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Novel Pt Support for Proton-Exchange Membrane Fuel Cell (PEMFC) Cathode and Anode Active Layer

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Abstract

Fuel cells continue to show great potential as a clean energy source for both mobile and stationary power, but considerable improvements are still necessary to reach this potential, primarily with respect to cost/power ratio. This project details an alternative membrane construction for the Proton-Exchange Membrane Fuel Cell (PEMFC) that will enable a reduction in the required platinum (Pt) mass, the most costly single component in the PEMFC. The key to this improvement comes from using a continuous array of aligned carbon channels for the Pt support in the electrode. The aligned carbon constitutes the active layer of the membrane assembly and when tested against the current technology demonstrated a 6-fold improvement per gram of Pt at peak power. The patent-pending method that was used to synthesize the Pt support allows a high degree of dimensional variability, such that the dimensions can be tuned to reach the optimum fuel cell output in future endeavors.

Introduction

There is a growing interest in the development of alternative power sources in all areas of energy production. A field that has shown remarkable technological progress over the past thirty years is the fuel cell, particularly the proton-exchange membrane fuel cell (PEMFC). Hurdles still exist in each step of this fuel cell system, but one area that requires particular attention is the high cost of using Pt in the active layer of the anode and cathode. The chemical reactions necessary for fuel cells to generate power do not occur at the temperatures of interest (60-120°C) without a catalyst, and Pt is the most efficient catalyst for both the hydrogen oxidation reaction in the anode and the oxygen reduction reaction in the cathode; there are currently no known cost-effective alternatives to this noble metal. The current target for a competitive PEMFC is \$45/kW by 2010 with an additional goal of \$30/kW set for 2015. According to an Arthur D. Little study, the current cost of precious metals alone in the present day fuel cell is \$65/kW, an estimated one-fifth of the total cost, which illustrates the necessity of marked improvement in this step alone (Carlson 2001). This project details a Pt support that is geared towards the optimization of the Pt in the fuel cell to derive the optimum power per gram of Pt used.

Technical Approach

PEMFCs are attractive because they can potentially generate more specific power (power normalized to the mass of fuel cell, e.g. W/kg) and power density (power normalized to the cross-sectional area of the electrodes, e.g. W/cm²) than any other fuel cell. The electrical power is generated through controlled chemical reactions in a stack of fuel cells consisting of: bipolar plates, catalyst containing electrodes, and proton exchange membranes (PEM). As previously mentioned, Pt is the best available catalyst for the hydrogen oxidation reaction at the anode, which proceeds according to the following mechanism:



The electrons flow out of the anode through an external circuit and then to the cathode, while the H^+ proton permeates through the PEM to the cathode. They then react with O_2 according to the following stoichiometry:



While the H_2 oxidation reaction and mechanism is well understood there is still not a well-established mechanism describing the O_2 reduction at the cathode, so only the overall reaction can be accurately displayed. A concern in PEMFCs is overpotential, or the loss of power through interactions that do not generate power, such as electrical resistance, reversible reactions, mass-transfer limitations, etc. In general, the number of steps in a process is proportional to the overpotential associated with the process; for instance, the overpotential in the cathode, a $4 e^-$ interaction, is generally an order of magnitude higher than in the anode, a $2 e^-$ interaction. Other contributions to overpotential arise from proton mobility, or diffusion, through the electrodes and PEM, and especially the transition between these phases; in fact, recent studies have shown that the impregnation of the PEM into a small portion of the electrodes lead to a 10-fold improvement in performance because the transfer mobility of reactants was improved (Gottesfeld 1997). This finding highlights the need to consider the diffusional characteristics of the system.

