

Research on Asphalt-Derived Carbon as a Catalyst for Proton Exchange Membrane Fuel Cell

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Abstract. As the society and technology advanced these years, the concern about Earth's energy and climate warming rose up. Meanwhile, the appearance of Proton Exchange Membrane Fuel Cell (PEMFC) promotes the development of many fields, like transportation and aerospace. However, PEMFC is limited by the performance and cost of oxygen reduction reaction (ORR), and relies on Platinum-based catalyst to improve the reaction efficiency, which is scarce, expensive, and may result in catalyst activity decrease under complex reaction environment. That greatly increases the production cost of PEMFC and encourage scientists to develop some non-Platinum catalysts that are friendly environmental, low-priced and abundant. Thus, carbon-based materials stand out due to their high conductivity, good stability and structural designability, including Asphalt-Derived Carbon, which can converse to porous carbon materials with excellent conductivity and adjustable structure. Consequently, this article aims to illustrate the advantages of asphalt-derived carbon, compare several designs of controlled carbonization process for asphalt-derived carbon and the future of asphalt-derived carbon.

Keywords: Carbon-based catalyst, Asphalt-Derived, Proton Exchange Membrane Fuel Cell, Oxygen Reduction Reaction

1. Introduction

The proton exchange membrane fuel cells (PEMFCs) have gained a lot of attention due to their very high efficiency and zero emissions as a result of the worldwide need for green energy. Nevertheless, platinum-based catalysts are still a major bottleneck for the development of fuel cells due to their high price and short stability. To lower the price and raise the ion performance of PEMFCs, scientists are investigating catalysts that do not contain any precious metals. Carbon materials made of carbon have turned out to be perfect solutions because of their conductive properties, structural flexibility, and stability.

Among them, asphalt-derived carbon has shown great promise. Asphalt, a byproduct of crude oil or coal, contains rich aromatic structures. These structures can form conductive networks and porous carbon frameworks after carbonization. Studies have shown that adjusting the carbonization process and doping elements such as nitrogen or sulfur can significantly improve catalytic performance. For

example, Zhang's research revealed that asphalt's polyaromatic structures contribute to ordered carbon formation. Cheng's work found that pre-oxidation improves nitrogen doping. These studies confirm the feasibility of asphalt as a carbon source for electrocatalysts.

This paper focuses on asphalt-derived carbon as a support material for oxygen reduction catalysts. It analyzes the structural features from different asphalt sources, discusses how processing methods affect performance, and compares various doping techniques. The goal is to explore efficient, low-cost ways to use asphalt in PEMFC electrocatalysts and support future applications in sustainable energy systems.

2. Influence of asphalt source on its performance

2.1. Background about proton Exchange Membrane Fuel Cell (PEMFC)

Proton Exchange Membrane Fuel Cells (PEMFCs) are a type of clean energy technology that generate electricity directly through the electrochemical reaction between hydrogen and oxygen, producing only water and heat as by-products. Because of these features, PEMFCs are considered an important pathway toward achieving a low-carbon energy future. Compared with traditional combustion-based power generation, PEMFCs offer several advantages, including higher energy efficiency, lower operating temperatures, and zero harmful emissions. In domains, like green vehicles, backup power, and portable electronic devices, the use of these new technologies have provided the world with the potential for many years. The last decade has seen an increase in the global need for clean energy, which, along with the greater impetus to reduce carbon emissions, directly led to much more focus and research on the PEMFC technology. But there still remain some difficulties in making the technology fully commercial, particularly regarding several challenges including the high costs of production, which is why its' development has been limited.

2.2. The principle of PEMFC

By implementing the synergistic reaction of hydrogen oxidation at the anode and oxygen reduction at the cathode, the proton exchange membrane fuel cell (PEMFC) system, as one of the most effective energy transformation devices, achieves its core working principle. Typically, in the membrane electrode assembly structure of the three layers, the proton exchange membrane plays the role of a solid electrolyte, thus it prevents gas crossing over and at the same time it enables proton conduction, while the catalytic layers for the anode and cathode provide electron transfer and mass transport through the three-phase boundary. Research indicates that "the voltage loss in PEMFCs primarily stems from the multi-step four-electron transfer process of the oxygen reduction reaction (ORR) at the cathode, where its sluggish kinetics result in an activation overpotential exceeding 300 mV." These characteristic limits the cell to releasing only 50%-60% of its theoretical potential at practical operating voltages (0.6-0.8 V), significantly constraining the improvement of energy conversion efficiency.

