Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.18 No.1, 2026

Sulfur Dioxide-Tolerant Oleylamine-Modified Pt/C Catalysts toward Oxygen Electroreduction

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Abstract

The Pt-based oxygen reduction reaction (ORR) catalyst for proton exchange membrane fuel cells (PEMFC) is highly prone to being poisoned and deactivated by air impurities SO_2. It is crucial to enhance its SO_2 tolerance. In this paper, we found that modifying the surface of Pt particles with oleylamine (OAm) can enhance the resistance to SO_2 poisoning. Detailed investigations demonstrate that the introduction of OAm is beneficial for the oxidation of SO_{2ad}, which accelerating the regeneration of the Pt surface. After SO_2 poisoning, the OAm-Pt/C catalyst maintains 71% ORR mass activity at 0.9 V and 60% electrochemical surface area (ECSA), much better than the Pt/C (38% mass activity, 30% ECSA remained). That indicates that the SO_2 tolerance of Pt after OAm modification is significantly improved. The OAm on Pt surfaces introduces a spatial hindrance effect, which physically impedes the access and subsequent adsorption of SO_2 on the Pt active sites, improving the SO_2 tolerance of other state-of-the-art Pt-based catalysts.

Keywords: Oxygen reduction reaction, Platinum-based catalyst, Sulfur dioxide tolerance

DOI: 10.7176/CMR/18-1-03
Publication date: February 28th 2026

1. Introduction

Although proton exchange membrane fuel cells (PEMFCs) have significantly improved in terms of cost and stability, and fuel cell vehicles have achieved initial commercialization, there is still a considerable gap from the goal of large-scale commercial application. Among them, the poor stability of air impurities in fuel cells is one of the main constraints. During actual operation, PEMFC usually uses a compressor to directly inject compressed air instead of O_2 into the cathode. However, impurity gases in the air, such as NO_x and SO_2 will flow into the stack with the air and strongly adsorb on the surface of the Pt catalyst, occupying the active sites for the oxygen reduction reaction (ORR), seriously affecting the performance and lifespan of the battery system [1]. SO_2 is regarded as the most toxic impurity for the cathode Pt-based catalyst, whose poisoning effect cannot be ignored.

Pt-based catalysts exhibit extremely excellent catalytic performance for ORR and are the most commonly used cathode catalysts in commercial PEMFCs. However, Pt-based catalysts are highly sensitive to SO_2. The strong interaction between SO_2 and Pt is the fundamental cause of the poisoning of Pt/C. SO_2 adsorbed on the Pt surface firmly occupies the active sites of ORR, preventing the adsorption and reduction of O_2. Moreover, SO_2 cannot be desorbed within the potential window (0.6–0.9 V) of the PEMFC cathode. Usually, multiple high-potential cyclic voltammetry scans (0.05–1.5 V) are required to completely remove SO_2, which will significantly affect the stability of Pt/C and the operating life of PEMFCs [2].

In this work, we notice that a small amount of oleylamine (OAm) adsorbed on the surface of Pt would interact with Pt electrically, enhancing the ORR performance of Pt/C. Triggered by this, we modify the surface of Pt/C catalyst with OAm and investigate the relationships among OAm, ORR activity, and SO_2 tolerance. It is inspired that the tolerance of SO_2 of the OAm-Pt/C catalyst has significantly increased. This work paves a new way to design SO_2-tolerant Pt-based ORR catalysts.

2. Experimental

2.1 Synthesis of Catalysts

2.1.1 Synthesis of Pt/C Catalysts

The Pt/C catalyst was prepared by the ethanol reduction method. 100 mg of carbon powder was dispersed into 60 mL of ethanol by ultrasonic treatment to form a homogeneous suspension. The mixture was transferred to a flask and heated at 110 ℃ with stirring and reflux for 90 minutes and then cooled to room temperature by stirring. Then, a certain amount of $H_2PtCl_6 \cdot 6H_2O$ was added to the mixture. The mixture was then heated and stirred at 80 ℃ for 1 hour. Add 4 mL of 0.08 mol L^{-1} NaOH aqueous solution to the above solution and stir for 25 minutes. After cooling to room temperature, the products were rinsed and dried in vacuum oven 58 ℃ for 2 hours to obtain the Pt/C catalyst.

