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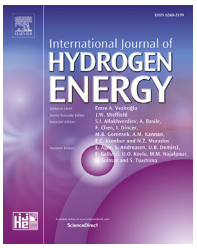

Pt nanoparticles sputter-deposited on TiO_2/MWCNT composites prepared by atomic layer deposition: Improved electrocatalytic activity towards the oxygen reduction reaction and durability in acid media

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ABSTRACT

Acid-treated multi-walled carbon nanotubes (MWCNTs) were decorated with TiO_2 using the atomic layer deposition (ALD) technique followed by uniform distribution of platinum nanoparticles (PtNPs) through magnetron sputtering. Surface analyses were performed by scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS). Electrochemical decontamination and characterization of the Pt-TiO_2/MWCNT electrodes were carried out by CO stripping followed by cyclic voltammetry in acid media. The oxygen reduction reaction (ORR) was studied in O_2-saturated 0.05 M H_2SO_4 solution using the rotating disk electrode (RDE) method. Durability of the prepared catalysts was examined by repetitive potential cycling. Electrochemical data obtained was analyzed and compared to that of the commercial Pt/C catalyst. It was revealed that the Pt-TiO_2/MWCNT catalysts possess higher ORR activity and better durability as compared to that of the commercial Pt/C.

Introduction

Since the past few decades, significant efforts have been devoted to develop advanced energy conversion devices in order to utilise renewable energy resources as an alternative to the conventional fossil fuels [1]. One of the most promising 21st century energy conversion devices is the polymer electrolyte membrane (PEM) fuel cell [2]. PEM fuel cell is preferred in both automotive and stationary applications because of its green and efficient operating system [3,4]. Platinum, being the

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most active catalyst for oxygen reduction reaction (ORR), has attracted significant attention in the respective research area [5–7]. To enhance the ORR activity and durability of the catalyst and to minimize the loading of the costly noble metal, Pt nanoparticles (PtNPs) are usually deposited onto suitable support materials [8–17]. It has been observed that carbon and oxide-based substrate materials increase the ORR activity of the metal catalyst [18–20]. Among the high-area carbon-based support materials, multi-walled carbon nanotubes (MWCNTs) are regarded as a suitable catalyst support due to their outstanding mechanical, chemical and electrical properties [21–24]. It has been previously reported that magnetron sputtering is a promising technique for the uniform distribution of PtNPs on a support surface [25–27].

It has been demonstrated by many groups that TiO_2-based support material enhances the ORR activity and durability of the Pt catalysts mainly because of the metal-support interaction [28–35]. Matsumoto and co-workers have recently reported PtNPs anchored on TiO_2/cup-stacked carbon nanotubes with enhanced ORR activity and durability [32]. The PtNPs were anchored to TiO_2 matrix by photodeposition. It was found that the induced electronic interaction between the TiO_2 and PtNPs resulted into increased ORR activity. Moreover, the durability of the electrocatalyst was attributed to the inhibition of agglomeration of the PtNPs due to TiO_2 support. Another group used different TiO_2 phase composition as support by applying heat-treatment at different temperatures followed by deposition of PtNPs through colloidal method [28]. They reported higher ORR activity of Pt deposited on TiO_2 annealed at 800 °C than that of the Pt supported on anatase TiO_2. Moreover, long-term stability test was performed by measuring cyclic voltammograms between 0 and 1.0 V vs reversible hydrogen electrode (RHE) at a scan rate of 20 mV s^{-1}. It was confirmed that more than 60% of the electrochemically accessible surface area was retained by Pt/TiO_2-800 even after 20,000 potential cycles. Zhao et al. reported Pt supported on TiO_2 modified graphitized nanodiamond as a more durable catalyst than Pt/C [36]. Additive-treated TiO_2 has been studied as an alternative to carbon-based support [29]. Three types of additives, namely urea, thiourea and HF were added through hydrothermal process and the results were compared to those of non-additive-treated TiO_2. It was observed through transmission electron microscopy (TEM), X-ray diffraction (XRD) analysis and cyclic voltammetry that the TiO_2 support treated with additives affects the Pt particle size distribution and thus changes the surface area of the catalyst. Furthermore, the ORR activity of the Pt supported on HF-treated TiO_2 was higher as compared to the others because of the formation of highly reduced electronic state. Deposition of thin films of TiO_2 and Pt on Nafion membrane has been carried out by thermal evaporation [30]. The prepared electrode was examined in PEM fuel cell. The ORR measurements showed that the activity of the catalyst increases by incorporating TiO_2 between Pt and Nafion membrane. Rajalakshmi and co-workers also studied durability of TiO_2 as a support for Pt catalyst [31]. The catalyst showed higher electrochemical activity and thermal stability as compared to Pt/C, which was attributed to the highly dispersed Pt atoms and controlled nanostructure of the catalyst on the TiO_2 layer.

