Nitrogen and sulfur co-doped mesoporous carbon as cathode catalyst for H₂/O₂ alkaline membrane fuel cell — effect of catalyst/bonding layer loading

Nengneng Xu a, Taishan Zhu a, Jinli Qiao a,*, Fengyuan Zhang b,**, Zhongwei Chen c

a College of Environmental Science and Engineering, Donghua University, 2999 Renmin North Road, Shanghai 201620, PR China
b Nanodynamics and High Efficiency Lab for Propulsion & Power, Department of Mechanical, Aerospace & Biomedical Engineering, University of Tennessee Space Institute, University of Tennessee, Knoxville (UTK), United States
c Department of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT

In this study, nitrogen and sulfur co-doped mesoporous carbon (N-S-MPC) materials are selected as the platform to demonstrate the potential of N-S-MPC to replace precious metal catalyst for fuel cell cathode oxygen reduction. Using both N-S-MPC and commercial available 40%Pt/C as cathode catalysts, the effects of catalyst and bonding layer in the catalyst layer (CL) on the power generation performances are thoroughly investigated for alkaline membrane fuel cells (AMFCs). Through single cell tests, several observations are reached as follows: (1) For N-S-MPC cathode, with increasing N-S-MPC loading from 1.00 to 5.00 mg cm⁻², the power density reached the maximum (21.7 mW cm⁻²) when the catalyst loading is 3 mg cm⁻². However, for Pt/C cathode the power density reached the maximum (21.3 mW cm⁻²) for a catalyst loading of 0.5 mg cm⁻², with increasing loading from 0.3 to 0.5 mg cm⁻²; (2) Increasing the thickness of catalyst layer resulted in an increase in power density. Thus, raising the local hydroxyl ion concentration was in favor of the process of oxygen reduction reaction. (3) The bonding layer also has a significant influence on the MEA fabrications, where the MEA using 30 μL bonding layer produced a maximum power density of 20.8 mW cm⁻².

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Introduction

The energy crisis and environmental pollution have stimulated significant research into new, efficient and sustainable energy sources to compensate and even replace traditional ones [1,2]. The polymer electrolyte membrane fuel cell (PEMFC) has been considered as promising green energy device due to its high energy conservation efficiency, the possibility of using regenerative fuels, low or zero levels of noxious emissions of environmental pollutants, a low operating temperature and a relatively quick start-up [3–5]. However, the
PEMFC need precious metals such as Pt as electrocatalyst, therefore, the major effort in fuel cell associated technologies have been devoted to reducing Pt loading in catalyst layer (CL) of electrode by exploring more active catalysts, and/or replacing Pt metal using other non-precious metals such as Fe, Co and Cu [6–8].

PEMFC can be divided into two kinds of systems, according to the media (proton or hydroxyl ion transport) the PEMFC operated. Recently, the growing interest in the application of alkaline membrane fuel cells (AMFCs) is principally motivated by the prospective use of cheap, easy to start, and relatively abundant non-precious metal catalysts [9,10]. Regarding non-precious metal catalysts, extensive work have been done to develop transition metal N-containing complexes, conductive polymer-based catalysts, transition metal chalcogenides, metaloxides/carbides/nitrates/oxynitrides/carbonitrides and enzymatic compounds [6,11,12]. However, compared with Pt-based catalysts, these alternatives usually suffer from high activation polarization and poor durability, partly caused by the instability of transition metals [13–15]. At the same time in the study of Pt-based noble metal catalysts, many efforts have been made to either enhance the performance of Pt-based catalysts through the shape and size control of the Pt or the fabrication of the carbonaceous support especially in cathode owing to its sluggish kinetics of oxygen reduction reaction (ORR) [16–18]. In the study of the above, nitrogen-doped carbon nanotubes have been seen to be much effective for performance enhancement, particularly in alkaline electrolytes. However, carbon is usually used as the carrier of Pt instead of the catalyst to catalyze the ORR [19,20]. More recently, certain types of heteroatom-doped nanocarbon materials, in particular nitrogen- and sulfur-doped ones, have shown high activity for the ORR [21,22], and the extensive research efforts have been made to explore N-doped non-noble metal or “metal-free” ORR catalysts [23]. S-doped ones as well as N and S co-doped carbon materials, on the other hand, have not been studied extensively [23–25]. For this reason, the study of power performances by applying N and S

Fig. 1 – A schematic of a typical AMFC (H2 as the fuel and O2 as the oxidant).