2.1.2 Synthesis of OAm-Pt/C Catalysts

The prepared 50 mg of Pt/C and a certain amount of OAm (with a molar ratio of 30% to Pt) were dispersed in 50 mL of ethanol and ultrasonicated for 10 minutes to form a mixture. The mixture was continuously stirred for 12 hours, then washed and dried under vacuum to obtain the the OAm-Pt/C catalyst.

2.2 Electrochemical Measurements

All electrochemical tests were conducted in a three-electrode system. The working electrode was a glassy carbon rotating disk electrode, the counter electrode was a Pt sheet, and the reference electrode was a saturated Ag/AgCl electrode. All the expressions regarding the electrode potential in this paper were made relative to the Reversible Hydrogen Electrode (RHE). The electrochemical performance was examined by cyclicvoltammetry (CV), linear sweep voltammetry (LSV). The working electrode was activated prior to formal testing by running CV scans from 0.05 to 1.0 V at 200 mV s^{-1} in an Ar-saturated 0.1 M $HClO_4$ solution, continuing until a steady-state CV curve was obtained. The ORR activity of the catalyst was evaluated using LSV. Measurements were conducted in an O_2-saturated 0.1 M $HClO_4$ electrolyte, with a potential scan from 0.05 to 1.0 V at a rate of 10 mV s^{-1} and a rotation speed of 1600 rpm.

3. Results and discussion

3.1 Characterization of Catalysts

The actual composition and metal loading of the Pt/C catalysts are characterized by inductively coupled plasma (ICP). The loading of Pt in the Pt/C catalyst is 20wt%. To characterize the crystalline structure of the Pt/C catalyst, X-ray diffraction (XRD) measurements were performed, and the resulting pattern is presented in the Figure 1. As shown in the Figure 1, the broad background signal at about 25° originates from the amorphous carbon support. The sharpest peak at 40°, 46°, 68°, and 81°corresponds to the (111), (200), (220), and (311) crystal plane of Pt, respectively, which exhibits characteristic diffraction peaks corresponding to the face-centered cubic (fcc) structure of Pt [3]. In addition, there are no other characteristic diffraction peaks of metals, indicating that the sample is the Pt/C catalyst.

To investigate the morphology and dispersion of Pt nanoparticles (NPs) in the Pt/C catalyst, transmission electron microscopy (TEM) characterization was conducted. Figure 2 shows the TEM and high resolution transmission electron microscopy (HRTEM) images of the Pt/C catalyst. As shown in the Figure 2(a), the Pt NPs exhibit excellent dispersion on the carbon support with no significant clustering. This uniform dispersion is consistent with the XRD result and suggests effective immobilization of Pt on the carbon matrix. The HRTEM image shows that Pt NPs exhibit a size range of ~2–6 nm and maintain good dispersion. The lattice fringe spacing is ~0.227 nm, which corresponds to the (111) crystal plane of Pt with fcc structure.

