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Article

MoS₂-rGO hybrid architecture as durable support for cathode catalyst in proton exchange membrane fuel cells

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ABSTRACT

Carbon black is utilized as a conventional electrocatalyst support material for proton exchange membrane fuel cells. However, this support is prone to corrosion under oxidative and harsh environments, thus limiting the durability of the fuel cells. Meanwhile, carbon corrosion would also weaken the linkage between Pt and the support material, which causes Pt agglomeration, and consequently, deterioration of the cell performance. To overcome the drawbacks of a Pt/C electrocatalyst, a hybrid support material comprising molybdenum disulfide and reduced graphene oxide is proposed and synthesized in this study to exploit the graphitic nature of graphene and the availability of the exposed edges of MoS₂. TEM results show the uniform dispersion of Pt nanoparticles over the MoS₂-rGO surface. Electrochemical measurements indicate higher ECSA retention and better ORR activity after 10000 potential cycles for Pt/MoS₂-rGO as compared to Pt/C, demonstrating the improved durability for this hybrid support material.

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1. Introduction

Recently, proton exchange membrane fuel cells (PEMFCs) have received increasing attention because of their unique advantages, such as excellent efficiency and zero emission. Despite this, some issues limit the widespread commercialization of PEMFCs, such as the production of durable electrocatalysts with sufficient catalytic activity as well as the high cost of the catalyst [1–4]. Efforts have been made toward the development of precious-metal-free catalysts for fuel cells, which can reduce the cost and facilitate commercialization of fuel cells [5–10].

Another cost reduction approach is to use supported Pt electrocatalysts, among which carbon black-supported platinum (Pt/C) is the most commonly used for PEMFC application. Though such supports have a high surface area, low cost, and adequate electrical conductivity, poor durability and low Pt utilization remain a challenge for the conventional Pt/C [11,12]. Degradation of the electrocatalyst is thought to occur due to Ostwald ripening, Pt metal dissolution, and carbon corrosion. Amongst these mechanisms, corrosion of carbon needs to be eradicated as it is more prominent, hence leading to the overall low performance. Corrosion of carbon occurs in the catalyst

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layer of the cathode at high potentials during shutdown and startup, as per the following reaction:

Moreover, it has been observed that the presence of Pt on the carbon-based support causes corrosion, which in turn results in the detachment of Pt and reduction of the electrochemically active surface area, consequently leading to a catastrophic performance [13,14].

In contrast with carbon black—the most commonly employed support material—graphene is determined to be a suitable candidate with better stability, higher electrical conductivity, and larger specific surface area derived from the unique shape of the sp^2 bonded carbon atoms arranged in the form of two-dimensional sheets. However, the inert nature of graphene nanosheets hinders the homogenous distribution of Pt nanoparticles over the graphene surface [15–19].

To overcome such issues, the graphene nanosheets are usually functionalized by introducing oxygen-containing groups, as the presence of oxygen functionalities could serve as an attraction for Pt nanoparticles. Additionally, these groups can cause hydrophilicity, which in turn results in a more uniform dispersion of graphene in the solvent and consequently leads to improved catalyst inks during electrode fabrication [20–22]. However, as the graphitic nature is critical for electrical conductivity and material stability, the existence of oxygen containing groups would sacrifice the stability of carbon-based support materials. Therefore, it is necessary to achieve a balance between the introduction of functional groups and maintaining the degree of graphitization [23–26].

Another approach to improve the durability of Pt-based electrocatalysts is to utilize non-carbonaceous materials such as metal oxides (WO_3 , TiO_2), nitrides (Mo_2N , CrN), carbides (WC), and conducting polymers (PANI) [27–36]. For instance, based on our previous study, tantalum-doped titania was prepared and adopted as a corrosive-resistant catalyst support for PEMFC, which facilitated greatly improved durability in comparison to Pt/C [28]. Nevertheless, the electrical conductivity for non-carbonaceous alternatives is much smaller than that for carbon, which lowers the catalytic activity, making it applicable only under special operation conditions, e.g., at a high operating temperature, or in the presence of a strong oxidant. Given the disadvantages of carbon-based and non-carbonaceous support materials, hybrid support materials that can potentially achieve high stability as well as high electrical conductivity are proposed.