Fig. 2 – Polarization and power density curves of H2–O2 AMFC based on N-S-MPC and Pt/C catalysts. MEA active area: 4.0 cm⁻²; N-S-MPC catalyst loading in cathode: 3 mg cm⁻²; Anode catalyst loading of 40%Pt/C: 0.3, 0.4, 0.5 mg cm⁻²; Membrane: Tokuyama A201.
co-doped carbon materials as cathode catalysts for AMFCs have not received much attention [26].

In a PEMFC system, the electrochemical reactions can only take place at the three-phase boundary, where the electrolyte, reaction material, and electrically connected catalyst particles contact together in a membrane electrode assembly (MEA), which is the heart of a fuel cell [27,28]. A high three-phase boundary electrode promotes a good gas and water diffusion, proton or hydroxyl ion transport and electron transport to and from the catalytic sites [29]. The quality of the three-phase boundary depends significantly on the fabrication procedure of the MEA; therefore, there has been considerable interest in the design and optimization of catalyst layers aiming at performance improvement and cost reduction, such as electrocatalyst loading, ionomer loading and bonding layer loading [30–33]. The effect of Pt catalyst loading on the performance of conventional electrodes has also been systematically investigated. It was shown that a higher catalyst loading at the membrane-catalyst layer interface can improve the power generation performance [31,34]. The optimal catalyst utilization occurs for a thin porous active layer with Pt nanoparticles close to membrane side [35].

As a bonding layer for AMFCs, in addition to provide a good adhesion, As-4 solution (Tokuyama Corp.) also has the function of the ion channel. A bonding layer is developed to improve the low interfacial stability between membranes and

**Table 1** Kinetic parameters for fuel cell test on N-S-MPCs catalysts at room temperature (Different Anode Catalysts (Pt/C) loading).

<table>
<thead>
<tr>
<th>Catalysts loading (Pt/C)</th>
<th>OCV (V)</th>
<th>Pmax (mW cm⁻²)</th>
<th>Imax (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 mg cm⁻²</td>
<td>0.91</td>
<td>18.0</td>
<td>52.5</td>
</tr>
<tr>
<td>0.4 mg cm⁻²</td>
<td>0.92</td>
<td>20.8</td>
<td>51.2</td>
</tr>
<tr>
<td>0.5 mg cm⁻²</td>
<td>0.94</td>
<td>21.3</td>
<td>50.7</td>
</tr>
</tbody>
</table>

*Pt/C was as the anode and N-S-MPC (3 mg cm⁻²) was used as the cathode.

**Fig. 3** Polarization and power density curves of H₂–O₂ AMFC based on N-S-MPC and Pt/C catalysts. MEA active area: 4.0 cm⁻²; N-S-MPC catalysts loading in cathode: 1, 2, 3, 4, 5 mg cm⁻²; Anode catalyst loading of 40%Pt/C: 0.4 mg cm⁻²; Membrane: Tokuyama A201.
electrodes [36]. In a unit cell test, the MEA with the different bonding layer loading shows the different power performance.

Inspired by the results achieved in our continuing effort, in this work, we seek to investigate and understand the influences of the different nonprecious electrocatalyst/bonding layer loading in CLs for the H2/O2 alkaline membrane fuel cell performances. Pt/C and the nitrogen and sulfur co-doped mesoporous carbon (N-S-MPC) catalyst-coated substrate by direct spray (CCS) were tested in H2/O2 AMFC using CO2-free air, with commercially available anion-exchange membrane. The same Pt/C and N-S-MPC CCS as typical representatives have been employed for precious metal and non-precious metal catalysts to understand the power generation performance differences of Pt and nitrogen and sulfur co-doped mesoporous carbon materials.

