Rational Design of High-Performance M-N-C Single Atom Catalysts

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Abstract

High-performance electrocatalysts are required because the sluggish kinetics of Oxygen Reduction Reaction (ORR) at the cathode in either Fuel Cell (FC) or Metal-Air Battery (MAB). The current most effective ORR catalysts are noble Pt-group metals, whose high price and low abundance severely hamper the widespread application of FC and MAB. Dispersively non-noble transition metal coordinated with nitrogen atoms doped in carbon nanomaterials (M-N-C) Single Atom Catalysts (SACs) have been considered as the most promising catalysts for the ORR. Here, the effect of typical morphology on the activity and stability of SACs was discussed firstly. Moreover, the effect of metal type, coordination nitrogen number, heteroatom decoration on the central metal atom were discussed. Based on the rate determining step (RDS), we propose the ideal characters that high-performance SACs should possess.

Introduction

The ever-increasing energy demands and environmental concerns caused by using traditional fossil fuels have stimulated enormous interests to develop environment-friendly fuel cells and metal-air batteries [1]. The Oxygen Reduction Reaction (ORR) at the cathode plays a very important role in their overall performance. Although noble metals and their alloys remain as outstanding candidates for catalyzing the ORR on the cathode, the large-scale applications have been significantly hampered by the prohibitive cost and scarcity of the precious metals. Therefore, it is important to develop high performance inexpensive catalysts to replace the noble metals. Dispersive metal atoms coordinated with nitrogen doped carbon nanomaterials (M-N-C), a kind of Single Atom Catalysts (SACs), is considered as a potential catalyst for ORR because of their high atomic utilization efficiency and low price compared with the precious metals. Unfortunately, due to the extremely high surface energy of the single atoms in SACs, the atoms are prone to aggregation during the synthesis process [2]. A suitable support which should anchor the isolated single atoms has to be designed to prevent the migration and aggregation of the dispersed single atoms. Meanwhile, a high TM loading is also important since the catalysts then can provide more active sites for the ORR. Moreover, the activity of SACs can be enhanced through tuning the unique unsaturated coordination environment of central TM atoms [3,4], including the intrinsic properties of metal atom itself, the number and the type of atoms coordinated with the central metal atom [5].

In this work, the effect of both the morphology of nitrogen doped carbon support and the coordination environments of central atom on the activity of M-N-C were discussed, and the general principles for the design of M-N-C catalyst was provided. The morphology study was focused on the construction of 3D hierarchical porous structure which provides not only a large specific surface area with more single-atom active sites but also a suitable surface which will facilitate the diffusion of the species in ORR. Moreover, the coordination environments including the atom type, the number of the coordinated nitrogen atom, the heteroatom decoration on the central metal were analyzed. It is expected that this mini review will provide insights into the design of high-performance catalysts towards ORR.

The Effect of Various Factors on the Stability and Activity of SACS Catalyst for ORR

Morphology

Generally, SACs can be synthesized through direct pyrolysis of the mixtures containing N, C precursors and metal salts and M-N_4 was considered as the active sites. However, during the pyrolysis process, the metal species are prone to agglomeration to form iron-based nanoparticles or clusters which are difficult to be removed, thus blocking the formation of the M-N_4 active sites [6,7]. Moreover, inaccessible pores will be generated owing to the random mixing of the NC precursors and transition metal salts, and the M-N_4 active sites may be buried, reducing the exposure of the SACs [8-10]. In addition, owing to the high surface energy of isolated single atoms, the dispersive atoms easily migrate and aggregate into particles during the catalytic process [11]. Thus, the stability of SACs with highly dispersive active metal atoms was very important. Li et al. [12] prepared the Fe SACs through a cage encapsulated-precursor pyrolysis method, and their catalyst exhibited a half-wave potential ($E_{1/2}$) of 0.900 V and a high kinetic current density (J_k) of 37.85 mA cm^2 at 0.85 V, only 2 mV decay after 5000 continuous cycles. The catalyst also perform good methanol tolerance. Moreover, a suitable porous network can facilitate the transport of electrons, oxygen molecule and liquid water. We designed a Three Dimensional (3D) ordered porous architecture which contains large-pore structure with suitable micropores and mesopores through SiO_2 and ZIF-8 template method. The synthesized nanoparticles exhibited excellent ORR catalytic activity and stability, the $E_{1/2}$ is 0.901 V and only 3 mV decay after 10 000 potential cycles from 0.6 V to 1 V. Furthermore, the ZAB with as-prepared 3D Fe-N-C as the cathode performed a high peak power density (140 mW cm^2) and a high specific capacity (786.6 mA h g^{-1}), benefiting from the 3D hierarchical porous structure with lots of accessible Fe-N_4 sites and large specific surface area(1357.8 m^2 g^{-1}) [13].