Presently, transition-metal dichalcogenides (TMDCs), including molybdenum disulfide (MoS_2), have been introduced as potential substitutes for graphene due to their similarly layered structures. For instance, MoS_2 has been adopted as a catalyst support in a solid oxide fuel cell and as a catalyst for the hydrogen evolution reaction (HER) in an alkaline environment because of its superior activity [37–41]. However, due to the restacking of existing MoS_2 layers, which would decrease the anchoring sites for Pt deposition, it cannot deliver high catalytic activity in PEMFC application. To exploit the mesh shape, electronic conductivity of graphene, and stability of MoS_2 , a hybrid

support material comprising of MoS_2 and reduced graphene oxide (MoS_2 -rGO) is proposed herein and prepared for use as the cathode in PEMFCs. This support is believed to deliver practicable catalytic activity along with stability after potential cycling. The solvothermal method is utilized to synthesize the hybrid material with its unique architecture, which is less resistant to charge transfer as compared to that of pure MoS_2 [42]. Moreover, homogeneous dispersal of Pt metal nanoparticles onto the support is realized due to the large number of exposed active sites for Pt deposition. As a result, the synergistic effect of MoS_2 and rGO leads to comparable catalytic activity and greatly enhanced stability of Pt/ MoS_2 -rGO as compared with conventional Pt/C.

2. Experimental

2.1. Synthesis of MoS_2 -rGO hybrid architecture

The hybrid support was simply prepared by the solvothermal method. In this setup, 25 mg of graphene oxide (Aladdin) was dissolved in 25 mL of dimethylformamide through sonication, followed by the addition of 55 mg of a MoS_2 precursor, $(\text{NH}_4)_2\text{MoS}_4$ (J&K Chemicals), under sonication. After obtaining a uniform solution, 0.25 mL of hydrazine monohydrate (Sinopharm Chemical Reagent Company) was added, trailed by sonication for at least 25 min. This solution was then transferred into a Teflon bottle, followed by heating in an oven at 180 °C overnight. The yield was washed using deionized water numerous times to completely remove the solvent. Eventually, the product was added to 12.5 mL of deionized (DI) water. This mixture was solidified using liquid N_2 and then lyophilized for 20 h [42,43].

Home-made Pt/C (40 wt%) and Pt/ MoS_2 -rGO (40 wt%) were produced by employing a slightly modified ethylene glycol process. In a given setup, appropriate amounts of potassium tetrachloroplatinate (Sigma Aldrich) were added to ethylene glycol and stirred till a homogenous solution was obtained. In another solution, Vulcan XC-72 R (supplied by Cabot Corporation) or MoS_2 -rGO was added to ethylene glycol while stirring followed by sonication until complete dispersion, and these two solutions were then intermixed. The starting pH for the abovementioned mixture was found to be 6, which was raised to 11 by adding 1.0 mol L^{-1} NaOH dropwise. Afterwards, the mixture was transferred to a three-neck bottle and heated in an oil bath at 140 °C for 3 h under reflux. After cooling to the ambient temperature, the solution was washed using DI water multiple times to separate impurities. Finally, the product was dried at 70 °C for 12 h. The schematic for the preparation of MoS_2 -rGO and Pt/ MoS_2 -rGO is presented in Fig. 1.

2.2. Characterization

The surface characteristics, including the morphologies of the prepared electrocatalysts, were analyzed using a transmission electron microscope (TEM) equipped with field emission microscope JOEL 2100F. The hexagonal structure of MoS_2 was analyzed by X-ray diffraction (XRD) using a D8 diffractometer

Fig. 1. Scheme representing the preparation of hybrid support MoS₂-rGO and Pt/MoS₂-rGO catalyst.

equipped with Cu K α radiation (the corresponding wavelength was 1.54×10^{-1} nm). The scan range was 10° to 70° , with a scan rate of 2° min^{-1} . To analyze the composition and chemical state of each element, X-ray photoelectron spectroscopy (XPS) was performed using a Shimadzu Kratos AXIS Ultra DLD Instrument. The XPS results also indicated the percentage of each element in the hybrid support. To further quantitate the Pt loading for these two different electrocatalysts, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using a Thermo iCAP6300 system.

