Magnetron Sputtered PtNP/MWCNT Composite Electrocatalysts for Oxygen Reduction Reaction

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Pt nanolayers were sputter-deposited onto multi-walled carbon nanotubes (MWCNT). Pt nanoparticle/MWCNT composites were used as catalysts for oxygen reduction reaction (ORR). Magnetron sputtering has a number of advantages over other physical methods, such ease of sputtering any metal, alloy or compound onto different substrates providing high-purity films, good adhesion on substrate with accurate control of metal loading [1]. Although the method is convenient, it is not frequently utilized in fuel cell catalyst preparation. Nevertheless, this method enjoys an increasing interest within both AEMFC and PEMFC communities [2]. The purpose of this work was to perform a systematic investigation for optimizing the use of the magnetron sputtering technique for the preparation of electrocatalytically active PtNP/MWCNT nanocomposite materials.

Anchoring of Pt nanolayers of different catalyst loading onto MWCNT support was performed by sputter-deposition with a Pt target in argon atmosphere. The nominal Pt film thicknesses were 4, 8 and 16 nm. In what follows, the prepared catalysts are designated as 1-PtNP/MWCNT; 2-PtNP/MWCNT and 3-PtNP/MWCNT, respectively. The CO oxidation experiments and cyclic voltammetry were used for cleaning and characterizing the surface of PtNPs attached to carbon nanotubes.

The rotating disk electrode (RDE) experiments were performed in O_2-saturated 0.5 M H_2SO_4 and 0.1 M KOH solutions in order to test the electrocatalytic properties of PtNP/MWCNT catalysts. The composite catalyst samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM micrographs show an excellent distribution of the Pt nanolayers on the surface of MWCNTs (Fig. 1).

The electrodes exhibited a high electrocatalytic activity for the four-electron reduction of oxygen to water (Fig. 2a). As expected, the overall ORR activity increases with increasing nominal Pt layer thickness. Linear Koutecky-Levich (K-L) plots were obtained from the RDE data and the value of *n* was found from the K-L slopes, which was close to four for each electrode. For the determination of kinetic parameters of O_2 reduction on PtNP/MWCNT catalysts the Tafel plots were constructed from the RDE data (Fig. 2b). Two Tafel regions with characteristic slopes close to −60 and −120 mV dec^{-1} were clearly distinguished. Similar slope values were observed for a bulk Pt electrode. This indicates that the reaction mechanism is the same for all the electrocatalysts tested. Specific activity (SA) values of PtNP/MWCNT composites are higher than that of bulk Pt electrode.

In order to confirm activity trends the ORR was also studied in alkaline media. The half-wave potentials of O_2 reduction in 0.1 M KOH were higher than in 0.5 M H_2SO_4 and this is the expected results considering the inhibiting effect of strongly adsorbed (bi)sulfate anions. The SA values of PtNP/MWCNT catalysts in 0.1 M KOH were comparable with that of bulk Pt. The Tafel behavior of O_2 reduction was also similar for these electrodes.

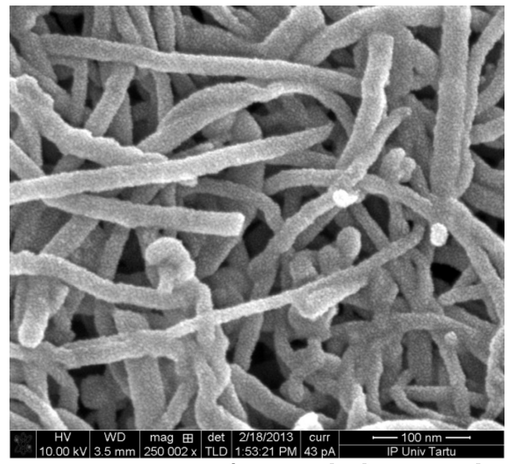

Figure 1. SEM image of 4 nm thick Pt nanolayer on multi-walled carbon nanotube support.

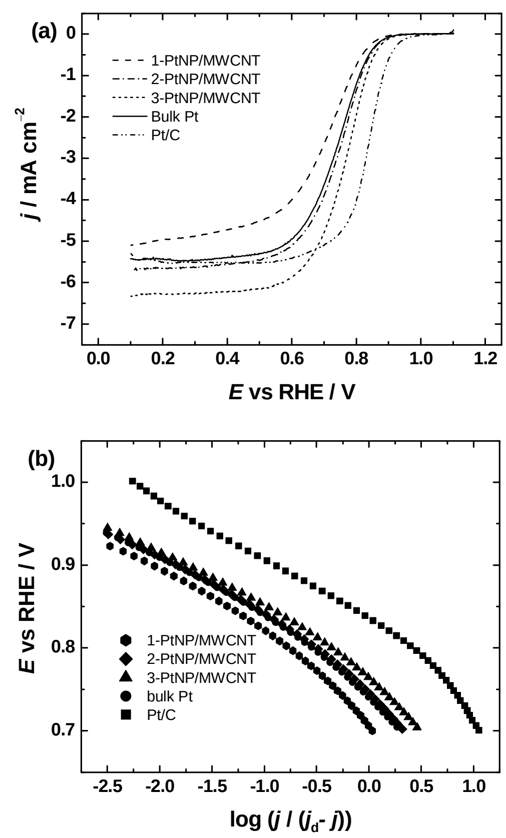

Figure 2. (a) Comparison of RDE results on O_2 reduction on PtNP/MWCNT and commercial Pt/C modified GC and bulk Pt electrodes in O_2-saturated 0.5 M H_2SO_4. v = 10 mV s^{-1}, ω = 1900 rpm. (b) Mass-transfer corrected Tafel plots for O_2 reduction on PtNP/MWCNT and commercial Pt/C modified GC and bulk Pt electrodes in 0.5 M H_2SO_4.

In summary, magnetron sputtering provided an easy and efficient deposition of Pt nanolayers on carbon nanotubes with controlled loading. This development confirmed that the sputtering method can be successfully utilized for the preparation of PtNP/MWCNT cathode catalysts for low-temperature fuel cells. Morphological and electrochemical characterizations provide a better understanding of changing catalytic properties of prepared composites.

References

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[2] K. Jukk, N. Alexeyeva, A. Sarapuu, P. Ritslaid, J. Kozlova, V. Sammelselg, and K. Tammeveski, *Int. J. Hydrogen Energy* **38,** 3614 (2013).