catalyst in PEMFC

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HIGHLIGHTS

- Titania–carbon core shell applied as a Pt support in PEMFC.
- Titania encapsulated in carbon nanospheres applied as a Pt support.
- Low amount of Pt sputtered on supports as catalyst.
- Fabricate a single cell and plot *I*–*V* curves.

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ABSTRACT

As catalyst supports play an important role in the performance, cost, and the stability of fuel cells, we focus on synthesis of novel nanocomposites via different designs to overcome durability and cost of electrocatalyst layer. In this paper, the researchers wished to report a simple and cost effective hydrothermal method for synthesizing titania encapsulated carbon, and carbon–titania core–shell structure. This comparison was conducted in an effort to find better structure of metal oxide–carbon, as a promising replacement for carbon in PEMFC catalyst supports. Different chemical reagents were applied in order to increase the surface area, and control the porosity of supports. All produced supports at each step were extensively analyzed and discussed. Carbon structure and morphology of nanospheres were studied through Raman characterization and scanning electron microscopy. Titania structure studied through X-ray diffraction indicated two phases including the main anatase phase and the minor rutile phase. Low amounts of platinum (0.05 mg/cm^2) were deposited on prepared supports via constant condition in comparison to the 0.2–0.3 mg/cm^2 platinum for standard membrane electrode assembly. The performances of PEMFC, consisting different prepared support-platinum as cathode, were compared depending on the measured polarization curves. TiO_2–Pt showed the lowest power density around 167 mW/cm^2 while the maximum power densities belonged to core–shell structure with 10 wt% titania around 410 mW/cm^2 which was comparable with Vulcan–Pt. Notably, titania encapsulated carbon with the same amount of titania gave the same performance as core–shell structure. However, the accelerated potential cycling test indicated that the carbon–titania core shell structure showed higher stability in comparison to titania encapsulated in carbon. This result was discussed through X-ray photoelectron spectroscopy.

1. Introduction

There is no denying that energy shortage and air environmental pollution are two of the gravest global challenges of the 21st century. Currently, fuel cells lie in the spotlight of intensive research seeing that they have several special merits to offer, such as high energy conversion efficiency, low noise, cleanliness, and low maintenance. These electrochemical devices have the ability of converting the chemical energy of a fuel into electricity with the aid of catalysts [1–3]. The main goal in this technology is performance optimization, durability promotion, and cost reduction. The polymer electrolyte membrane fuel cell (PEMFC) is considered to be a proper power sources candidate in stationary and mobile applications of the future thanks to its portability and high power density. However, slow kinetic of ORR is one of the most important impediments to the fuel cells' commercialization. Moreover, for fuel cell electric vehicles (FCEV) application, fuel cell must be

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stable for approximately 5000 h. The durability and performance of fuel cell largely depends on carbon support corrosion, platinum dissolution, and membrane thinning [4–7].

Generally speaking, Pt supported on carbon black (Vulcan XC-72) is the most widely-used electrocatalyst in PEMFC. Owing to its high surface area and electrical conductivity, Carbon is commonly used as a support. However, it suffers from main drawbacks: first, small amounts of Pt are deposited due to the dense structure of carbon, which limits mass transfer; and second, corrosion at the cathode side, due to oxidation under operational conditions of fuel cells such as low pH or high amounts of water. With carbon oxidation, Pt particles would detach from the surface of the carbon and agglomerate into large clusters, which results in a decrease in the surface area, and as a result, in the performance of the cell. In other word, smaller Pt nanoparticles due to higher surface energy tend to dissolved sooner at lower potential. If these detached Pt nanoparticles redeposied on larger Pt nanoparticles, platinum cluster can be formed which is called Ostwald ripening [8,9].

Recently, researchers have made concerted efforts to find novel supports that are able to increase the catalytic activity, and as well, are stable. In addition to these two characteristics, the ideal support should also have a high surface area, high porosity, and good electrical conductivity. To address these properties, different approaches have been developed, including the use of different carbon nanostructures such as nanotubes, nanofibers, nanospheres, and the like [10–15].

In the recent years, transition metal oxides such as titanium oxide, tin oxide, indium tin oxide, tungsten oxide, niobium oxide, and antimony oxide have witnessed growing interest in PEMFC application as supports. These materials stage excellent mechanical resistance and durability in low pH and oxidative environments. However, in comparison to carbon nanomaterials, these supports have lower electrical conductivity and surface area. In order to overcome these problems, doping with conductive materials, heat treatment, and novel synthesis method were suggested by the researchers [16–20].

