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博士論文の要約

Design and Fabrication of Porous Graphene Materials for Advanced Supercapacitors

（先進スーパーキャパシター用多孔グラフェン材料の設計及び創製）

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Graphene, a one-atom-thick two-dimensional carbon material, due to its exceptional physical, chemical, and mechanical properties, has been a promising candidate for a broad range of applications. Graphene offers large specific surface area, high conductivity, excellent mechanical flexibility and outstanding chemical stability. These characteristics make graphene an attractive electrode material for supercapacitors. However, the graphene sheets tend to restack due to the strong π-π interactions and van der Waals forces between them, which cause significant decrease in the electrochemically active surface area and the inter-graphene channels accessible to electrolyte, leading to lower specific capacitance. To address this problem, one effective strategy is to synthesis of graphene electrode materials with a desired morphology/structure for easing the restacking. Here, in this thesis, we have developed a series of graphene electrodes with different micro-structures and architectures. These rational designed graphene structures show many advantages, i.e., large specific surface area, favorable pore structure, or high conductivity, when they are used for supercapacitor applications.

We first successfully assembled graphene nanosheets into hollow spherical shells and tested them as electrode material for supercapacitors. Compared with planar stacked graphene sheets, the hollow spherical graphene shells can provide more free space between the spheres and therefore reduce effectively restacking of graphene sheets. More accessible surface area will also be produced for ion adsorption. Electrochemical characterization shows that the graphene hollow spheres exhibit impressive specific capacitance of 273 F g^{-1} at a low current density of 0.5 A g^{-1} and 197 F g^{-1} at a high current density of 10 A g^{-1}, respectively. Moreover, when it was charged and discharged repeatedly at a high current density of 10 A g^{-1}, 95% of

its initial capacitance was retained even after 5000 cycles. These findings indicate that the graphene hollow spheres are promising as electrode material for supercapacitors.

Then we prepared a single-walled carbon nanotube spaced graphene aerogel (SSGA), in which the SWCNTs are sandwiched between graphene sheets to realize a high specific capacitance together with a high rate capability. The aerogel provides a macro-porous structure and the numerous large pores make the electrode be wetted quickly by the electrolyte to ensure high rate performance; The SWCNTs are placed between the graphene layers to prevent the restacking of graphene sheets and more accessible surface area is made available for ion adsorption; The introduction of highly conductive SWCNTs can also reduce the resistance of the SSGA electrode to further increase the rate capability and promote stable cycling performance. Electrochemical characterization showed that the composites exhibited a high specific capacitance of 245.5 F g^{-1} at a current density of 2.5 A g^{-1} and a high specific capacitance of 197.0 F g^{-1} at a high current density of 80 A g^{-1} in aqueous electrolyte. After 2000 times of repeated charge and discharge cycles at a high current density of 10 A g^{-1}, 97% of its initial capacitance was retained. A high capacitance of 183.3 F g^{-1} at 0.5 A g^{-1} and a high energy density of 80 Wh kg^{-1} were achieved using an ionic liquid ($EMIMBF_4$) as the electrolyte.

We also prepared curved graphene sheets by ionic liquid mediate chemical reduction of graphene oxide in aqueous electrolyte. Electrochemical test results show that the relaxation time and charge transfer resistance at electrode-electrolyte interface for curved graphene electrode is one third and one forth of that for common graphene electrode, respectively, indicating the improved compatibility between the electrode and the electrolyte. Benefited from that, the capacitance retention of curved graphene electrode from current density of 0.5 A g^{-1} to 20 A g^{-1} is 84.4 %, which is extremely higher than that of common graphene electrode (52.9 %), highlighting its enhanced rate capability in ionic liquid electrolyte.