Changing to TiO_x Based Nanostructured Catalyst Support Materials for PEM Fuel Cells Utilizing ALD and PEALD

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Two challenges currently inhibiting the progression of proton exchange membrane fuel cell (PEMFC) technologies utilizing Pt on carbon catalyst materials, are carbon corrosion^{1,2} and electrode flooding.³ These two processes (associated with typical colloidal carbon supports) lead to poor catalyst performance over time thereby inhibiting the long term efficiency of PEMFCs. Consequently, the current work investigates strategies for overcoming these two challenges. It is suggested that by changing the catalyst support material and structure the undesirable consequences of these processes can be avoided. TiO_x and Nb enhanced TiO_x (Nb-TiO_x) are suggested as potential carbon support replacements due to their high conductivity and corrosion resistance.

High aspect ratio $TiO_x/Nb-TiO_x$ nanostructures (up to 100:1) were formed using atomic layer deposition (ALD) over anodic aluminum oxide (AAO) and silicon nanowire (SiNW) templates (see Figure 1). To increase conductivity $TiO_x/Nb-TiO_x$ films underwent post deposition oxygen reducing anneals in hydrogen. Four point probe and x-ray photoelectron spectroscopy (XPS) measurements of annealed films indicate a substantial increase in conductivity corresponding with a subtle but consistent decrease in oxygen. The maximum conductivity (~400 S/cm) was obtained for a O/Ti ratio of ~1.75. $TiO_x/Nb-TiO_x$ films were observed to be stable in both oxidizing and acidic environments.

Since minimizing the loading of Pt is a necessary route to reducing fuel cell costs, it is useful to be able to maximize the catalyst's surface area (i.e., maximize the catalyst's efficiency). Hence, plasma enhanced atomic layer deposition (PEALD) exists as a powerful technique for coating 3-D surfaces with catalyst particles which are highly size controllable and evenly distributed. For contrast in the current work, catalysts were deposited using both PEALD and a liquid phase deposition technique. Electrochemical analysis of resulting catalyst coated nanostructured materials was performed using cyclic voltammetry (CV) and rotating disk electrode (RDE) analysis. Results indicate higher catalyst specific activity on $TiO_x/Nb-TiO_x$ structures than what is typical of Pt on carbon materials.

¹ J. Wang, et al., J. Power Sources **171**, 331 (2007).

² T. Ioroi, et al., J. Electrochem. Soc. **155**, B321 (2008).

³ H. Li, et al., J. Power Sources **178**, 103 (2008).



Figure 1: SEM of Pt Coated Supports: Micrographs of the three step fabrication process of Pt/TiO_x coated SiNWs where (a) is the as grown SiNWs, (b) is the same wires coated with TiO_x and (c) is the PEALD Pt coated TiO_x. In (d) a micrograph of liquid phase deposited Pt coatings on Nb-TiO_x tubes formed from AAO templates are shown.