### Experimental

**Preparation of catalysts**

The procedure for the preparation of N-S-MPC catalysts was analogous to what reported by our group [37]. The N-S-MPC was synthesized by dispersing FeSO4·7H2O and PEI onto the surface of SiO2 (HangzhouWanjing New Material Co., Ltd 10–15 nm in diameter). Typically, 4.5 g PEI was added to a calculated silica solution (the PEI content with respect to the silica was 45 wt.%) under magnetic stirring and sonicated condition. Then an aqueous solution of FeSO4·7H2O (Sinopharm Chemical Reagent Co., Ltd Fe:PEI = 1:3) as activation reagent was added into the SiO2-PEI solution under magnetic stirring to form a reddish-brown nitrogen-iron chelate, and further sonicated for 8 h in the sonobath. After that, a uniform and viscous solution of PEI-silica-Fe was placed in a drying oven overnight at 85 °C, and heated at 800 °C for 1 h in a tubular furnace under N2 atmosphere with a heating rate of 20 °C min⁻¹ to accomplish the activation, pyrolysis and carbonization process. The SiO2 was then leached out using excess amount of 40 wt.% hydrofluoric acid (HF) for 24 h, and the resulting powder was washed with D.I. water until neutral, and dried overnight. In order to further improve the electrochemical performance, the resulting powder was again refluxed in 0.5 M H2SO4 at 80 °C for 8 h. The final NSMCs were obtained after re-pyrolyzing at 800 °C for 1 h under a N2 atmosphere.

**Treatment of A-201 membrane**

Prior to fabrication of the electrodes, A-201 membrane (Tokuyama Corp) were treated with 3 wt.% H2O2 at 60 °C for 1 h, then in de-ionized water at 60 °C for 1 h and, go on in 1 mol L⁻¹ NaOH at 60 °C for 1 h, respectively. Finally, it was immersed in at 60 °C for 1 h to eliminate the sodium ion.

**Preparation of electrocatalyst ink**

For AMFC testing, catalyst ink was prepared by mixing catalyst (40%Pt/C, Johnson Matthey) or N-S-MPC with 5 wt.% As-4 solution (Tokuyama Corp) and isopropanol, and then sonicated for 4 h to get a homogeneous solution, where the ratio of the catalyst to As-4 solution was 3:1.

**Preparation of MEA**

For the CCS technique, the electrocatalyst ink was sprayed directly onto the gas diffusion layer (GDL) by a spray gun (Crescendo, Model 175-7™) and then dried in air at 60 °C for 30 min. Next, the As-4 solution as the bonding layer was applied on the electrocatalyst surfaces of two electrodes by a brushing procedure. Afterwards, the two surfaces of the treated membranes were aligned and then compressed to form an MEA by a compression mold (LP 20-Labtech) at 60 °C and 2 MPa for 2 min. The catalyst layer with catalyst (40%Pt/C) loading of 0.4 mg cm⁻² was for the anode and, the catalyst layer with catalyst (N-S-MPC) loading of 1, 2, 3, 4, 5 mg cm⁻² for the cathode, respectively. The active electrode area for a single cell test was 4.0 cm².

**H2/O2 AMFC test**

The cell configurations: H2 | Pt/C | Tokuyama membrane | Pt/C or N-S-MPC | O2, were used for single-cell tests. The membrane electrode assembly (MEA) was inserted into fuel cell hardware. Pure hydrogen and oxygen gas were supplied as the anode and cathode fuel to enter the channel with a gas flow rate of 100 and 70 mL min⁻¹, respectively, through a humidifier held at room temperature under ambient pressure. Polarization curves were obtained using a fuel cell evaluation system (GE/FC1-100).
Results and discussion

The MEA, which is composed of anode, membrane, and cathode, is a key unit in fuel cells. The MEA is normally prepared by sandwiching a membrane between an anode and cathode under hot pressing. Before hot pressing, the membrane usually needs to be pre-treated in order to remove impurities. The hot-pressing process (also called MEA bonding) is a simple way to assemble the anode, cathode and membrane together, and ensures interfacial contact between the electrode and the membrane. To illustrate the work principle, Fig. 1 presents a schematic of a typical AFC (H₂ as the fuel and O₂ as the oxidant). Under the operation conditions, the catalytic oxygen reduction reaction generated lots of the hydroxide ions in the cathode and then transported through the anion-exchange membrane (AEM) to the anode, in the end hydroxide ions react with H₂ to produce H₂O and electrons. In order to the cell reaction to continue, not only need the number of three-phase boundary but also the logistics of hydroxide, electron, reactant, and product transport is important. The electrode preparation will make a great impact on the electrode structure and three-phase boundary, further affect the performance of the cell.

