



Non-platinum nanocatalyst on porous nitrogen-doped carbon fabricated by cathodic vacuum arc plasma technique



Reungruthai Sirirak^{a,b}, Thapanee Sarakonsri^{a,b,*}, Min Medhesuwakul^c

^a Material Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^b Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

^c Plasma & Beam Physics Research Facility, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

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ABSTRACT

Polymer electrolyte membrane fuel cells (PEMFCs) convert chemical energy directly into electrical energy where catalysts composing of non-noble transition metals, nitrogen, and carbon compounds are the most promising materials to replace the expensive platinum catalysts for oxygen reduction reaction (ORR). In this research, cathodic vacuum arc plasma (CVAP) technique was used to fabricate porous nitrogen doped carbon (NC) and non-platinum catalyst on porous NC (Fe-NC) directly on ion exchange membrane for being used as an ORR catalyst at the cathode. The porous NC layer was fabricated on silicon wafer at 0.05 mTorr, 0.1 mTorr, 0.5 mTorr, 1 mTorr, and 5 mTorr of nitrogen gas inlet. The AFM, and SEM images are observed to be regularly big with quite high hillocks and thin NC layers; these results indicate that the optimum process pressure of nitrogen gas inlet is 5 mTorr for porous NC fabrication. The SEM-EDS detects Fe, N, and C elements in the prepared catalysts, and the XRD pattern reviews the iron nitride and the carbon nitride phases. The SEM images in the backscattered electron mode (BSE) reveal good dispersion of very small metal particles (bright spots) on the highly porous coral-like carbon film. The TEM images clearly show the spherical Fe nanoparticles (64 nm) dispersed on the porous carbon film. However, the XANES (X-ray absorption near edge structure) analysis specifies that the prepared Fe is in the form of iron(III). As a result of no FeN standard for confirmation, both the XRD and the XANES results are used to confirm the Fe(III) compound. In preparing the catalyst as FeN, all these results specify that the CVAP technique can be used to produce the catalyst on the membrane.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) is drawing more attention as an environmentally innocuous power source for stationary and mobile applications [1,2]. The oxygen reduction reaction (ORR) at the cathode is a sluggish and complicated four-electron reaction. Platinum supported on carbon (Pt/C) has been used in cathode catalysts for ORR [3,4]. However, even on pure platinum (Pt), the over potential for ORR exceeds 300 mV. In addition, Pt is a precious metal of low abundance, and it is thus of great interest to develop non-platinum cathode catalysts for PEMFC.

Several Pt-free catalysts such as chalcogenides [5,6], Pd-based alloys [7], transition metal oxides [8], carbides, nitrides [9,10] and

transition metal macrocyclic compound-based catalysts [11–13] have been proposed as potential alternative catalysts for ORR. Due to the relatively good ORR activity and the low price of non-platinum catalysts, there has been considerable research on transition metal macrocyclic compound-based catalysts in the past several decades. In particular, the presence of transition metals may facilitate the incorporation of pyridinic-N and quaternary-N into the carbon matrix with a strong Lewis basicity, which can increase the electron-donor property of the N-doped carbon. Thus, the O–O bond will be weakened via the bonding between oxygen and nitrogen and/or the adjacent carbon atom. Consequently, the catalytic activity of the N-doped carbon-based catalysts toward the ORR [14] will be increased. Some researchers have proposed that the Fe-N₄/Fe-N₂ center bound to the carbon support is catalytically active, and that the central Fe plays a crucial role in the ORR [15,16]. Others have proposed that the transition metal (e.g., Fe or Co) may not itself be part of the active sites [17,18]. While there is disagreement concerning the active sites for ORR, there is agreement

* Corresponding author at: Material Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

E-mail address: tsarakonsri@gmail.com (T. Sarakonsri).

concerning the requirements for preparing N-doped carbon-based non-precious metal catalysts for ORR, such as (i) carbon, (ii) surface nitrogen, and (iii) a transition metal. Recently, Dodelet et al. [19] reported the synthesis of the iron-based catalysts possessing ORR activity to be similar to Pt catalysts. Based on their consumption on the structure of the active sites, they believed that the micropores in the N-doped carbon-based non-precious metal catalysts were also important factors for the synthesis of active oxygen-reduction catalysts.

The processes such as heat treatment [20,21], microwave irradiation [22], solution route [23,24], and reflux [25] were reported to synthesize nano-catalysts. Recently, Liu et al. [26] developed an ultrasonic spray pyrolysis technique (USP) to synthesize efficient macrocycle catalysts with good dispersion of the active sites on the carbon surface. Another new preparation strategy, plasma treatment, was first presented by Bogdanoff et al. [27] and Herrmann et al. [28]. Their results showed that plasma technique is effective in preparing active ORR catalysts. Normally, conventional heat treatment at high temperatures can cause aggregation of the carbon-supported catalyst particles, reducing the active surface. However, the plasma technique suppresses particle aggregation and allows the formation of smaller average particle sizes [29].

