CARBON-BASED ELECTRODES: LEARN FROM TRADITIONAL POROUS CARBON TO DESIGN INNOVATIVE GRAPHENE-BASED NANOSHEETS

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Introduction

Carbon electrodes have attracted considerable attentions in the electrochemical fields, such as lithium ion batteries, supercapacitors, and molecular/ionic target sensing/diagnoses. The abundant surface chemical property, complicated porous texture and variable electronic structure of carbon materials introduce the wide feasibility to engineer the electrochemical performance of carbon electrodes.

Porous carbon is one of the most conventional carbon materials that have wide electrochemical applications. From the numerous investigations regarding porous carbon electrode, it is known that the porous texture, surface chemical property and electronic conductivity affect the electrode performance significantly. Graphene as the atomic thick building block of carbon materials has been successfully fabricated by chemical exfoliation from graphite at a mass scale [1]. The chemically modified graphene-based nanosheets have been utilized for energy storage and electrochemical sensing [2, 3]. In spite of the atomic thick characteristic, chemically modified graphene-based nanosheets also demonstrate the features of surface chemistry, porous texture and electronic structure. Consequently, the knowledge from traditional porous carbon electrodes can provide foreseeable insights to the design of innovative graphene-based electrodes.

In this proceeding, we will briefly revisit our previous works on the properties of conventional porous carbon electrodes in supercapacitors, and introduce how the knowledge guides us to design the novel graphene-based electrodes for supercapacitors.

Porous Carbon Electrodes

The electrode processes occurred on the porous carbon materials involve 1) the ion transport in the porous texture, 2) the electric double layer and 3) the redox charge storage by surface modification. The inner-pore ion transport has been well studied due to their significant effects on the power performance of carbon-based supercapacitors. Our previous studies utilized ordered mesoporous carbon (CMK-3) as a model electrode material to probe the geometrical and surface chemical influences of the porous texture on the ion transport efficiency [4-7]. Research results revealed that the inner-pore ion transport depends on 1) the regularity of the mesopore [4], 2) the aspect ratio of the mesopore [5], and 3) the surface polarity of the mesopore (with specific focus on aqueous electrolyte) [6, 7]. Inspired from the mesopore-aspect-ratio concept, a kind of hierarchical porous carbon was prepared with reduced aspect ratio and highly enhanced power performance [8]. The interfacial capacitance including the double layer capacitance and the redox capacitance associated with oxygen functional groups was studied with regard to the surface modification of CMK-3 carbon using nitric acid oxidation and boron-doping [6, 7]. The results showed that the capacitance increased as the oxygen functional groups aggregated, however the power performance depends on both the pore regularity and the pore surface polarity.

Graphene-based Electrodes

Number of Stacking Layers [9]: The electric double layer capacitance is a function of the Helmholtz layer capacitance and the space charge layer capacitance. The Helmholtz layer capacitance depends on the electrolyte type and concentration, and hence can be treated identically for electrodes prescribed to the same electrolyte. The space charge layer capacitance is related to the stacking thickness (positive dependence) and the screening length (negative dependence) of the graphene nanosheets. Previous studies concluded the screening length increases in thicker graphene sheets because of the decreased charge carrier concentration. However, this increment is not quite significant because only 3~4 times increase have been noticed from few layer graphene to bulk graphite. This result suggests that the space charge layer capacitance, and hence the interfacial capacitance, will increase as the number of layers, i.e. stacking thickness increases. We analyzed the number of layers for graphene nanosheets after different treatments. By correlating these data with their interfacial capacitance, we confirmed the above relationship.

Oxygen on Graphene Nanosheets: The oxygen functional groups on graphene oxide nanosheets can be removed by applying a reducing potential over the electrode from graphene oxide sheets. In this way, the surface chemistry and electric conductivity can be simultaneously tailored. Our work showed that by reducing the oxygen functional groups, the capacitance was increased with great contributions from the enhanced electric conductivity.

Conducting Polymer on Graphene Nanosheets [10]: The surface chemical property of graphene nanosheets has been modified by polyaniline, a kind of conducting polymer with high redox capacitance. The polyaniline decoration distributed homogeneously over the graphene nanosheets. The paper electrode assembled from the polyaniline-modified graphene nanosheets shows combined advantages of high gravimetric capacitance, high volumetric capacitance and also good mechanical tensile strength, in comparison with the pure graphene-based paper electrode.

Mesoporous Cobalt Oxide on Graphene Nanosheets: Cobalt oxide can contribute significant redox capacitance to graphene nanosheets. By a hydrothermal treatment, mesoporous cobalt oxide was deposited onto graphene nanosheets. Owing to the contribution from oxide, the mesoporosity and capacitance of the novel hybrid graphene-based nanosheets was dramatically improved.

Conclusions

To summarize, based on the lessons from conventional porous carbon electrodes, we have attempted to probe the following electrochemical properties of novel nanoassembly electrode based on graphene nanosheets: 1) the electronic structure and the stacking thickness of graphene nanosheets, 2) the redox capability of oxygen functional groups anchored on graphene-based nanosheets, 3) paper-like electrode from polyaniline decorated graphene nanosheets, and 4) the hybrid graphene-oxide nanosheets with tailored porosity and increased capacitance.

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