Electrochemical measurements for Pt/C and Pt/MoS₂-rGO (each of a catalyst with 40 wt%) were carried out using a CHI 660e electrochemical work station. In the rotating disc electrode (RDE), an electrode consisting of glassy carbon (GC) acted as a working electrode with an area of $1.96 \times 10^{-1} \text{ cm}^2$. A thin Pt wire was employed as a counter electrode, and the standard calomel electrode (SCE) was used as a reference electrode. To prepare the catalyst ink for the electrochemical measurements, a few milligrams of the prepared catalysts were added to an appropriate amount of abs. ethanol mixed with Nafion solution (20%-Nafion dissolved in IPA, Nafion provided by DuPont). A homogenous suspension was achieved after sonication for about 50 min. Afterwards, 3 μL of the catalyst ink was poured onto a clean surface of a GC electrode and then

Fig. 2. The XRD spectra of MoS₂-rGO hybrid architecture.

dried in air. The same procedure was repeated after a few minutes. The final Pt loading was determined to be $0.030 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ for the prepared catalysts. For the cyclic voltammetry (CV) and linear sweep voltammetry (LSV), $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ (purchased from Sigma-Aldrich) purged with N₂/oxygen was used. The scan rate was kept at 0.02 V s^{-1} for electrochemical measurements. During the accelerated durability tests (ADT) of the prepared electrocatalysts, the scan rate was slightly increased to 0.2 V s^{-1} with a scan range of 0 to 1.2 V (vs. RHE). The potential cycling was performed for 10000 cycles using N₂ enriched $0.1 \text{ mol L}^{-1} \text{ HClO}_4$. Both catalysts were tested in the same environment, and all electrochemical characterization was recorded at the ambient temperature. Moreover, the electrodes were activated before each electrochemical measurement.

3. Results and discussion

The XRD pattern for the synthesized hybrid architecture is shown in Fig. 2. Basically, MoS₂ has different polymorphs ex-

Fig. 3. XPS spectra for (a) MoS₂-rGO hybrid architecture, (b) C 1s, (c) Mo 3d, and (d) S 2p.

Fig. 4. XPS spectra of (a) Pt/MoS₂-rGO, (b) Pt 4f (c) C 1s, (d) Mo 3d, and (e) S 2p.

isting in nature, amongst which, a 2H phase (six sulfur atoms arranged hexagonally) is found to be thermodynamically stable [39]. The diffraction peaks of Fig. 2 correspond to the nanosized MoS₂ with a 2H phase (PDF card number 37-1492), which is consistent with the previous study [42].

The chemical states and interactions between the different elements of the hybrid support material and supported catalyst were investigated by XPS. Fig. 3a shows the overall spectra for the hybrid support. The peak occurrence at a binding energy of 285 eV that corresponds to C 1s is indicated in Fig. 3b, whereas, Fig. 3c shows peaks at approximately 229 and 232.5 eV, which correspond to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. The peaks near 161.5 and 163.5 eV refer to the S 2p_{3/2} and S 2p_{1/2}, respectively, as depicted in Fig. 3d. Additionally, XPS results also affirm the transformation of GO into rGO and the transformation of molybdenum(VI) into molybdenum(IV) [44]. The atomic percentages of the different elements were found to be C

62.9%, S 23%, and Mo 14%.

To affirm the presence of MoS₂ after the deposition of Pt NPs, XPS plots were obtained again. The peaks corresponding to the binding energies of Pt, molybdenum, and sulfur can be noted in Fig. 4.

Figs. 5 and 6 represent the TEM and high-resolution transmission electron microscopy (HRTEM) images of MoS₂-rGO and

Fig. 5. HRTEM and TEM images of MoS₂-rGO hybrid architecture.