2.3. The function of catalyst in pemfcs

In proton exchange membrane fuel cells (PEMFCs), catalysts play a decisive role in ensuring the efficient progress of electrochemical reactions. At the anode, catalysts accelerate the oxidation reaction of hydrogen, promoting the decomposition of hydrogen into protons and electrons. At the cathode, catalysts significantly speed up the rate of the oxygen reduction reaction (ORR)—a reaction that is inherently kinetically slow; without a catalyst, efficient reaction progression is

difficult to achieve [1]. For instance, research from the Dalian Institute of Chemical Physics (DICP) of the Chinese Academy of Sciences (CAS) indicates that commonly used platinum (Pt)-based catalysts can greatly reduce reaction activation energy and enhance reaction rates [2].

The item of a PEMFC catalyst with a high enough activity that would lead to a power density rise and total performance improvement of the battery would be the perfect one from the point of application requirements. It should also have excellent stability to operate stably for a long time under complex conditions (e.g., changes in temperature and humidity) and reduce performance degradation. Additionally, it needs good anti-poisoning ability to prevent impurities in fuel gas (e.g., CO) from deactivating the catalyst [1]. According to a research paper on PEMFC catalysts published in the journal *Nature*, developing new catalyst materials and structures—such as platinum-based alloys and single-atom catalysts—can meet the above requirements and promote the large-scale application of PEMFCs in fields like transportation and distributed power generation [1].

2.4. The source of asphalt

Asphalt is a byproduct of petroleum refining and coal coking industries. Its source and structural characteristics significantly impact the catalytic performance of the resulting carbon materials. In global oil refining processes, asphalt primarily comes from the residual fraction of crude oil after vacuum distillation, accounting for 15% to 30% of the processed crude. The chemical composition of asphalt varies greatly depending on the origin of the crude oil. For instance, asphalt derived from Middle Eastern crude contains higher proportions of saturated and aromatic hydrocarbons, whereas asphalt from Venezuelan heavy oil has a greater fraction of resins and asphaltenes [3]. These compositional differences make asphalt precursors unique in molecular design.

Research by Wenjing Zhang indicates that the polycyclic aromatic structures in asphalt can form highly ordered carbon frameworks through π - π stacking during pyrolysis, providing a structural foundation for constructing conductive networks [4]. Additionally, coal tar pitch, a byproduct of coking, typically has a higher content of condensed aromatic hydrocarbons than petroleum asphalt, along with abundant heteroatoms such as oxygen and nitrogen. This gives coal tar pitch an advantage in preparing nitrogen-doped carbon materials [5].

2.5. Structural influence

At the microscopic level, the molecular alignment of asphalt precursors directly affects the topological features of the carbonized products. In petroleum asphalt, alkyl side chains break first during low-temperature carbonization (300–500 °C), generating free radicals that promote lateral growth of aromatic layers. In contrast, the rigid fused-ring structure of coal pitch facilitates the formation of vertically aligned graphite microcrystals at higher temperatures (>700°C) [6].

This difference leads to distinct pore connectivity in carbon materials derived from the two types of asphalt. Petroleum asphalt-derived carbons typically exhibit a three-dimensional interconnected mesoporous network, whereas coal pitch-derived materials are dominated by slit-shaped micropores. Research by Jiasheng Han shows that the electron transfer efficiency at the metal-carbon interface is closely related to the topological structure of the carrier pores [7]. This explains why petroleum asphalt is generally more suitable as a support material for M-N-C catalysts.

2.6. Influence of impurities

The impurity distribution in asphalt precursors has dual effects on active site formation. Sulfur may poison transition metal active centers, yet during carbonization, SO_x gases generated from sulfur can create pores and increase edge defect density. Metal impurities such as calcium and nickel may promote carbon graphitization, but excessive amounts can lead to particle agglomeration.

