Applied Catalysis B: Environmental 198 (2016) 32–37

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Effect of silica morphology on the structure of hard-templated, non-precious metal catalysts for oxygen reduction

Jacob Anibal[a], Henry G. Romero[b], Nathaniel D. Leonard[a,1], Cenk Gumeci[a,2], Barr Halevi[b], Scott Calabrese Barton[a,*]

[a] Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA
[b] Pajarito Powder, Albuquerque, NM 87102, USA

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form 8 May 2016
Accepted 18 May 2016
Available online 19 May 2016

Keywords:
Fuel cells
Oxygen reduction reaction
Non-precious catalysts
Pore size distribution
Membrane-electrode assembly

ABSTRACT

With extensive development over the past ten years, non-precious metal (NPM) catalysts have become promising alternatives to platinum catalysts in fuel cell cathodes, but have been challenged by severe transport limitations. Hard template synthesis, also called the sacrificial support method, promises to improve transport properties introducing a sacrificial template to form mesopores. To further understand hard template transport properties, the relationship between template morphology, resulting catalyst pore structure, and overall fuel cell performance was investigated. Porous carbon materials and catalysts were synthesized using four different silica templates. Nitrogen physisorption and scanning electron microscopy were used to characterize pore diameter and morphology. The catalysts displayed pores approximately half the diameter of the template particles, and a geometric model is proposed to describe pore collapse. Catalyst electrochemical performance was characterized in membrane electrode assemblies using the hard templated materials in gas-diffusion electrodes for oxygen reduction. An optimum pore diameter was observed at approximately 9 nm.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Increasing petroleum prices within the last decade have drastically increased interest in fuel cells as an alternative technology. Despite the high energy density and efficiency imparted by platinum electrocatalysts, the cost of the precious metal continues to limit the feasibility of fuel cells in vehicle powertrains. Metal-Nitrogen-Carbon (MNC) catalysts produced using high temperature pyrolysis offer a promising, inexpensive alternative to platinum catalysts. Despite their lower costs, MNC catalysts have not found widespread use due to their low activity relative to platinum [1,2]. Many researchers have contributed to improved performance, but MNC catalysts still have performance well below platinum [3].

Recently, a key focus of MNC development has been enhancement of transport within the carbon support structure [4,5]. Producing a catalyst with optimum transport properties requires a synthesis technique with control over a catalyst's physical properties. Hard templating is one such technique. Developed in the late 1980's [6], hard template synthesis controls the pore size, shape and structure via a template particle.

Hard templating consists of a three to four step process. The process begins with the deposition of an organic precursor onto template particles. The template is often either silica particles or polymer materials. After deposition, the precursor is decomposed by pyrolysis to form a carbonaceous material over the template surface. The template is then removed, either by chemical reagents or high temperatures, leaving a highly porous, carbon product. An additional carbonization step often follows template removal to fully solidify the porous carbon material. More extensive reviews of hard templating are given by Lee et al. [7] and Xia et al. [8].

Pylypenko and coworkers extended the hard template process to catalyst synthesis. They used a sacrificial support method to produce a metal-nitrogen-carbon catalyst from metal macrocycles [9]. The hard template catalysts showed excellent oxygen reduction activity and a high degree of mesoporosity. Subsequent work by researchers in the Atanassov group improved catalyst activity by optimizing process parameters and varying the carbon-nitrogen precursor [10–14]. Despite the promise of hard template catalysts, little is known about their physical structure or its effect on catalyst performance. This work investigates the relationship between hard

* Corresponding author.
E-mail address: scb@msu.edu (S. Calabrese Barton).
[1] Current Address: Technische Universität Berlin, Germany.
[2] Current Address: Nissan Technical Center North America, Farmington Hills, MI, USA.

http://dx.doi.org/10.1016/j.apcatb.2016.05.038
0926-3373/© 2016 Elsevier B.V. All rights reserved.

Silica	Particle Diameter (nm)	Surface Area ($m^2 g^{-1}$)
Aerosil® OX-50 [24]	40	50 ± 15
Cab-O-Sil® L-90 [24]	20	90 ± 10
Cab-O-Sil® LM-150 [25]	18	160 ± 15
Cab-O-Sil® M-5P [24]	14	200 ± 15

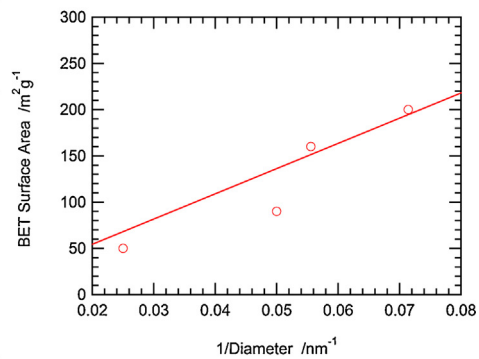

Fig. 1. Summary of the silica particle properties. The plot shows the relationship between silica surface area and particle diameter with a comparison to the theoretical geometric relationship for spheres [24,25].

template catalyst pore structure and silica precursor morphology. Four hard template catalysts were synthesized using silica particles with modal diameters between 14 and 40 nm. Catalyst pore structure was analyzed using nitrogen physisorption and scanning electron microscopy and compared with the precursor structure. Membrane electrode assembly (MEA) tests followed physical characterization to relate catalyst performance and structure.