Effect of anode catalyst loading on the single cell performance

The fuel cell polarization and power density curves with different Pt/C anode catalyst loadings are shown in Fig. 2. The cathode catalyst is N-S-MPC, of which the loading is controlled at 3 mg cm⁻². In order to compare the results, a summary of correlation parameters are also provide in Table 1. It can be seen that the cell performances are increased with increasing Pt/C catalyst loading on the anode under the identical test conditions of H₂/O₂ cell, however, the changes are very different. As shown in Fig. 1 and Table 1, under H₂/O₂ the maximum peak power density of the cell made by Pt/C loading of 0.5 mg cm⁻² is 21.3 mW cm⁻², which is much larger than that for a Pt/C loading of 0.3 mg cm⁻² (18 mW cm⁻²). However, the cell performance made by Pt/C loading of 0.4 mg cm⁻² is only 0.5 mW cm⁻² lower than that for Pt/C loading of 0.5 mg cm⁻². The complexity of the MEA preparation and the other influence factors (such as the catalyst ink, spraying technology, hot-press temperature and pressure) may lead to these differences between the different catalyst loadings.

Table 4 – Kinetic parameters for fuel cell test on NSMCs catalysts at room temperature (Different Bonding layer Loading).

<table>
<thead>
<tr>
<th>Bonding layer</th>
<th>OCV (V)</th>
<th>P_max (mW cm⁻²)</th>
<th>I_max (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 µL</td>
<td>0.91</td>
<td>17.6</td>
<td>53.5</td>
</tr>
<tr>
<td>30 µL</td>
<td>0.92</td>
<td>20.8</td>
<td>51.2</td>
</tr>
<tr>
<td>40 µL</td>
<td>0.91</td>
<td>15.3</td>
<td>50.8</td>
</tr>
<tr>
<td>50 µL</td>
<td>0.82</td>
<td>11.4</td>
<td>50.1</td>
</tr>
</tbody>
</table>

Fig. 4 – Polarization and power density curves of H₂–O₂ AMFC based on N-S-MPC catalyst and Pt/C catalyst with different bonding layer loading. MEA active area: 4.0 cm⁻²; N-S-MPC catalyst loading in cathode: 1, 2, 3, 4, 5 mg cm⁻²; Anode catalyst loading of 40%Pt/C: 0.4 mg cm⁻²; Membrane: Tokuyama A201.
indicates that when the Pt/C loading reached 0.4 mg cm\(^{-2}\), the reaction rate of hydrogen oxidation reaction has reached maximum. Thus, continuing to increase the Pt/C loading, the power generation performance is no obvious increase.

**Effect of cathode catalyst loading on the single cell performance**

Fig. 3 shows current density–voltage and current density–power density curves obtained for AEM electrode assemblies with different catalyst loadings using N-S-MPC as the cathode under H\(_2\)/O\(_2\) condition, while control the Pt/C loading at 0.5 mg cm\(^{-2}\). The electrode performance is commonly evaluated and compared according to the peak power density. For a convenient comparison, a summary of correlation parameters are provide in Table 2. It can be seen that the N-S-MPC with a loading of 3 mg cm\(^{-2}\) can give an initial cell performance with a peak power density of 21.7 mW cm\(^{-2}\) (Fig. 3), which is the highest value in all tested catalyst loading samples, for example, 1, 2, 4 and 5 mg cm\(^{-2}\) for power densities of 12.6, 17.2, 19.8 and 16.2 mW cm\(^{-2}\), respectively. Although their single cell performances are still much lower than the one, where both sides are made of Pt/C catalyst (0.5 mg cm\(^{-2}\) on each side) (Fig. 3), the OCV values are very promising (all larger than 0.9 V in Table 1). In addition, it can be observed that the power density increased with increasing the catalyst loading until 3 mg cm\(^{-2}\), then began to decrease when the catalyst loading was further increased. For the research, we further measure the effect of the catalyst layer thickness on the cell performances. For a good comparison, a summary of the catalyst layer thickness are provide in Table 3. To our interest, the catalyst layer thickness is found to be increased with the increase in catalyst loading, therefore, the power density was observed to increase with the thickness of catalyst layer. However, the power density growth leveled off when the thickness of the catalyst layer was increased so much, for example, larger than 90 \(\mu\)m. This can be explained by the fact that the reaction zone was limited by mass transfer. The increase of the power density with increasing the thickness of the catalyst layer is largely due to the increase of the total area of triple phase boundaries, at which ORR occurs. On the other hand, the decrease in power density when catalyst layer was thicker than 90 \(\mu\)m can be ascribed to the increase of diffusion resistance of the reactants, since thinner catalyst layer was favorable for gas transport. Hence, an increase in the thickness of catalyst layer produced the higher local hydroxyl ion (OH\(^{-}\)) concentration which is favorable for the process of ORR, thus resulted in an increase in the power density. As a consequence, when the thickness of the catalyst layer was increased, the promoting contributions from the increase of local OH\(^{-}\) concentration also increased.