Fig. 6. TEM and HRTEM images of Pt/MoS₂-rGO (from (a) to (d)) and related particle size distribution of Pt (e).

Fig. 7. Comparison of the cyclic voltammograms of Pt/MoS₂-rGO and Pt/C. N₂ enriched 0.1 mol L⁻¹ HClO₄ used as the electrolyte, scan range 0–1.2 V vs. RHE, scan rate 0.02 V s⁻¹.

Pt/MoS₂-rGO. It can be observed that MoS₂ is deposited on a graphene sheet, whereas some folded edges of MoS₂ with several layers are also depicted in Fig. 5c. In Fig. 5d, lattice fringes of MoS₂ with a hexagonal shape along with a sufficient number of open edges can be observed. The TEM images shown in Fig. 6 represent the successful loading of Pt nanoparticles onto the surface of the hybrid architecture. A hundred randomly selected nanoparticles were used to calculate the mean particle size of Pt, and it was determined to be 3.4 nm. Additionally, coalescence of the Pt nanoparticles was found to be at a minimum, which was ascribed to the effective distribution of MoS₂ with active edges that act as attaching sites for Pt nanoparticles. It is widely known that the particle size of Pt ranging from 3 to 5 nm is ideal for the ORR activity [45,46]; therefore, Pt/MoS₂-rGO fulfilled the size requirements for the reaction.

Inductively coupled plasma-optical emission spectroscopy was further used to determine the loading of Pt nanoparticles onto the hybrid support, and it was deduced to be 42 wt% for Pt/MoS₂-rGO, which is quite close to the theoretical value.

To compare the electrochemical performance of the supported catalysts, 40 wt% Pt/C was also synthesized. Fig. 7 shows the cyclic voltammograms of Pt/MoS₂-rGO and Pt/C, where it can be observed that the Pt decorated on the hybrid support has a comparable electrochemical surface area in contrast with Pt/C. The homogeneous distribution of Pt NPs onto

Table 1

Electrochemically active surface area for Pt/MoS₂-rGO and Pt/C after 5 and 10000 potential cycles.

Electrocatalyst	ECSA (m ² g ⁻¹)		Loss in ECSA (%)
	5 cycles	10000 cycles	
Pt/MoS ₂ -rGO	32.0	17.2	46.2
Pt/C	68.4	29.0	57.6

the surface of the hybrid support may be due to the presence of the fringes/edges of MoS₂ [47]. The ORR performance for the above electrocatalysts is as illustrated in Fig. 8a. Pt/MoS₂-rGO shows better performance in comparison with Pt/C. It can be clearly seen that the onset potential for Pt/MoS₂-rGO is more positive, and hence, this catalyst has better activity [48]. The corresponding mass activities, which are usually measured at a slightly higher potential values to avoid inaccuracies, have been calculated and demonstrated in Fig. 8b, affirming the better performance of Pt/MoS₂-rGO.

To investigate the stability and durability of electrocatalysts, ADTs were performed. The number of potential cycles was 10000, and the scan range used was 0–1.2 V (vs. RHE) with N₂ purged 0.1 mol L⁻¹ HClO₄ as an electrolyte. Meanwhile, the ORR plots and cyclic voltammograms for these two catalysts were recorded after 5 and 10000 cycles. Moreover, the area corresponding to the hydrogen adsorption plot was utilized to measure the electrochemically active surface area (ECSA) in accordance with the following equation:

$$\text{ECSA} = Q_{\text{ad}} / (Q_{\text{mo}} \cdot m_{\text{ct}}) \quad (2)$$

where Q_{mo} and Q_{ad} represent charge stored for a single layer and charge for H₂ adsorption, respectively, and m_{ct} represents Pt loading [49,50]. The electrochemically active surface area for both catalysts decreased with the increasing number of cycles. The ECSA loss for Pt/MoS₂-rGO and Pt/C was revealed to be 46.2% and 57.6%, respectively, and it is summarized in Table 1. The enhanced stability of Pt/MoS₂-rGO can be ascribed to the strong electrical and chemical binding between the reduced graphene oxide and MoS₂. Moreover, the MoS₂ nanoparticles over the rGO surface served as active sites for the Pt nanoparticles anchorage, leading to strong interactions as well as suppression of Pt aggregation. The cyclic voltammograms for Pt/MoS₂-rGO and Pt/C after 5 and 10000 cycles are illustrated in Fig. 9.

