

Fuel Cell Catalysts Based On Core-Shell Nano-particles

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ABSTRACT

In this work, we used platinum black to improve the dispersion mechanisms onto highly oriented pyrolytic graphite substrates by using different solvents in order to develop a methodology to disperse core-shell Pt nanoparticles. With this technique, we found that pure isopropyl alcohol exhibited better dispersion onto graphite in comparison with a mixed solution. Although SEM and STM images revealed in general a poor dispersion, some aggregates and few individual particles scattered onto the graphite surface were observed.

Keywords: fuel cell, catalysts, Pt, nanoparticles

1 INTRODUCTION

Reducing the costs of fuel cell components is a key issue in the commercialization and broad application of fuel cell technology. Particular focus is on the catalyst: Platinum is still the most effective material for both the fuel and air electrodes in PEMFC systems [1]. However Pt is one of the most expensive metals on earth and extensive use of the technology in the future will only aggravate the situation [2]. Thus, strategies of how to use the limited Pt resources more efficiently are currently being researched extensively. One option is to increase the surface area of the catalyst, since it is the surface, rather than the bulk atoms, which is catalytically active. Nanoparticles are thus a viable alternative to bulk metals, since they exhibit a large surface-to-volume ratio. This increases the fraction of (Pt) surface atoms and ensures a higher efficiency, relative to the amount of catalyst material used. Nevertheless, a significant amount of Pt still remains in the centre of the particle and does not take part in the catalytic process. A potential alternative is to employ the so-called “core-shell” nanoparticles, where the bulk is composed of a suitable inexpensive material (e.g. Co) [3] and only the surface is covered with Pt metal. Such catalysts would require a minimal amount of Pt, while still providing sufficiently high catalytic activity. The investigation of such core-shell nanoparticles, including their physical and chemical properties is thus of key interest to the fuel cell community.

2 EXPERIMENTAL

Platinum black nanoparticles (JOHNSON MATTHEY) were ultrasonicated in either isopropyl alcohol or a 1 :1 mixed solution of isopropyl alcohol (C_3H_8O , AnalaR NORMAPUR) and butyl acetate ($C_6H_{12}O_2$, SIGMA-

ALDRICH). Two solutions were employed in this study. The concentration of 1mg: 1ml was employed for the pure alcohol while a 1mg: 1ml was used for the mixture. The 1 x 1 x 0.2 cm of Highly Oriented Pyrolytic Graphite (Agar Scientific) was used as a substrate material. Graphite was cleaved before each experiment prior to the deposition of a drop of solution. Samples were left to dry for 2 hours before each characterization. Scanning electron microscopy (SEM) images were obtained with LEO 420 equipment. Finally, an Agilent Scanning Tunnelling Microscope (STM) was used in the constant current mode to investigate the particle dimensions and the aggregation state of the system (Figure 1). The tunnelling conditions include: the tunnelling current 0.200nA, the bias voltage 0.800V and the scan rate 814nm/s.

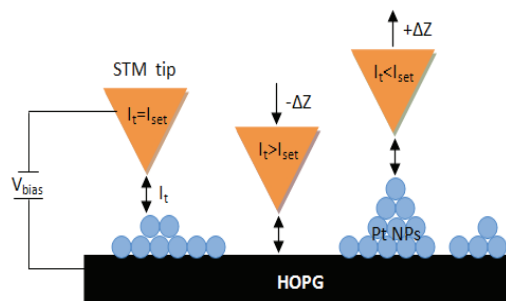


Figure 1: The constant-current mode in STM.

3 RESULTS

From Figure 2, a relatively even dispersion on the graphite surface is observed. It is possible to distinguish clusters from 100 nm to 5 microns in diameter. At higher magnification, smaller clusters can be seen although the resolution of the SEM microscope is still too low to detect individual particles. On the other hand, high resolution images, Figure 4, by STM show individual particles between the aggregates. A profile analysis of the features showed a distribution between 1.5 to 2.5 nm in height.