**Effect of the bonding layer on the single cell performance**

The amount of polyelectrolyte binder used in the catalyst layer (CL) is not as large as that in the membrane, however, the amount is important because it is closely related to CL performance, catalyst utilization and MEA durability. The reactant must be transported through three-phase interface before it arrives at the reaction sites to carry out reactions, and therefore the binder in the CL must be reactant-permeable to avoid reactant mass transport limitations. The resistance of the CL could be reduced at the optimized catalyst loading and bonding layer, increasing the utilization of the catalysts. Fig. 4 shows the polarization curves of single cell with the bonding layers as compared with the different loading. Also, for a convenient comparison, a summary of correlation parameters are provide in Table 4. The maximum power density of 20.8 mW cm\(^{-2}\) was found for the MEA with a bonding layer of 30 \(\mu\)L (Fig. 4), which was the highest value among all the prepared MEAs. This indicates that that bonding layer has a great influence on MEA performance. It is believed that a bonding layer can increase the interfacial adhesion and improve the interfacial stability between membranes and electrodes. The bonding layer also has the function of the ion channel and gas permeability. With the bonding layer loading increase, the ion channel increases and the ion conductivity is accelerated, leading to a decrease in the interfacial resistance. From Fig. 4, it can be seen that when the bonding layer loading increased from 20 \(\mu\)L to 30 \(\mu\)L, the power density increased to 20.8 mW cm\(^{-2}\). However, lower performance was observed in the bonding layer of 40 \(\mu\)L and 50 \(\mu\)L, with power densities of 15.3 mW cm\(^{-2}\) and 11.4 mW cm\(^{-2}\), respectively. This may be due to the fact that the bonding layer loading has been increased to the limit, where the ion channels were blocked and oxygen permeability was significantly inhibited, thus leading to the poor power density. As a consequence, the thin bonding layer can not only increases the interfacial adhesion, but also enhances the power generation performance.

**Conclusions**

In conclusion, with both N-S-MPC and Pt/C as typical representatives for non-precious metal and precious metal catalysts, respectively, the effects of catalyst and bonding layer loading on the fuel cell power generation performances were systematically studied. Through H\(_2\)/O\(_2\) AMFCs test, it was found that when N-S-MPC was used as the cathode, the power density increased with increasing carbon materials loading from 1.00 to 5.00 mg cm\(^{-2}\), and reached the maximum (21.7 mW cm\(^{-2}\)) when the catalyst loading is 3 mg cm\(^{-2}\). For Pt/C cathode catalyst, on the contrary, the power density increased with increasing Pt/C loading from 0.3 to 0.5 mg cm\(^{-2}\), and reached the maximum (20.8 mW cm\(^{-2}\)) when the catalyst is 0.4 mg cm\(^{-2}\). In addition, an increase in the thickness of catalyst layer resulted in increasing the power density, thus raising the local hydroxyl ion concentration is very important, which was favorable for the ORR process. It is noted that the bonding layer has a great influence on the MEA performances, and the MEA with 30 \(\mu\)L of bonding layer produced a maximum power density of 20.8 mW cm\(^{-2}\).

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