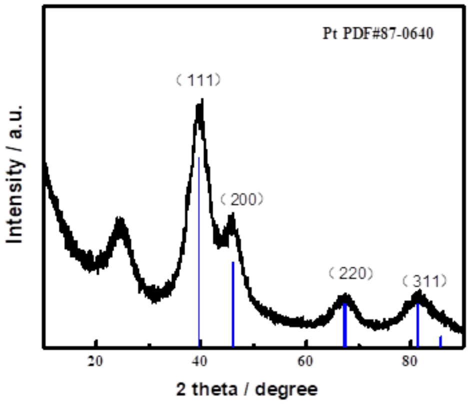

Figure 1. XRD analysis of Pt/C

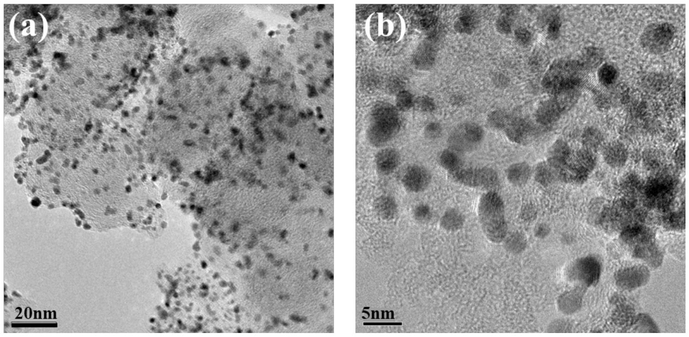

Figure 2. (a) TEM and (b) HRTEM images of Pt/C

3.2 Electrocatalytic Performance

Figure 3(a) shows the CV curves of Pt/C and OAm-Pt/C in 0.1 M HClO4. Compared with the CV curve of Pt/C, the hydrogen adsorption and desorption area is decreased of OAm-Pt/C, indicating that OAm has indeed been modified on the surface of Pt. Figure 3(b) shows the CV curves of OAm-Pt/C in four cycles. The curves of the four cycles are almost completely overlapping and the electrochemical surface areas (ECSAs) almost have no change, indicating that the OAm modified on the surface of Pt cannot be oxidized and desorbed within the potential range of 0.05-1 V.

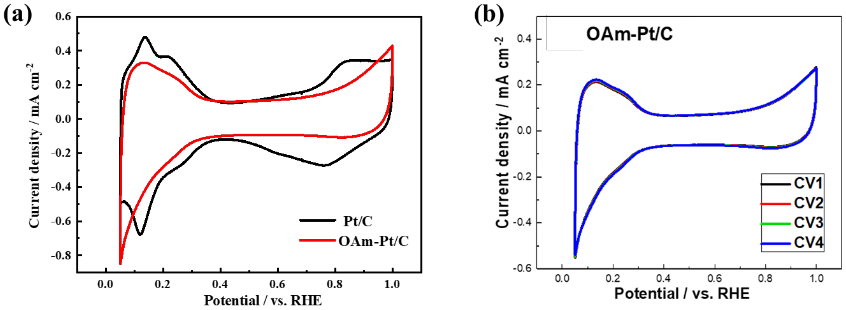

Figure 3 (a) CV curves of Pt/C and OAm-Pt/C; (b) CV curves of OAm-Pt/C in four cycles

The CV curves of Pt/C and OAm-Pt/C before and after SO_2 poisoning are compared, as shown in Figure 4. Under the same poisoning conditions, the (ECSAs) are all decreased after SO_2 poisoning because of the active site occupation by SO_2. Calculations indicated that the ECSA of Pt/C decreased by 70%, while that of OAm-Pt/C decreased by 40% lower than Pt/C. It indicates that the introduction of OAm effectively prevent the adsorption of SO_2 on the Pt surface. It is worth noting that as the number of cycles increases, the ECSA of OAm-Pt/C gradually expands, as shown in Figure 4(b). By comparing with Figure 3(b), it can be seen that the gradual regeneration of the clean Pt sites is caused by the desorption of SO_{2ad} rather than OAm, which cannot be desorbed within the potential range of 0.05-1 V. Other researchs have shown that SO_{2ad} cannot be oxidized and desorbed from the Pt surface within the 0.05-1 V potential range, causing irreversible poisoning [4-5]. Therefore, the introduction of OAm is beneficial for the oxidation of SO_{2ad} and the regeneration of the poisoned Pt surface.

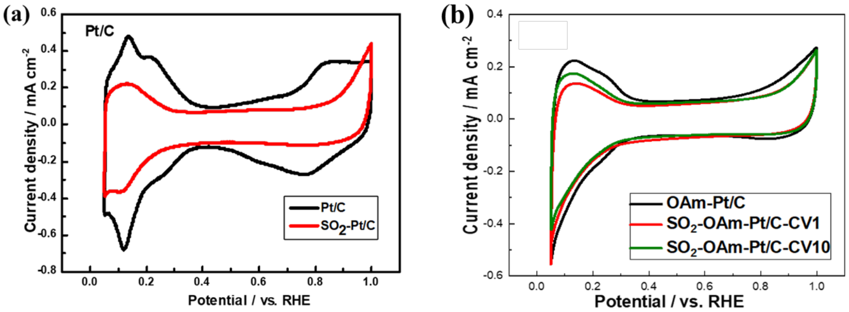

Figure 4 CV curves of (a) Pt/C and (b) OAm-Pt/C before and after SO_2 poisoning.