As the platinum concentration increased, the aggregation became more important regardless of the solvent employed. For instance, when the platinum concentration was doubled, the size of the aggregates increased up to 8 microns in diameter as seen in Figure 3. From this image, we can also notice a low surface coverage between the aggregates which complicate the imaging by STM.

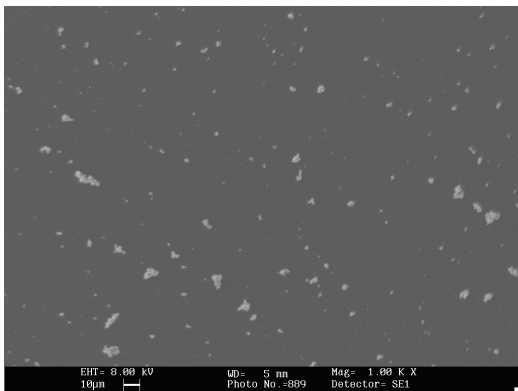


Figure 2: SEM image of Platinum black particles onto HOPG (Pt: solvent=1mg:1ml).

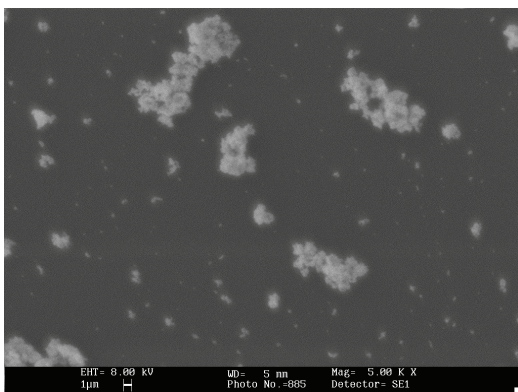


Figure 3: SEM image of Platinum black particles onto HOPG at higher concentration (Pt: solvent=2mg: 1ml).

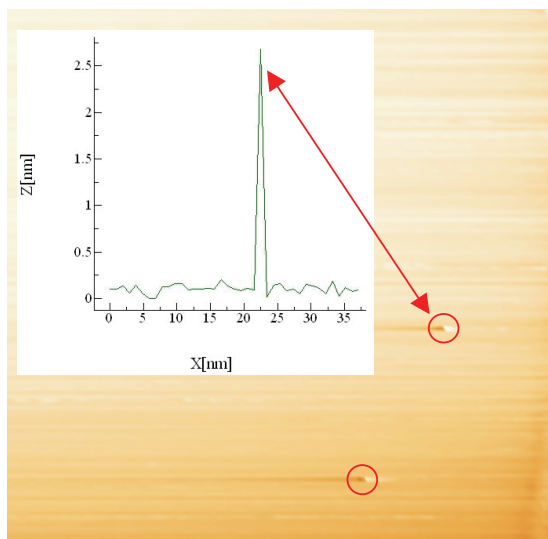


Figure 4: The platinum black particles (in red cycles) on HOPG as seen by STM (0.200nA, 0.800V, 814nm/s). The inset shows the profile of one Pt particle. Image size is 29 x 29 nm.

4 CONCLUSIONS

The results show that pure isopropyl alcohol provides better dispersion than the mixed solvent. On the other hand, lower concentrations improve the dispersion onto HOPG in comparison with higher concentrations.

Although these experiments are at an early stage, the current results demonstrate that because of the high hydrophobicity of HOPG, the method of direct dispersion onto a graphite surface is not very satisfying since platinum black particles tend to agglomerate during the solvent evaporation. Future work needs to be done in order to improve the dispersion ability of the solvent. This will reduce the mean diameter of the aggregates and hopefully increase efficiency of the catalyst.

5 FUTURE WORK

1. We will continue using the dispersion technique by using the drop technique with different solvents and mixtures. The different concentration will also be investigated.
2. We will investigate the particle deposition in situ by using the liquid cell of the STM. In this case organic and aqueous solutions will be employed.
3. The electrochemical properties of Pt black nanoparticles and Pt / Co core/shell nanoparticles will be investigated and compared. These include the in-situ electrochemical STM imaging and cyclic voltammetry.
4. Finally, fuel cell test will be performed to investigate the catalytic performance under or close to operating conditions.

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