The current membrane electrode assemblies (MEA) use Pt clusters (2-3 nm) dispersed on carbon black supports that have a diameter of about 0.1 μm . Carbon black (CB) is used for its high porosity and high surface area ($\sim 150 m^2/g$), which enables high power densities. These Pt-coated particles are held together with a binder to constitute a 10-60 μm thick active layer of the anode and cathode. Diffusion is not optimized with these Pt supports since the porous structure is highly irregular and tortuous in carbon black, and the Pt is dispersed throughout the pores. The reactant gases must diffuse into these meandering pores and the products must diffuse out. The extent that the pore structure effects diffusion is defined as tortuosity, τ :

$$\tau = \frac{\text{actual distance molecule travels between two points}}{\text{shortest distance between two points}} \quad (5)$$

Tortuosity is inversely proportional to the effective diffusion of a molecule, and can have a dramatic effect on the overall fuel cell efficiency if molecular transport to and from the reaction sites is a limiting factor, such as the case at high loads. In other words, since most of the gas does not diffuse to the center of the carbon black particle, the Pt in the center is not efficiently utilized, so the overall output per gram of Pt decreases. Thus, diffusion is minimized as τ approaches unity.

This project focused on the development and fuel cell demonstration of an alternative support system for this Pt-rich active layer, i.e. the layer where chemical reactions occur. The new technology is based on a recently reported method of aligned carbon nanotubule deposition in the pore structure of anodized alumina, often referred to as the template method (Martin 1996, Kyotani 1996, and Miller 2001). This technique allows the synthesis of an active layer with aligned carbon nanotubules as the Pt support (with outside diameters circa 20 nm), and it results in electrodes comprised of a continuous array of these nanotubules. These aligned nanotubules have theoretical tortuosity of unity for the entire active layer of the electrodes, which minimizes the diffusional constraints of the catalyst support. The fabrication method allows flexibility in controlling the nanotubule diameter (by selection of the alumina pore size), wall thickness (varying deposition time), and location of the Pt particles, either solely on the interior walls, or on all surfaces. This flexibility allows the fine-tuning of the support's pore structure to achieve optimal diffusion, such that the effectiveness of each Pt reactive site would increase. The details of the fabrication are patent pending (ID 1072) and can not be fully disseminated in this medium;

however, it should be noted that the process involves inexpensive pyrolysis of hydrocarbons (HC) that deposit carbon nanotubes inside pores of commercially available alumina templates. These nanotubes and their application in the MEA are the fundamental difference between the current PEMFC technology and the one demonstrated in this project. The scope of the project entailed the following steps:

Task 1. Nanotubule Deposition Study.

Task 2. Pt Deposition and Alumina Removal.

Task 3. Characterization of Pt-coated Nanotube Arrays.

Task 4. MEA synthesis and PEM Fuel Cell testing.

The end result of this project is a direct comparison of the current technology PEMFC against the novel minimal diffusion PEMFC.

Results and Discussion

The deposition rate of carbon on the walls of the alumina pores was fully mapped out for HC pyrolysis on alumina templates, and the rates were verified with High Resolution Transmission Electron Microscopy (HRTEM) at ORNL's High Temperature Materials Laboratory (HTML). The HRTEM also verified a constant deposition rate regardless of pore size (20-300 nm), i.e. the channel thickness is constant throughout the membrane. Template removal using HF was executed for a wide array of carbon supports, and the method underwent modifications to ensure the integrity of the nanotubular array. It was determined that a minimum wall thickness of 4-5 nm was necessary to ensure the mechanical integrity of the carbon nanotubular array. Using the wet impregnation technique, platinum (H_2PtCl_6 precursor) was added to the nanotubular array both before and after removal of the template. It was determined that Pt deposition before template removal was the best technique to achieve well dispersed Pt crystals; particle size and deposition was verified by HRTEM. Pt crystals of 2-5 nm were obtained in the carbon arrays with an average particle size of 3 nm, which indicates approximately 1/3 of the Pt atoms are surface atoms available for catalytic activity.