The LSV plots for the ORR of the prepared electrocatalysts

Fig. 8. (a) ORR plots for Pt/MoS₂-rGO and Pt/C electrocatalysts. The electrolyte utilized oxygen-purged 0.1 mol L⁻¹ HClO₄ with a scan rate of 0.02 V s⁻¹ and a rotational speed of electrode 1600 rpm. (b) Comparison of Pt mass activity for Pt/MoS₂-rGO and Pt/C catalysts at 0.75 and 0.8 V.

Fig. 9. Cyclic voltammograms after 5 and 10000 cycles for (a) Pt/MoS₂-rGO and (b) Pt/C, showing a smaller decline in the ECSA for Pt/MoS₂-rGO. N₂ enriched 0.1 mol L⁻¹ HClO₄ used as an electrolyte, scan range 0–1.2 V vs. RHE, scan rate 0.02 V s⁻¹.

Fig. 10. ORR curves after 5 and 10000 potential cycles for (a) Pt/MoS₂-rGO and (b) Pt/C. Oxygen enriched 0.1 mol L⁻¹ HClO₄ used as an electrolyte, scan rate 0.02 V s⁻¹, rotational speed of electrode 1600 rpm.

prior to and after ADT tests are depicted in Fig. 10. As illustrated, Pt/MoS₂-rGO showed better performance when the catalytic activities were compared after 5 and 10000 cycles. To further confirm this, the half-wave potential (value of potential referring to half of the diffusion current, $E_{1/2}$) method was used. It was observed that $E_{1/2}$ was higher for Pt/MoS₂-rGO after 5 potential cycles and decreased further for Pt/C after 10000 potential cycles, indicating better stability for Pt/MoS₂-rGO. The reduction in $E_{1/2}$ is summarized in Table 2.

In Fig. 11, the mass activities for Pt/MoS₂-rGO and Pt/C at a potential of 0.75 V before and after the ADT tests are depicted. These activities were estimated by employing raw experimental data along with correction for mass transport [51]. It could be observed that Pt/MoS₂-rGO shows higher mass activities after 5 and 10000 cycles, in contrast with the Pt/C. The mass activity decreased to 25% of its initial value for Pt/C, whereas it decreased to only 75% of its preliminary value for Pt/MoS₂-rGO, confirming the improved stability.

The poor performance of Pt supported on carbon can be ascribed to the electrochemical corrosion of the support, which ultimately leads to the creation of oxygen functionalities over

the Pt/C surface [52,53]. Keeping in view the lower loss in ECSA and better mass activities for Pt/MoS₂-rGO, it can be concluded that this electrocatalyst is more stable compared to Pt/C.

4. Conclusions

A robust hybrid material consisting of MoS₂ and reduced graphene oxide was prepared by a facile solvothermal method to take advantage of individual supports, and employed as a catalyst support for the cathode in PEMFCs. Electrochemical performance measurements indicated that the supported cata-

Fig. 11. Comparison of Pt mass activities for Pt/MoS₂-rGO and Pt/C at a potential of 0.75 V.

Table 2

$E_{1/2}$ comparison for Pt/MoS₂-rGO and Pt/C after 5 and 10000 potential cycles.

Electrocatalyst	$E_{1/2}$ (V)	
	5 cycles	10000 cycle
Pt/MoS ₂ -rGO	0.82	0.79
Pt/C	0.78	0.72

lyst had high activity for the ORR and considerable durability during long-term testing. A large number of exposed edges of the MoS₂ nanoparticles constituting a uniform dispersion of Pt nanoparticles, the mesh structure of graphene that hindered the leaching of Pt, graphitic nature, and excellent electronic conductivity of the reduced graphene oxide collectively contributed to the higher electrochemical performance. This study showed that MoS₂-rGO hybrid architecture could meet the durability targets without compromising on the catalytic activity when employed as an electrocatalyst support. Additionally, the study opens new horizons for exploring other transition-metal dichalcogenides with graphene as alternative electrocatalyst supports as well as for other catalytic applications.