Titania–carbon nanocomposites reveals promising characteristics as catalyst support in PEMFC. In 2012, in separate works, Akalework and Huang [21,22], reported multiwall carbon nanotubes (MWCNTs) doped with titania had unique characteristics that enabled them to serve as an effective Pt support that could increase durability and ORR activity compared to Pt–C and MWCNTs–Pt. This development was explained by the homogeneous dispersion of Pt on the Pt–MWCNTs–TiO_2. In 2013, Tiido et al., synthesized grahene–TiO_2 composite as a Pt support. The Pt–TiO_2–graphene depicted a relatively high electro-catalytic activity through four electron reduction of oxygen [23].

In the present study, a new family of high surface area supports was prepared through simple and cost-effective hydrothermal method, and applied as a Pt support in cathode side of PEMFC. Carbon–titania core–shell structure and titania encapsulated in carbon nanospheres with different concentration of titania were produced. Ultra-low amount of Pt was deposited on supports in order to reduce the costs as well as to increase the stability. To the best of the researchers' knowledge, no study has ever targeted this empirical procedural line of work.

2. Experimentation

2.1. Materials and targets

Titania (TiO_2) nanoparticles, and α-D(+)-Glucose ($C_6H_{12}O_6$), sodium hydroxide (NaOH), and Potassium hydroxide (KOH) were purchased from Sigma Aldrich. Nafion solution (10 wt%) was used as a binder and proton conductive agent. Platinum targets with 99.9% purity were purchased from Kurt J. Lesker Canada Inc. Company. Dupont Nafion 212 was utilized as an electrolyte. Moreover, Teflonised carbon paper (SGL, 35 BC Sigracet) was applied as gas diffusion layer (GDL).

2.2. Carbon nanospheres (CNS)

Carbon nanospheres were prepared by simple, and straightforward hydrothermal method. In this method, proper amounts of glucose was dissolved in distilled water to form 0.5 M solution. The solution became clear after 10 min of stirring with the help of magnetic blender. The clear solution was sealed in a 60 ml

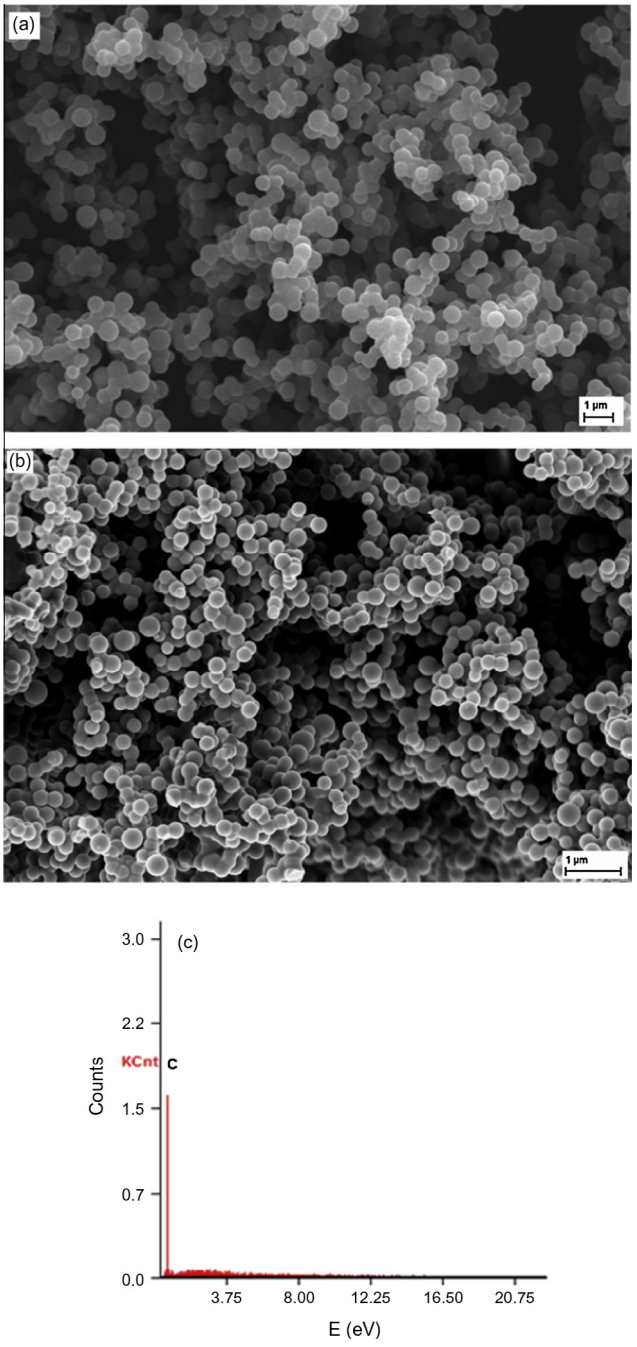

Fig. 1. SEM image of produced CNS (a) after 180 °C, (b) after 500 °C, (c) EDX analysis of CNS.