2. Experimental

2.1. Synthesis

Porous carbon materials and catalysts were synthesized by Pajarito Powder, Inc. using a proprietary technique based on the methodology of Serov et al. [12]. Briefly, porous carbon materials were prepared by mixing a carbon-nitrogen precursor with fumed silica particles, followed by pyrolysis in inert atmosphere (900 °C, 1 h). The silica was then etched with hydrofluoric acid and a second pyrolysis occurred in an inert atmosphere. Nicarbazin was used as the carbon-nitrogen precursor in all syntheses [14]. Catalysts were synthesized in the same manner as the porous carbon materials, but had iron nitrate added to achieve 20 wt% Fe prior to the first pyrolysis. Following etching, the resulting iron content was 0.5 wt%. Porous carbon materials and catalysts were synthesized using four different fumed silicas: Evonik Aerosil® OX-50, Cabot Cab-O-Sil® L90, Cab-O-Sil® LM150, and Cab-O-Sil® M5P, respectively. Fig. 1 summarizes the silica particle properties as reported by the manufacturers. The silica particles show moderate specific surface areas which generally agree with geometric predictions for hard body spheres. The L90 silica does deviate from the theoretical trend, possibly due to greater fusion between the silica particles. Boldridge gives an in-depth geometric characterization of the L90 silica [15].

2.2. Physical characterization

Nitrogen adsorption isotherms for the hard template materials were obtained using a Micromeritics ASAP 2020 Nitrogen adsorption analyzer. The surface area of the porous carbons and catalysts was measured using the Brunauer-Emmett-Teller (BET) methodology [16]. Pore size distributions were obtained from the isotherms using the Barrett-Joyner-Halenda (BJH) [17] and Nonlocal Density Functional Theory (DFT) [18,19] approaches. BJH calculations were performed using the desorption branch of the isotherm, while DFT used the adsorption branch.

Scanning electron microscopy (SEM) was performed using a JEOL 7500 F ultra-high resolution scanning electron microscope equipped with Scandium image processing software. Each specimen was mounted on conductive carbon tape atop a 15 mm aluminum stub. Materials were imaged at 5 kV with a 20 μA emission current and a typical working distance of 5 mm. All hard-templated materials (porous carbon and catalyst) were conductive and did not require coating.

2.3. MEA fabrication and testing

Catalyst layers were constructed by spraying catalyst ink onto a 5 cm^2 Sigracet 25BC GDL using a Sono-tek Exacta-Coat automated spray system. The ink contained 500 mg catalyst per 20 mL solvent with a 9:11 mass ratio of Nafion to catalyst. After drying, the catalyst coated GDL was assembled with a 211 Nafion membrane and 0.2 mg_{Pt}/cm^2 anode to form the Membrane Electrode Assembly (MEA). Following assembly, the MEAs were hot pressed at 131 °C and 90 psi for six minutes.

Following fabrication, MEAs were sandwiched between two, single serpentine pattern flow plates and tightened with 4.5 Nm torque to form fuel cells for performance testing. Tests were performed using Fuel Cell Technologies (Albuquerque NM) test stands at 80 °C, with 30 psi back pressure, and a feed rate of 200 sccm. Prior to testing, each cell was broken in by holding the potential at 0.3 and 0.6 V for 15 min each. MEA performance was measured potentiostatically, with potentials ranging from an open circuit to 0.25 V, and with 60 s stabilization time before recording the cell current.

3. Results and discussion

Nitrogen physisorption characterization of the porous carbons and catalysts indicated highly porous materials, with total adsorbed Nitrogen above 400 cm^3/g STP near saturation pressure, as shown in Fig. 2. All of the hard template materials displayed type IV isotherms with significant hysteresis loops [20].

BJH and DFT pore size distributions were obtained from the nitrogen adsorption isotherms, as shown in Fig. 3. The BJH pore size distributions displayed broad peaks in the mesoporous range. The peak locations varied among the different precursors, but were nearly identical for each porous carbon-catalyst pair, indicating a very weak effect of iron nitrate on the hard template's structure. The iron precursor's only noticeable effect was a slight decrease in catalyst mesoporosity, most noticeable for the L-90 catalyst. The pore size distribution widths also offered insight into the pore formation mechanism. The distribution widths correlated strongly with pore size. Fumed silica particle distributions follow a similar correlation, widening with increasing particle size [21]. This similarity reflects the expected direct impact of silica particle size on catalyst pore size.

The DFT pore size distributions displayed similar general characteristics to the BJH distributions, exhibiting unimodal peaks in the mesoporous region. The DFT distribution also showed large, sharp peaks around two nanometers, indicating significant microporos-

Download English Version:

https://daneshyari.com/en/article/44713

Download Persian Version:

https://daneshyari.com/article/44713

Daneshyari.com