Electroreduction of Oxygen on Pt Nanoparticles Supported onto TiO₂/Graphene in Acid Media

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Due to its remarkable properties, such as large surface area, good conductivity and mechanical strength, graphene has attracted a lot of attention including the fuel cell catalyst research area [1]. Various nanoparticles have been anchored to graphene in order to create advanced materials for different applications, such as batteries, sensors and fuel cells [2].

A number of studies reported that the dissolution of the Pt catalyst particles and the corrosion of the carbon support are responsible for the performance degradation of proton-exchange membrane fuel cells (PEMFCs) [3]. Agglomeration and growth of the typically nano-sized Pt particles (PtNP) have also been shown to result in a lower electro-active Pt surface area and in a loss of the oxygen reduction reaction (ORR) mass activity of the catalyst. Furthermore, Pt can catalyze the oxidation of the carbon support [2].

In order to avoid degradation of carbon support and eliminate Pt agglomeration possibility functionalization of graphene nanosheets with TiO_2 was utilized in the present study. It is believed that although oxide supports do not participate in the catalytic reaction, they play an important role in the activation of the O_2 molecule.

A nano-sized Pt catalyst supported onto titanium dioxide functionalized graphene support (PtNP/TiO₂-FGS) was prepared using the polyol method [4] and utilized for a catalyst activity investigation toward the oxygen reduction reaction. This work is focused on systematic investigation of PtNP/TiO₂-FGS catalyst material properties toward ORR.

The studies were carried out in a three electrode cell setup using a 40 wt.% PtNP/TiO₂-FGS catalyst. Standard electrochemical techniques as cyclic voltammetry and the rotating disk electrode methods were performed in acidic solution in order to investigate the electrocatalytic behavior of the prepared catalysts. The composite catalyst samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showing a good dispersion of the Pt particles at the surface of the graphene supported TiO₂ particles. The average Pt particle size was 11 ± 2 nm.

Functionalization provided efficient way to keep the nanosheets of graphene exfoliated and more easily accessible for nanoparticle uniform deposition. Functionalized graphene was easily dispersible and had a better adhesion with catalytic nanoparticles. This development confirmed that functionalized graphene sheets used for the preparation of cathode catalysts for ORR is more preferable support than pure graphene.

The values of specific activity (SA) and other kinetic

parameters were determined from the Tafel plots taking into account the real electroactive area of each electrode.

The electrodes exhibited a relatively high electrocatalytic activity for the four-electron oxygen reduction reaction to water. Tafel analysis revealed that the mechanism of O_2 reduction on PtNP/TiO₂-FGS is the same as on bulk platinum. The knowledge obtained by studying electrocatalytic trends on electrode surfaces can be used to provide a fundamental basis for the improvement of existing cathode nanocatalysts.



Figure 1. Annular Dark-Field Scanning transmission electron microscopy PtNP/TiO₂-FGS catalyst



Figure 2. RDE voltammetry curves for oxygen reduction on PtNP/TiO₂-FGS modified Au electrode in O₂ saturated 0.1 M HClO₄. $\nu = 10$ mV s⁻¹.

Acknowledgements

The authors thank Dr. Patrick R. L. Malenfant from Institute for Chemical Process and Environmental Technology, National Research Council Canada (NRC-ICPET) for synthesis of graphene nanosheets and Dr. Martin Couillard (NRC-ICPET) for performing TEM measurements.

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