Design and Fabrication of Non-Noble-Metal Electrocatalysts for Oxygen Reduction Reactions

Ji Liang

School of Chemical Engineering

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Abstract

Fuel cell is a device that can directly convert the chemical energy in fuels into electricity and it has the advantages including high efficiency, high energy density and zero waste emission. However, a current fuel cell requires noble-metal catalysts (in most cased platinum, Pt) to accelerate the electrode reactions. As a result of the high cost of Pt, the commercialization of fuel cell has been severely hindered. Thus, it is exceptionally important to search for an alternative low-cost catalyst, especially on the cathode when the sluggish oxygen reduction reaction (ORR) occurs and much larger amount of Pt is employed, to bring down the over-all price of a fuel cell. With this aim, this Ph.D thesis has demonstrated the design and synthesis of a serial of high –performance Pt-free catalysts based on carbon materials. These researches include:

(1) We firstly designed and constructed a series of porous g-C_3N_4/C composite with different pore size ranging from large mesopores (*ca.* 12 nm) to large macropores (*ca.* 400 nm) and studied the structural impact of these hybrid materials on their ORR performance. In this study, we have for the first time revealed that macropores would be more favorable for ORR in such materials rather than the conventionally believed mesopores.

(2) Then, we integrated short-range ordered mesopores into the walls of macropores to form a hierarchical pore structure. By incorporating graphene into this system, its electric conductivity can be enhanced. This is the first study to natively grow graphene on porous carbon. It is found that this material shows an excellent ORR performance with synergistically enhanced activities. Tafel analysis confirms that the good performance was brought from its unique structural advantages.

(3) To further enhance the catalytic activity of the above materials with ideal hierarchical structures for ORR, we have introduced high active Fe-N species into the system during the fabrication. By delicate tuning of the Fe content, we are able to control the carbon nano-materials on the hierarchical porous carbon to form graphene or carbon nanotube. As a result, the catalyst has obtained a similarity high performance as Pt as a result of the successful combination of the desired merits for ORR on it.

(4) Besides the optimization of materials structure, we have also doped graphene with both N and S, and studied the influence of dual dopants on its ORR activity. We found that a significant performance enhancement was achieved by dual-doping. From density function theory calculation, we found the synergistic effect was from the spin and charge densities redistribution brought by dual-doping of S and N, leading to a larger number of ORR active sites.

The studies in this thesis have provided a thorough understand of the kinetic and mechanism of the ORR process on the Pt-free catalysts. The research has not only provided materials with optimized structure and high performance for ORR, but also showed an avenue on the materials' design and construction for further study.

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