Having synthesized the active layer it was possible to assemble the rest of the MEA with commercially available materials. Nafion[®] 117 (18 mm thick) was used for the proton exchange membrane, and Toray carbon paper (0.19 mm thick) was used for the gas diffusion layer. The diffusion layer, active layer and membrane were pressed together at 1250 psig and 150°C for 5 minutes in a Carver Press with heated platens. This results in a MEA that must be kept under high humidity to minimize disruption, since Nafion[®] is hygroscopic and is susceptible to curling in transient humidity environments.

To accurately compare the nanotubule array MEA to the current technology, it was necessary to synthesize an MEA with the current technology, but using the same Pt dispersion technique, and MEA assembly protocol. CB with 80 m²/g specific surface area was used as the catalytic support, and Pt was added using the wet impregnation technique with H_2PtCl_6 . HRTEM analysis of the resulting Pt/CB displayed relatively large Pt particle sizes, 5-9 nm, so when comparing the two MEAs all results were normalized to surface Pt. This results in the most accurate comparison, and due to the similarity of the MEA synthesis allows the comparison to be made where the only variant is the geometry of the Pt support.

Having developed the synthesis technique for the MEAs, fuel cell testing was now possible. A miniature single cell PEM fuel cell from H₂ Economy was obtained with a cross sectional area of 5 cm². This representative fuel cell consists of a collector plate, a bipolar plate (with a serpentine pathway), and a gasket for each side of the MEA. The fuel cell was easily disassembled, so

switching MEAs was trivial. H₂ and O₂ were humidified at 28 and 30 psig respectively, by passing the gases through a sparger at 10 sccm to achieve saturation and introduced to the fuel cell through heated. The fuel cell was operated both at 25°C, indicative of startup operation, and the generally accepted maximum output temperature of 85°C. The most widely accepted test that indicates operation dynamics of a fuel cell is a plot of voltage versus current (an I-E plot) where resistance is applied to draw current. The higher the current is at a given voltage the better the fuel cell is operating, i.e. overpotential is minimized. The fuel cell was equipped with a resistor bank that allows application of a resistance from 0.2 to 10⁶ Ω. As shown in Figure 1, the aligned carbon support has considerably better performance than the Pt/CB electrode; at 85°C and 0.4V the current generated for the novel support is 6 times greater than the Pt/CB support. Similarly, the maximum work from the aligned carbon MEA is 6.4 versus 1.1 W/g_(surface Pt) for the Pt/CB MEA. These results are very promising and satisfy the proof of principle needed for the patent technology; however, we believe there is still room for further improvements that were unable to be addressed at this time. The pending follow-on funding should allow us to bring this potential to realization as well.

Benefits

Improvements in the PEMFC is a key thrust to DOE's Energy Efficiency and Renewable Energy (EERE) and this project ties directly into this area which is the likely prime mover for FreedomCar. It is relevant to the energy resources and the environmental quality missions of DOE. Many other federal agencies are investigating the usefulness of PEMFCs. The primary barrier of which is their high cost. If this success aids the implementation of PEMFCs as a viable power source, multiple other federal agencies (Department of Defense, Department of Transportation, etc.) could benefit.

The results of this project have been disseminated throughout ORNL, and Tim Armstrong (ORNL's representative for EERE's Hydrogen, Fuel Cells and Infrastructure Technologies Program) further distributed the results to DOE Headquarters. The new project has been included in ORNL's Annual Operating Plan FY2005 that is currently pending Congressional action. Other contact has been made with industry, although the proprietary nature of the project tends to inhibit full cooperation; however, a Non-Disclosure Agreement is in place with United Technologies Research Center.

References

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Figure Caption

Fig. 1. I-E plot comparing the existing technology Pt support system (Simple Pt/CB) to the improved aligned carbon support. Depicts 6-fold increase in specific current at 0.4V and 85°C. Test conditions: 25 or 85°C, 30 psig O₂, 28 psig H₂, steam saturated at 80°C, 5 cm² cross-sectional area.