References

- [1] Y. Chen, J. Wang, H. Liu, R. Li, X. Sun, S. Ye, S. Knights, *Electrochem. Commun.*, **2009**, 11, 2071–2076.
- [2] S. Y. Huang, P. Ganesan, B. N. Popov, *Appl. Catal. B*, **2009**, 93, 75–81.
- [3] Q. X. Wu, Z. F. Pan, L. An, *Renew. Sustain. Energy Rev.*, **2018**, 89, 168–183.
- [4] P. Li, W. Chen, *Chin. J. Catal.*, **2019**, 40, 4–22.
- [5] R. Mei, J. Xi, L. Ma, L. An, F. Wang, H. Sun, Z. Luo, Q. Wu, *J. Electrochem. Soc.*, **2017**, 164, F1556–F1565.
- [6] R. Mei, L. Ma, L. An, F. Wang, J. Xi, H. Sun, Z. Luo, Q. Wu, *J. Electrochem. Soc.*, **2017**, 164, F354–F363.
- [7] J. Xi, F. Wang, R. Mei, Z. Gong, X. Fan, H. Yang, L. An, Q. Wu, Z. Luo, *RSC Adv.*, **2016**, 6, 90797–90805.
- [8] Z. F. Pan, L. An, T. S. Zhao, Z. K. Tang, *Prog. Energy Combust. Sci.*, **2018**, 66, 141–175.
- [9] F. Ahmad, L. Luo, X. Li, H. Huang, J. Zeng, *Chin. J. Catal.*, **2018**, 39, 1202–1209.
- [10] X. Tang, D. Fang, L. Qu, D. Xu, X. Qin, B. Qin, W. Song, Z. Shao, B. Yi, *Chin. J. Catal.*, **2019**, 40, 504–514.
- [11] A. L. Dicks, *J. Power Sources*, **2006**, 156, 128–141.
- [12] F. Barbir, T. Gómez, *Int. J. Hydrogen Energy*, **1997**, 22, 1027–1037.
- [13] L. M. Roen, C. H. Paik, T. D. Jarvi, *Electrochem. Solid-State Lett.*, **2004**, 7, A19–A22.
- [14] X. Yu, S. Ye, *J. Power Sources*, **2007**, 172, 133–144.
- [15] D. Chen, L. Tang, J. Li, *Chem. Soc. Rev.*, **2010**, 39, 3157–3180.
- [16] A. K. Geim, K. S. Novoselov, *Nat. Mater.*, **2007**, 6, 183–191.
- [17] G. A. Ferrero, K. Preuss, A. B. Fuentes, M. Sevilla, M. M. Titirici, *J. Mater. Chem. A*, **2016**, 4, 2581–2589.
- [18] L. Zhang, X. Wang, R. Wang, M. Hong, *Chem. Mater.*, **2015**, 27, 7610–7618.
- [19] K. Sakaushi, T. P. Fellingner, M. Antonietti, *ChemSusChem*, **2015**, 8, 1156–1160.
- [20] L. Dong, R. R. S. Gari, Z. Li, M. M. Craig, S. Hou, *Carbon*, **2010**, 48, 781–787.
- [21] Y. Li, L. Tang, J. Li, *Electrochem. Commun.*, **2009**, 11, 846–849.
- [22] F. Coloma, A. Sepúlveda-Escribano, J. L. G. Fierro, F. Rodríguez-Reinoso, *Appl. Catal. A*, **1997**, 150, 165–183.
- [23] D. He, K. Cheng, T. Peng, X. Sun, M. Pan, S. Mu, *J. Mater. Chem.*, **2012**, 22, 21298–21304.
- [24] Y. Li, Y. Li, E. Zhu, T. McLouth, C. Y. Chiu, X. Huang, Y. Huang, *J. Am. Chem. Soc.*, **2012**, 134, 12326–12329.
- [25] M. T. Anwar, X. Yan, M. R. Asghar, N. Husnain, S. Shen, L. Luo, J. Zhang, *Int. J. Energy Res.*, **2018**, 1–28.
- [26] G. Li, B. Huang, Z. Pan, X. Su, Z. Shao, L. An, *Energy Environ. Sci.*, **2019**.
- [27] H. Chhina, S. Campbell, O. Kesler, *J. Electrochem. Soc.*, **2007**, 154, B533–B539.
- [28] M. T. Anwar, X. Yan, S. Shen, N. Husnain, F. Zhu, L. Luo, J. Zhang, *Int. J. Hydrogen Energy*, **2017**, 42, 30750–30759.
- [29] H. Zhong, H. Zhang, G. Liu, Y. Liang, J. Hu, B. Yi, *Electrochem. Commun.*, **2006**, 8, 707–712.
- [30] M. Yang, R. Guarecuco, F. J. Disalvo, *Chem. Mater.*, **2013**, 25, 1783–1787.
- [31] H. Chhina, S. Campbell, O. Kesler, *J. Power Sources*, **2007**, 164, 431–440.