Cathodic vacuum arc plasma (CVAP) technique has been successfully used for the fabrication of dense metals, ceramics, and compound coating of films [30]. This technique enables the production of metal and carbon compound dense coatings on films from a solid conductor. Consequently, composite dense films can be deposited from mixed metals, carbon, and gas plasma. Because of the above-mentioned reasons, the CVAP technique was applied to fabricate the porous NC and Fe-NC catalyst directly on the proton exchange membrane for the ORR catalysts. This technique aims to develop nanoarchitectures of the

mentioned ORR catalysts with highly active sites and good electrical properties.

The present work focuses on (i) using the CVAP technique to fabricate porous NC films on proton exchange membrane, (ii) studying the effect of nitrogen gas inlet pressure on NC architectures, and (iii) applying the CVAP technique to fabricate non-precious catalysts on porous nitrogen-doped carbon (Fe-NC) directly on the proton exchange membrane which can be used as the ORR catalyst for PEMFC.

2. Materials and methods

The filtered cathodic vacuum arc system was installed in a cylindrical vacuum chamber of diameter 60 cm and height 55 cm. The chamber was evacuated by using a rotary backing pump together with an oil diffusion pump. A cold trap was installed at the entrance of the oil diffusion pump to prevent back diffusion of the pumping oil, which could contaminate the substrate. The base pressure of the chamber was 5×10^{-5} Torr. The process chamber and its pumping system are shown in Fig. 1.

2.1. Porous carbon fabrication

The experimental setup is shown in Fig. 1(b) and Fig. 2(a). The plasma source consists of a 6-mm diameter graphite rod, which was used as a cathode, surrounded by an insulated cylinder made of ceramic. The anode is made of stainless steel and acts as the support of the source. A conductive layer of graphite was applied on the surface of the insulating ceramic in order to make a conducting path between the cathode and the anode. The resistance between the anode and the cathode was around 500 Ω –1000 Ω . A pulse-forming network was used to power the source. The pulse width was around 120 μ s. The peak voltage was 600 V to initiate the

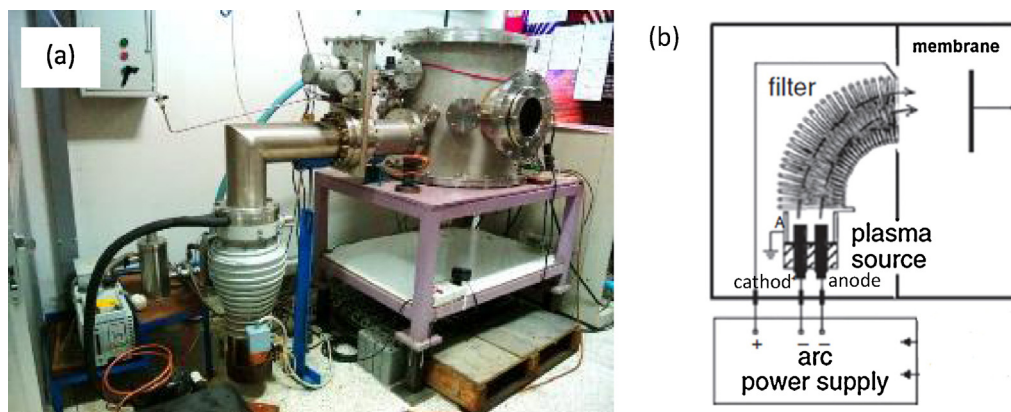


Fig. 1. (a) The process chamber and the pumping system. (b) Schematic diagrams of CVAP technique setup [30].

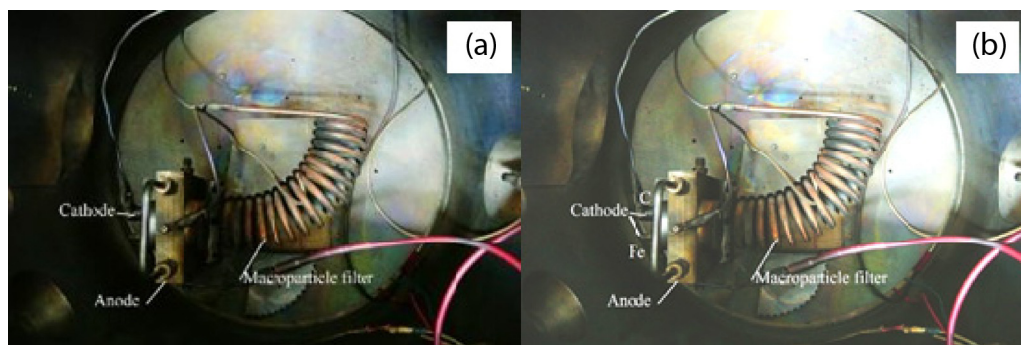


Fig. 2. The top view of (a) nitrogen-doped carbon and (b) Fe-NC experiment setup.

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