学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Preparation of Nitrogen-doped Hierarchically Porous Carbon for Electrochemical Energy Storage and Conversion
（電気化学的エネルギー貯蔵と変換に資する窒素ドープ階層型多孔質炭素の作製）

The electrochemical energy conversion and storage devices, such as metal-air batteries and electrical double layer capacitor (EDLC), have been considered to play an important role in the efficient use of sustainable energies. Carbon materials are the most important electrode materials in these devices, which can be active materials or electrocatalysts. Generally, the electrochemical reactions occur at the electrode/electrolyte interfaces. A hierarchical pore structure containing a multi-porous architecture of interconnected micro (<2 nm), meso (2 nm~50 nm) and even macropores (>50 nm) is considered to be effective in enhancing the performance, because such a structure can provide a shortened ion-transport pathway, large accessible surface areas and abundant active sites for the electrochemical processes. Moreover, heteroatom doping, especially nitrogen (N) doping, of carbon has arisen interest in enhancing the electrochemical properties, which can modify the intrinsic structure and active sites of carbon.

In this study, a facile and efficient strategy to produce N-doped hierarchical porous carbon (NHPCs) is introduced for electrochemical oxygen reduction reaction (ORR) and EDLC applications. The production involves a redox exothermic reaction of metal nitrate-carbohydrates using biomass cellulose and urea as raw materials. The incorporation of magnesium nitrate-urea-cellulose or magnesium/potassium nitrate-urea-cellulose endows the doping with N, exfoliates the fibers to fine 3D porous powders, and creates a large number of pores at various scales simultaneously.

Chapter 1 is the general introduction of this thesis. An overview of various carbon materials for electrochemical energy conversion and storage is introduced and the objective of this thesis is described.

In Chapter 2 and Chapter 3, the nitrate-induced exothermic reaction was employed for the preparation of NHPCs and the ORR characteristics of the NHPCs were examined in KOH solutions. Magnesium nitrate and urea were absorbed in the cotton cellulose fibers, and upon heating a vigorous exothermic reaction occurred, which exfoliated cellulose fibers to highly porous particles. After the exothermic pre-pyrolysis, the samples were further carbonized at high temperatures and finally washed with an acid solution to obtain NHPCs. The influence of four preparation parameters on the porous and N-doping properties were comprehensively investigated, including magnesium salt species, carbonization temperature, urea amount, and magnesium salt amount (MgO template amount). The following conclusions are obtained. (1) From the comparison of magnesium nitrate and magnesium acetate precursors, it was confirmed that the use of nitrate introduced exothermic reactions, which could promote the pyrolysis at a low temperature and quickly exfoliate the cellulose fibers to a highly porous architecture, making a highly active ORR catalyst; however, the magnesium acetate-induced reaction was endothermic and the corresponding pyrolyzed samples were less porous with low specific surface area (SSA) and low pore volume. (2) The carbonization temperature greatly influenced the doping amount of N, the doping species of N, and the graphitization degree of carbon, and it was concluded the NHPCs prepared at 1000℃ showed the best ORR performance. (3) The importance of urea addition in the raw materials was obvious since it offered the doping source for N element and promoted the complete exfoliation of cellulose fibers; however, excess addition of urea in the raw materials would decrease the SSA of the final carbon. (4) MgO template was important for the creation of micro-

and mesopores; after acid washing, micro- and meso-pores were largely introduced because of the dissolution of MgO nanoparticles. The NHPCs obtained at optimized precursor composition and carbonization temperature were high BET SSA (1173 $m^2 g^{-1}$) and the high ORR performance that was comparable to the best reported carbon-based ORR catalysts in alkaline electrolyte.

For obtaining an EDLC electrode with high capacitance, porous carbons with further increased SSA are needed. In **Chapter 4**, the NHPCs with very high BET SSA of larger than 2700 $m^2 g^{-1}$ were produced by controlling the use of magnesium and potassium nitrate in the precursors. The pore size distribution and SSA of the obtained carbons were quite dependent on the magnesium/potassium ratio in the precursors. The addition of potassium nitrate in the raw materials greatly increased the BET SSA to larger than 2000 $m^2 g^{-1}$, as compared to the magnesium nitrate added sample with BET SSA of around 1100 $m^2 g^{-1}$. This was due to the corrosive activation effect of potassium in creating numerous small micro-mesopores (< 4 nm). The simultaneous additions of magnesium nitrate and potassium nitrate produced continuous and interconnected micro-meso-macro hierarchical pores and very high BET SSA of 2600 $m^2 g^{-1}$.

In Chapter 5, the EDLC properties of the NHPCs with tunable pore structures were investigated in 6 M KOH electrolyte. The NHPCs prepared from the precursors containing both magnesium nitrate and potassium nitrate exhibited the specific capacitance as high as 280 F g^{-1}, being comparable to the highest capacitance of the N-doped carbon material reported so far. The good capacitive performance of the NHPCs obtained in this study is due to their advantageous characteristics including high surface area, hierarchical pore structure, and N-doping.

Chapter 6 is the general conclusion of this thesis. The facile production and outstanding electrochemical performance of the NHPCs are promising for application to electrochemical energy storage and conversion devices including metal-air batteries and EDLC.