Graphical Abstract

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MoS₂-rGO hybrid architecture as durable support for cathode catalyst in proton exchange membrane fuel cells

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To overcome the shortage and poor durability of commonly used carbon-black support, a MoS₂-rGO hybrid support material is proposed and prepared that enables both improved activity and durability relative to carbon-black supported electrocatalysts.

- [32] E. Antolini, E. R. Gonzalez, *Solid State Ionics*, **2009**, 180, 746–763.
- [33] S. Chen, Z. Wei, X. Qi, L. Dong, Y. G. Guo, L. Wan, Z. Shao, L. Li, *J. Am. Chem. Soc.*, **2012**, 134, 13252–13255.
- [34] N. Cheng, J. Liu, M. N. Banis, D. Geng, R. Li, S. Ye, S. Knights, X. Sun, *Int. J. Hydrogen Energy*, **2014**, 39, 15967–15974.
- [35] N. Rajalakshmi, N. Lakshmi, K. S. Dhathathreyan, *Int. J. Hydrogen Energy*, **2008**, 33, 7521–7526.
- [36] M. Gustavsson, H. Ekström, P. Hanarp, L. Eurenus, G. Lindbergh, E. Olsson, B. Kasemo, *J. Power Sources*, **2007**, 163, 671–678.
- [37] M. Chhowalla, H. S. Shin, G. Eda, L. J. Li, K. P. Loh, H. Zhang, *Nat. Chem.*, **2013**, 5, 263–275.
- [38] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, M. S. Strano, *Nat. Nanotechnol.*, **2012**, 7, 699–712.
- [39] S. Presolski, M. Pumera, *Mater. Today*, **2016**, 19, 140–145.
- [40] J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Nørskov, *Faraday Discuss.*, **2008**, 140, 219–231.
- [41] Y. H. Chang, C. T. Lin, T. Y. Chen, C. L. Hsu, Y. H. Lee, W. Zhang, K. H. Wei, L. J. Li, *Adv. Mater.*, **2013**, 25, 756–760.
- [42] Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *J. Am. Chem. Soc.*, **2011**, 133, 7296–7299.
- [43] H. Wang, J. T. Robinson, X. Li, H. Dai, *J. Am. Chem. Soc.*, **2009**, 131, 9910–9911.
- [44] J. H. Nielsen, L. Bech, K. Nielsen, Y. Tison, K. P. Jørgensen, J. L. Bonde, S. Hørch, T. F. Jaramillo, *Surf. Sci.*, **2009**, 603, 1182–1189.
- [45] H. A. Gasteiger, S. S. Kocha, B. Sompalli, F. T. Wagner, *Appl. Catal. B*, **2005**, 56, 9–35.
- [46] C. D. Valentin, G. Pacchioni, A. Selloni, *Chem. Mater.*, **2005**, 17, 6656–6665.
- [47] H. Yan, [PhD Dissertation], **2016**.
- [48] W. Xia, A. Mahmood, Z. Liang, R. Zou, S. Guo, *Angew Chem. Int. Ed.*, **2016**, 55, 2650–2676.
- [49] O. Reid, F. S. Saleh, E. B. Easton, *Electrochim. Acta*, **2013**, 114, 278–284.
- [50] L. Li, Y. Xing, *J. Phys. Chem. C*, **2007**, 111, 2803–2808.
- [51] S. L. Gojković, S. K. Zecevic, R. F. Savinell, *J. Electrochem. Soc.*, **1998**, 145, 3713–3720.
- [52] M. Dou, M. Hou, D. Liang, W. Lu, Z. Shao, B. Yi, *Electrochim. Acta*, **2013**, 92, 468–473.
- [53] Z. Chen, M. Waje, W. Li, Y. Yan, *Angew Chem. Int. Ed.*, **2007**, 46, 4060–4063.