The team led by Qingqing Cheng found that pre-oxidation treatment of asphalt can alter the valence state distribution of heteroatoms, thereby optimizing subsequent nitrogen doping efficiency. This precursor pretreatment strategy offers a new approach to balancing the conductivity and active site density of carbon materials, particularly for high-sulfur vacuum residue asphalt [8].

A major technical challenge lies in precisely controlling the content of mineral impurities like silicon and aluminum in asphalt feedstocks. These inorganic compounds form insulating phases after high-temperature carbonization, severely hindering charge transport [4,6].

3. Design of controlled carbonization process for asphalt-derived carbon

It has been found that the molecular arrangement of asphalt primer most definitely influences the geometrical configuration of the carbonized product obtained at the end of the process. At the stage of dehydrogenation polycondensation at 300-500 °C, petroleum asphalt is subjected to the process of alkyl side chain cleavage [9]. This reaction liberates a multitude of free radicals, which, during subsequent steps, provide ample opportunity for the lateral fusion of aromatic lamellae. Therefore, a 3D continuous network structure is established. The case of coal tar pitch is quite different. For instance, coal tar pitch generally contains the number of QI that are not soluble in quinoline (QI > 5%). Within the temperature range mentioned above, the pitch of the coal tar mainly converts to a nematic liquid crystalline phase. Flow-textured characteristics resulting from this process can be captured clearly with a polarizing microscope. By raising the temperature further to 500-700°C, both types of asphalt have their aromatic rings condensed and undergo π - π stacking. This action causes the mesophase microspheres to form with the size between 1 and 10 μm . One phenomenon worthy of note is that adjusting the heating rate to ≤ 2 °C/min can greatly promote the uniformity of the microspheres diameter and even surpass 40% in improvement. Also, when the graphitization progress is in the high stage (temperature > 700 °C), molecular chains in petroleum asphalt become more flexible and ultimately lead to the 3D network mesoporous with pore size of 4-10 nm of the main parts. Nitrogen adsorption isotherms follow a typical Type IV curve. Coal tar pitch contains a firm condensed ring skeleton. This skeleton favors the directional aligning of graphite crystals mainly along the vertical direction. The full width at half maximum (FWHM) of the diffraction peak of the (002) crystal plane in the X-ray diffraction pattern can shrink to 1.2° as a result of this structure. The direct consequence of this structural differentiation are the different ion transport performances of the two materials [9, 10].

3.1. Activation strategy

To achieve optimal pore structure and surface chemical characteristics, one needs to combine the chemical activation process with the doping strategies in a synergistic manner [11]. The KOH activation method whereby the ratio of the mass of asphalt to KOH is 1:2 is the best way to increase the specific surface area up to 2100 m^2/g . At the same time, this technique also generates a hierarchical pore network made up of micropores and mesopores [11]. A Pt catalyst (20 wt%) supported on carbon derived from petroleum asphalt achieved a peak power density of 1.15 W/cm^2

in PEMFC cathode tests (80 °C, 100% RH) [1]. This is 35% higher than commercial Pt/C. The reason is that mesopores (2-10 nm) speed up oxygen diffusion. At the same time, micropores hold Pt particles in place and stop them from clumping together [12]. When it comes to sulfur-containing asphalt as the source of carbon, the thiourea vapor deposition is an appropriate method to be used. This operation at 600°C allows to carry out the co-doping of nitrogen-sulfur. Such a procedure can push up the content of pyridinic nitrogen to 4.7 at.%. Under these conditions, sulfur does not negatively affect the active sites [13]. Rather it is a sulfur that, as a result of a synergistic interaction of the edge thiol groups and the pyridinic nitrogen, is the one that leads the oxygen reduction reaction (ORR) activity to the higher level [3]. The combined effect of sulfur edge groups and pyridinic nitrogen makes the material's ORR half-wave potential reach 0.78 V vs. RHE in acidic media [14]. When used as the PEMFC cathode, with a loading of 0.5 mg/cm², it achieves a power density of 0.41 W/cm². What's more, its ability to resist methanol poisoning is better than that of Pt/C [6].