Atomic layer deposition (ALD) is one of the most promising techniques used by many groups for the deposition of TiO_2 [27,37–40]. Our group has previously studied the electrochemical oxygen reduction behavior of PtNPs sputter-deposited on vertically-aligned MWCNTs coated with TiO_2 through ALD technique [27]. It was revealed that Pt-TiO_2/MWCNT modified electrode shows slightly higher ORR activity and durability in acidic medium than Pt/C while the Tafel slope values revealed that the ORR on both types of electrodes followed the same mechanistic pathway. Similar work was performed by another group who grew vertically-aligned carbon nanotubes by the chemical vapor deposition (CVD) method followed by TiO_2 deposition using the ALD technique and annealing in a tube-furnace at 600 °C for 4 h [41]. The catalyst showed higher specific capacitance and power density as compared to bare MWCNTs, which is attributed to the addition of faradic charge transfer mechanism due to TiO_2. The effect of various defect sites on the vertically aligned CNTs on the formation of TiO_2 nanoparticles has recently been studied [40]. Various mass fractions of TiO_2 were grown on the pristine CNTs, plasma-treated CNTs and N-doped CNTs using the ALD technique and the composite material was studied by TEM, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis and Raman spectroscopy. It was observed that the nucleation of the TiO_2 is affected by the distribution of the carbon-heteroatoms defect sites rather than structural defects. In order to obtain complete coverage of the MWCNTs with ultrathin coatings of TiO_2, Utke and co-workers introduced a new technique of temperature-step ALD [42]. They reported that the surface morphology of the anatase layer can be controlled by tailoring the deposition temperature during the ALD process. Moreover, complete coverage of the MWCNTs with continuous TiO_2 layer was achieved by applying a temperature of 60 °C during nucleation and 220 °C in the growth phase. Similar work has also been reported by another group for the engineering of HfO_2 thin films on Si substrate [43]. Lee and co-workers prepared TiO_2 coated Pt/C catalyst for ORR in PEM fuel cell using ALD [37]. The ORR activity and durability of the catalyst prepared at different ALD cycles were studied and compared to that of commercial Pt/C. They concluded that the TiO_2/Pt/C catalyst prepared with 10 ALD cycles of TiO_2 was more durable than Pt/C. Durability of the Pt catalyst deposited on TiO_2-decorated functionalized MWCNTs has recently been studied in PEM fuel cell [44]. It was observed that TiO_2-based catalyst support is more corrosion-resistant as compared to that without TiO_2.

In this work we aimed to investigate the role of TiO_2 used as a supplementary support for Pt catalyst. TiO_2 nanoparticles were deposited on MWCNTs using ALD technique followed by sputter-deposition of PtNPs on the TiO_2/MWCNT surface. The main advantages of the two deposition techniques include high reproducibility and controlled deposition, which are vital to investigate the role of TiO_2 as support and corrosion-resistant substrate for the Pt catalyst. Different loadings of Pt and TiO_2 are used for the electrochemical measurements to observe their influence on the ORR activity and durability of the Pt-TiO_2/MWCNT catalysts. Surface characterization of the prepared Pt-TiO_2/MWCNT electrodes is carried out by XPS,

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