二硫化钼-还原氧化石墨烯复合材料用作高稳定性燃料电池阴极催化剂载体

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摘要: 碳黑是质子交换膜燃料电池中最常用的电催化剂载体材料。然而, 由于燃料电池内部环境苛刻(强酸性、强氧化性、湿度大、温度高、电位高等), 碳材料易被氧化腐蚀, 同时还可能进一步引起Pt催化剂颗粒脱落和团聚, 造成催化性能衰减, 继而影响电池性能与稳定性。为了克服碳载体腐蚀的问题, 提高碳材料的石墨化程度是一种可行方法, 然而, 石墨化程度提高的同时伴随着含氧官能团的减少, 这减少Pt离子的沉积位点, 造成Pt团聚和颗粒过大等问题, 导致催化剂质量比活性过低。另一种方法是开发金属氧化物(WO₃, TiO₂)、金属氮化物(Mo₂N, CrN)、金属碳化物(WC)和导电聚合物(PANI)等非碳载体。然而, 这些载体材料的电导率远低于碳, 造成催化剂活性较低, 只适用于高温和使用强氧化剂(如纯氧、双氧水)等特殊工况。针对上述问题, 本文设计合成了二硫化钼-还原氧化石墨烯(MoS₂-rGO)复合材料作为燃料电池阴极催化剂的载体材料, 利用MoS₂的高稳定性及还原氧化石墨烯优异的导电性能与适量的含氧官能团, 实现了Pt颗粒的均匀沉积并提高了催化剂活性与稳定性。

XRD表征结果显示, 使用溶剂热法制备的复合材料同时具有石墨烯与二硫化钼的特征峰, 证实MoS₂-rGO成功合成。XPS结果进一步证实了六价钼向四价钼及氧化石墨烯向还原氧化石墨烯的转变。TEM与HRTEM显示, MoS₂以多层形式存在并成功沉积在rGO表面, 和rGO相互搭接形成了连续的电子传输网络, 保证了载体良好的导电能力。使用改进的乙二醇还原法制得MoS₂-rGO负载Pt催化剂(Pt/MoS₂-rGO), TEM显示Pt颗粒均匀分布在载体表面, 且Pt颗粒平均粒径为3.2 nm。这主要归功于MoS₂充分暴露的活性边缘及rGO表面存在的适量含氧官能团为Pt离子提供了充足的沉积位点。电化学测试显示, 在催化ORR反应中, Pt/MoS₂-rGO相比于碳载铂(Pt/C)具有更高的起始还原电位, 表明MoS₂-rGO载体有助于Pt催化剂活性的提升。此外, 经历10000圈加速衰减循环后, Pt/C电化学活性面积损失57.6%。相比之下, Pt/MoS₂-rGO活性面积损失为46.2%。同时, 衰减后Pt/MoS₂-rGO半波电位高于Pt/C, 进一步确认基于复合载体的Pt催化剂具有更好的稳定性。

关键词: 燃料电池; 复合催化剂载体; 碳腐蚀; 负载型催化剂; Pt电催化剂

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