3.2. Supercritical strategy

Supercritical carbon dioxide (Sc-CO₂) activation technology is a brilliant idea for the eco-friendly transformation of materials. In particular, carbon dioxide is delivered at the critical point (31.1 °C, 7.38 MPa) for the purpose of penetrating the carbon skeleton. After that, a rapid depressurization is carried out. Therefore, the rapid decompression effect creates a regular distribution of micropores with sizes ranging from 0.5-2 nm, which correspond to more than 80% of the porosity. In contrast to the traditional KOH method, this method not only can be the best, but it also completely gets rid of the problem of phenolic wastewater generation. In particular, the chemical oxygen demand (COD) is reduced from "above 80,000 mg/L" when conventional methods are used to "non-detectable levels". For instance, in a study by Bayrakçeken, supercritical CO₂-deposited Pt nanoparticles on Vulcan carbon supports exhibited remarkable performance in proton exchange membrane fuel cells (PEMFCs). The Sc-CO₂-treated carbon materials achieved Pt particle sizes as small as 1.2–2 nm with uniform distribution, significantly enhancing Pt utilization [15]. Electrochemical tests revealed a mass activity of 0.45 A/mg_{Pt} for the hydrogen oxidation reaction (HOR) at 0.9 V vs. RHE, nearly 80% higher than commercial Pt/C catalysts (0.25 A/mg_{Pt}). After accelerated aging tests (30000 cycles), the Sc-CO₂-derived catalyst retained 82% of its initial electrochemical surface area (ECSA), far exceeding the 63% retention of conventional Pt/C [15]. This stability is attributed to the micropore confinement effect (0.5–2 nm) created by Sc-CO₂ activation, which physically restricts Pt nanoparticle migration and agglomeration. The technology also eliminates toxic phenolic byproducts, aligning with its eco-friendly profile. These results underscore Sc-CO₂ activation as a transformative approach for sustainable energy materials [16].

For instance, when the asphalt contains metallic impurities, a new method comes to the fore which makes use of FeCl₃ that acts as a catalyst for the graphitization process. This catalytic effect can raise the electrical conductivity of the material up to 185 S/cm. Hence, the strategy of this method is to accomplish effective resource utilization.

4. Limitation of asphalt-derived carbon

While it is true that they have some good features, the asphalt-derived carbons are still far from the perfect ones. The main problem is the inconsistency that is inherent in the composition of the precursor (e.g., petroleum vs. coal-tar pitch, QI content, heteroatom concentration), affecting the performance of the final carbon's structure and properties, and the problem of standardized

production that is created due to this issue. Precise control of the pore size distribution is particularly challenging, especially when trying to achieve the highest possible fraction of desired mesopores (e.g., 4-10 nm) combined with the minimum of micropore dominance or macropore formation. Moreover, the graphitic crystallinity, even after intensive high-temperature treatment (>2500 °C), usually does not reach that of synthetic graphite or graphene, thus the electrical conductivity and the electrochemical stability are limited, especially in the fields of challenging applications like Li-metal anodes or high-power supercapacitors. The chemical activation methods (e.g., KOH) aim at getting ultra-high surface areas (>2000 m²/g). However, these methods produce highly corrosive substances and intensive washing is needed to remove them, leading to environmental and cost issues. On the other hand, the green approaches (e.g., Sc-CO₂ activation) are very clean, but they can hardly compete with the real target of chemical activation: surface area and pore volume [17]. The published results show that ongoing research into specific precursor alteration, controlled activation pathways, and scalable green synthesis is essential.

5. Conclusion

In summary, asphalt-derived carbon materials show strong potential as low-cost supports for ORR catalysts in PEMFCs. With proper control of asphalt source, carbonization process, and doping strategy, carbon materials with high surface area, good conductivity, and tunable pore structures can be achieved. This study discussed how differences in precursor composition affect the carbon's structure, and how various processing routes influence pore distribution and active site exposure. The results support the idea that asphalt is a flexible and effective carbon source. However, challenges remain. The composition of asphalt is complex and varies, making it hard to control the carbon structure precisely. In addition, large-scale preparation methods still face environmental and technical difficulties. Future research should focus on improving precursor consistency, developing green synthesis techniques, and optimizing structure-performance relationships. These improvements will help asphalt-derived carbon materials play a greater role in fuel cell technology.

Authors contribution

All the authors contributed equally and their names were listed in alphabetical order.

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