Type of central atom

The metal atomic center is usually considered as the active center site of ORR, which is a direct and effective method for selecting appropriate metals to adjust the intrinsic properties of SAC. Other transition atom coordinated with nitrogen doped carbon materials also perform good activity and stability towards the ORR. Wu et al. [14] prepared atomically dispersed nitrogen-coordinated single Mn sites on nitrogen doped carbon (Mn-N-C) with a two-step doping and adsorption approach. The Mn-doped ZIF-8 precursors were carbonized and then leached with an acid solution to get a partially graphitized carbon host with optimal nitrogen doping and microporous structures. And then additional Mn and N sources were adsorbed into the as-prepared carbon host to generate increased density of MnN_4 after a thermal activation. The Mn-N-C catalyst exhibited a half-wave potential of 0.80 V which is a little bit lower than that of Fe-N-C catalysts, along with significantly enhanced stability in acidic media. Wu et al. [15] developed Co-N-C catalyst with a core-shell structure via a surfactant-assisted metal-organic framework approach. The cohesive interactions between the surfactant and the Co-doped zeolitic imidazolate framework (ZIF-8) nanocrystals play a very important role in leading to the unique confinement effect. The Pluronic F127 block copolymer derived Co-N-C@F127 perform the best activity and the half wave potential ($E_{1/2}$) is 0.84V, which is much better than the Mn-N-C catalyst but still is not as good as the Fe-N-C catalyst. Normally, the lower the d-band center of the metal central atom, the weaker the binding between oxygen-containing intermediates and metal atoms. Generally speaking, the d orbitals of metal atoms and the 2p orbitals of oxygen containing intermediates undergo chemical reactions, resulting in a decrease in the energy of the anti-bonding state, which weakens the binding between metal and oxygen. Osmieri et al. [16] reported that the ORR activity of various M-N-C follows the order of $FeN_4 > CoN_4 > CuN_4$, while the oxygen adsorption strength is $CuN_4 > FeN_4 > CoN_4$, which indicates that the adsorption of oxygen-containing species by metal centers cannot be too strong or too weak, and an appropriate adsorption and desorption state needs to be reached, which is beneficial for ORR catalytic reactions.

Number of coordinated nitrogen atoms

The number of the coordinated nitrogen atoms with central metal atom also affect the activity of M-N-C. Li et al. [17] studied the active center coordination number of Fe-NC SACs through a combination of experimental and theoretical calculations, and summarized the effect of nitrogen atoms on the ORR performance and found the order was $Fe-N_4 > Fe-N_3 > Fe-N_2 > Fe-N_1 > Fe-N_5$. Among them, $Fe-N_4$ exhibits the highest ORR activity due to the moderate hybridization between O 2p and Fe 3d ($Fe-N_4$), resulting in a moderately strong Fe-O bond, while the ORR overpotential is minimal in the Rate Determining Step (RDS).

Second metal

The introduction of a second (or multiple metal) atom to form a bimetallic (or polymetallic) center can improve the activity and stability of SACs by regulating the electronic and geometric structure, and utilizing the synergistic effects between bimetallic sites [18]. Tong et al. [19] synthesized diatomic Cu/Zn-NC catalysts through high-temperature pyrolysis method. Due to the fact that Zn atoms donate electrons to the d-orbitals of Cu, the O-O bond on the Cu active site was stretched and cleaved, accelerating the reaction process of the RDS OOH*. This finding solve Osmieri's [16] idea that only Cu-N-C was not suitable for the ORR.

Yang et al. [20] synthesized a bimetallic SACs using Co and Fe sites as the core and shell, respectively. The Co site in the core was responsible for a significant stability, while the Fe site in the shell was responsible for a high activity. By controlling the inner or outer layer components to achieve synergistic effects, it is beneficial to increase the density of available electrochemical active sites and promote mass/charge transfer in electrochemical reactions. The initial and half wave potentials are 0.98V and 0.87 V, and the half wave potential only decreased 16 mV after 30 000 potential cycles from 0.6 V to 1.0 V. Huang et al. [21] embedded the FeN_4-MnN_3 double site into N-doped porous carbon to form an Fe-Mn-N-C bimetallic atomic catalyst. Theoretical calculations have confirmed that the introduction of MnN_3 species into the FeN_4 group significantly enhances the adsorption of *OOH through co adsorption. In ORR testing, Fe/Mn-N-C showed excellent performance, with half wave potentials of 0.79 V and 0.93 V in acidic and alkaline environments, respectively. The proton and anion exchange membrane fuel cells assembled with Fe Mn N-C as cathode catalysts have power densities of up to 1.048 W cm^{-2} and 1.321 W cm^{-2}, respectively. We designed bimetallic Zn/Fe-NC SACs through pyrolyzing Polyvinyl Pyrrolidone (PVP) coated on Fe doped ZIF-8. Benefiting from a proper architecture and a synergistic effect between Zn and Fe sites, the Zn/Fe-NC catalyst provides good ORR activity with a half-wave potential of 0.875 V and

only 8 mV decay after 10,000 cycles. Moreover, the ZABs with Zn/Fe-NC catalyst at the cathode possess a remarkable power density (186 mW cm^{-2}) and speciffc capacity (815 mAh g^{-1}). Zn alleviates the adsorption of OH* intermediates through synergistic effect, thus promoting the overall ORR electrocatalytic activity [22].

Conclusion

Developing efficient, affordable, and reliable clean energy conversion and storage devices is the main method to address energy scarcity and environmental pollution issues. It is meaningful to seek the development of a low-cost, superior activity, and strong stability non precious ORR metal catalyst to replace traditional platinum-based catalysts. Transition metal nitrogen carbon (M-N-C) single atom catalysts have the advantages of nitrogen doped carbon carriers with high conductivity and the ability to coordinate with different metals to form active centers. The atomic utilization rate is close to 100%, which can effectively achieve efficient ORR catalytic processes. However, the immaturity of the synthesis process and the aggregation of active centers have led to poor electrocatalytic activity and insufficient stability of M-NC. The optimum M-N$_4$ should possess a morphology with a large exposure of M-N$_4$ sites, and 3D hierarchical structure may be a good method to enhance the activity and stability through morphology engineering. Moreover, the geometric and electronic structure affected by the type of central atom, the number of the coordinated nitrogen atom, the type coordinated central atom and the effect of second metal atom.

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Page 3/3