The ORR LSV curves before and after SO_2 poisoning of Pt/C and OAm-Pt/C are shown in Figure 5(a) and (b). After being poisoned by SO_2, the ORR curve of Pt/C shows a significant negative shift, and the limiting diffusion current becomes smaller, as shown in Figure 5(a). In comparison, the negative shift of the ORR curve of OAm-Pt/C after poisoning is smaller, and the limiting diffusion current increases, as shown in Figure 5(b). The ORR activities in terms of mass activity at 0.9 V of the two catalysts before and after poisoning are calculated, and the results are shown in Figure 5(c). Since a few active sites of the clean OAm-Pt/C are occupied by OAm, its ORR activity is lower than that of Pt/C, but its tolerance to SO_2 is significantly improved. Obviously, the Pt/C is the most vulnerable to SO_2 poisoning, whose mass activity decreases from 0.236 A mg^{-1}_{Pt} to 0.09 A mg^{-1}_{Pt} with a loss of 62%. However, the mass activity of OAm-Pt/C after poisoning decreases from 0.213 A mg^{-1}_{Pt} to 0.151 A mg^{-1}_{Pt}, only loss 29%, which is much less than that of Pt/C. The OAm on Pt surfaces introduces a spatial hindrance effect, which physically impedes the access and subsequent adsorption of SO_2 on the Pt active sites. Therefore, the OAm-Pt/C catalyst exhibits strong resistance to the poisoning by SO_2.

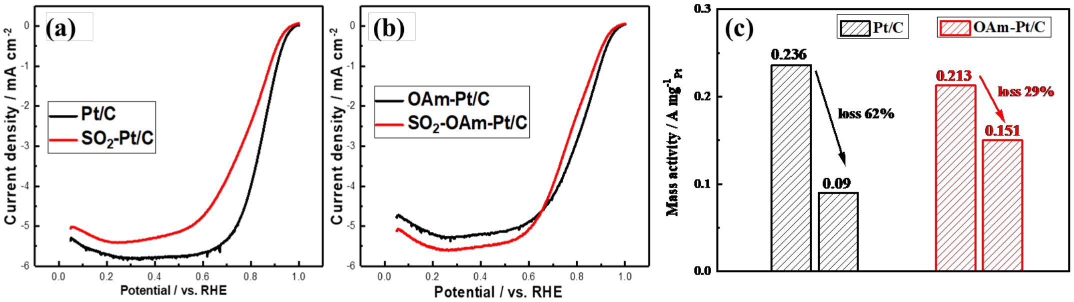

Figure 5 LCV curves of (a) Pt/C and (b) OAm-Pt/C before and after SO_2 poisoning; (c) the mass activity at 0.9 V of Pt/C and OAm-Pt/C for the ORR before and after SO_2 poisoning.

4. Conclusion

In this paper, OAm-Pt/C catalysts have been designed and synthesized to investigate the relationships among OAm, ORR activity, and SO_2 tolerance. The introduction of OAm is beneficial for the oxidation of SO_{2ad} and the regeneration of the poisoned Pt surface. Besides, the OAm-Pt/C exhibits a better SO_2 tolerance than Pt/C. The ORR mass activity of OAm-Pt/C only loss 29% after SO_2 poisoning much better than the SO_2 tolerance of Pt/C that loss 62% mass activity under the same poisoning condition. The OAm on Pt surfaces introduces a spatial hindrance effect, which physically impedes the access and subsequent adsorption of SO_2 on the Pt active sites. Consequently, the OAm-Pt/C catalyst demonstrates enhanced tolerance against SO_2.

Acknowledgements

The authors gratefully acknowledge the support from Natural Science Foundation of Jiangsu Province (BK20230720), the Project of Education and Teaching Reform from Yancheng Teachers University (2025YCTCJG57).

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