V.A.12 Mesoporous Non-Carbon Catalyst Supports of PEMFC (SBIR I)

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Overall Objectives

- Produce high surface area platinum–metal carbide (Pt-MC) mesoporous powders by a nanocasting route.
- Determine morphology of Pt-MC material.
- Evaluate electrochemical performance of Pt-MC as an alternative catalyst support material for use in proton exchange membrane fuel cells (PEMFCs).

Fiscal Year (FY) 2017 Objectives

- Demonstrate minimal loss in electrocatalytic activity in Pt-MC catalyst and membrane electrode assembly.
- Reduce required loading level of platinum.
- Evaluate alternate precursor materials to determine feasibility of producing mesostructured support material.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

Technical Targets

This project is addressing the following (Table 1) technical targets related to the durability of catalyst supports in PEMFCs.

TABLE 1. Technical Targets: Electrocatalysts for Transport Applications

Characteristic	Unit	2015 Status	2020 Target
PGM total content	g/kW @ 150 kPA	0.16	0.125
PGM loading	mg PGM/cm^2	0.13	0.125
Mass activity	A/mg PGM @ 900 mV	>0.5	0.44
Loss in initial catalytic activity	% mass activity loss	66	<40
Loss in performance at 0.8 A/cm^2	mV	13	<30
Electrocatalyst support stability	% mass activity loss	41	<40
Loss in performance at 1.5 A/cm^2	mV	65	<30
PGM-free catalyst activity	A/cm^2 @ 900 mV	0.024	<0.044

PGM – platinum group metal

FY 2017 Accomplishments

- Evaluated several fabrication routes to a durable, mesoporous metal carbide powder using new precursors.
- Achieved fabrication of a high surface area metal catalyst product to be used as a support material (565 m^2/g).

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INTRODUCTION

PEMFCs are promising energy conversion systems that harness energy from hydrogen and air with clean emissions. A big obstacle preventing the commercialization of PEMFCs is the significant decrease in performance over long-term operation. Lack of durability of catalyst supports has been attributed as a major source of overall fuel cell performance deterioration. Metal carbides are promising alternative materials to carbon black, the most commonly used catalyst support. A mesoporous metal carbide in particular is attractive because of its high active surface area and favorable transport properties.

Although metal carbides are fabricated commercially for a variety of applications, no process exists to produce a mesoporous material with such a high surface area. In this project, the development of such a process was investigated through the use of a series of unique precursor polymers integrated with a templating method to achieve mesoporosity.

APPROACH

The focus of this research effort is to evaluate the feasibility of using a non-carbon support material in PEMFCs and to establish a method of producing the alternative support that is cost effective. With respect to utilizing a metal carbide support as the substitute material, the overall approach is defined in two stages: investigation of synthesis routes to a mesoporous metal carbide and electrochemical analysis of the metal carbide with platinum functionalization. Although research is ongoing to replace platinum with a cheaper catalyst, this is not within the scope of this project.

Four types of precursor materials were synthesized and converted into the associated metal carbide products, utilizing a silica template and a developed heating process. The morphologies of the resulting products were analyzed to determine the best fabrication route. Once the ideal process is established, electrochemical activity of a Pt-MC catalyst will be assessed by functionalizing the surface of the metal carbide with Pt and performing basic testing including rotating disk and lab-scale membrane electrode assembly cyclic voltammetry. From this data, we will establish the proof of concept of the Pt-MC catalyst support in terms of both production and performance.

RESULTS

Three polymeric and one molecular precursor were synthesized according to prior literature. These precursors had been used to prepare metal carbide products, but not with a mesoporous structure. The difficulty in fabrication of mesoporous metal carbides is that often high temperatures are required for the reaction of the precursor to complete, but high temperatures will cause the mesoporous structure of a template material to degrade. The precursor must be successfully infiltrated into a mesoporous template, heated to an appropriate temperature, and then the product must be etched to remove the template. This unique process is outlined in Figure 1.

It was found that the MCM-41 (silica) was the best candidate for use as a template because of its stability and high surface area (931 m^2/g). Figure 2 shows X-ray diffraction patterns of this material at 600°C and 1,150°C. The relative stability of the low angle peaks (indicative of mesopores) and the retention of the broad amorphous peaks at higher angles suggest good stability for use in heat treatment procedures.

In addition to the method of silica template, one alternative procedure was explored, utilizing a cotton T-shirt as both a carbon source and a template to produce metal carbide nanowires. When combined with a nickel catalyst, this process produced a partially crystalline metal carbide product (Figure 3) with moderately high surface area (Table 2). Surface area analysis was conducted on the metal carbide products prepared using the silica or fiber template and a moderate temperature heat treatment (<1,200°C).

A high surface area of 565.5m^2/g was obtained for one sample type using the MCM-41 template, which should give good electrochemical activity as it is comparable to typical carbon based supports. The effect of different types of infiltration is clearly shown in Table 2, resulting in significantly different surface areas. It is vital to ensure proper filling of the template pores to produce a high surface area product.

CONCLUSIONS

Preparation of a high surface area metal carbide was demonstrated, establishing the groundwork of a process for making a mesoporous Pt-MC catalyst material. Once these high surface area carbides are functionalized with platinum, electrochemical testing will be conducted to determine the performance and durability of the supports.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Jacob Coppage-Gross "Mesoporous Non-Carbon Catalyst Supports of PEMFC." Department of Energy Annual Merit Review, July 2017.

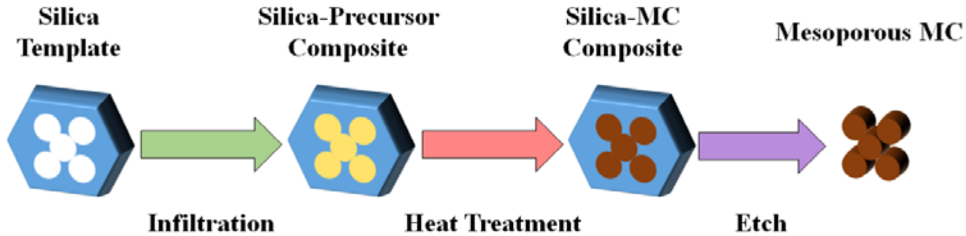

FIGURE 1. Schematic of templating process for producing mesoporous MC

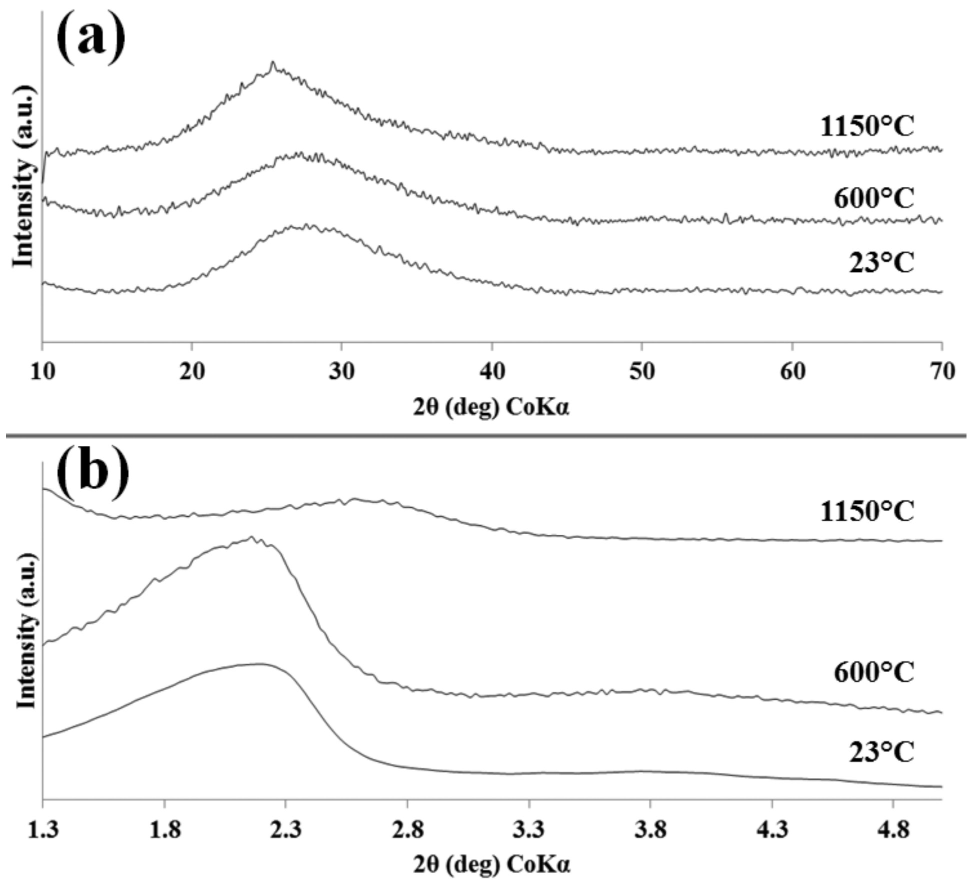

FIGURE 2. X-ray diffraction patterns of MCM-41 at (a) high angles and (b) low angles

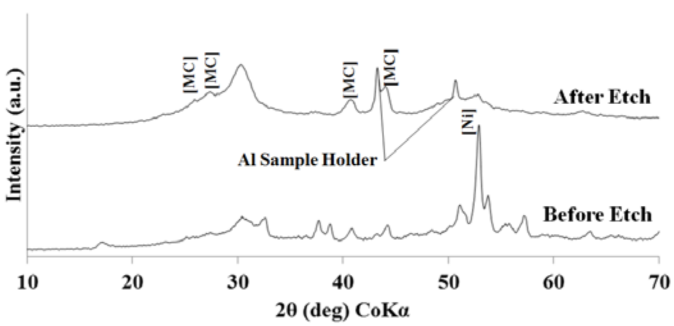

FIGURE 3. X-ray diffraction pattern of MC nanowire product before and after etching

TABLE 2. Calculated Surface Areas of Metal Carbide Products

Precursor	Infiltration Method	BET Surface Area
Type 1	No template	47.66 m^2/g
Type 1	Type 1	17.3 m^2/g
Type 1	Type 2	31.49 m^2/g
Type 1	Type 3 (SBA-15 template)	352.7±19.2 m^2/g
Type 1	Type 3 (MCM-41 template)	565.5 m^2/g
Type 2	Solution Infiltration	156.4 m^2/g
Type 3	T-Shirt	91.3±13.1 m^2/g

BET – Brunauer–Emmett–Teller