Development of Highly Porous Carbon Electrode for "Water-in-Salt" Electrolyte-based High-Voltage Supercapacitors

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The threat of climate change to human due to the rising of CO_2 level in atmosphere has stimulated continuing research and development of environmentally friendly energy storage devices, such as lithium-ion batteries and supercapacitors (SCs). SCs, which generally compose of activated carbon electrode and high-voltage non-aqueous electrolytes, are widely used in electric vehicles and renewable energy systems due to their high-power density, rapid charge/discharge, long cycle life, etc. At present, organic SCs are dominating at commercial market, which can offer operating voltage windows over 2.5 V, but the organic electrolytes suffer from low ion conductivity, flammability and toxicity. In recent years, many researches have been focused on expanding the operating voltage of aqueous electrolyte beyond the electrochemical stable window (ESW) of water. Especially, extremely high concentration of salts, so-called "water-in-salt" (WIS), such as 17 m $NaClO_4$ and 20 m LiTFSI, were found to have ESW over 2.0 V, because the activity of water is suppressed in WIS where water molecules are basically attached to the ions and there were almost no free water molecules. It is expected that the environmentally friendly SCs using WIS electrolyte have high energy density comparable to nonaqueous SCs but have higher power density in lower cost.

Because there are not sufficient water molecules for the complete hydration of ions, hydrated ions clusters form in WIS. The larger hydrated ion clusters would exhibit different behavior from those in regular aqueous electrolyte when forming electric double layers. The highly porous carbon with relatively large pores are considered as suitable electrode materials for large hydrated ion clusters in WIS electrolytes. In this dissertation, the research purpose is to develop two types of porous carbon, including mesoporous carbon derived from sulfonated resorcinol-formaldehyde and exfoliated graphene oxides by microwave irradiation, as the electrodes of 17 m $NaClO_4$ WIS electrolyte based SCs, and investigate the electrochemical behavior of the porous carbon on different current collectors Pt, stainless and graphite in the SCs. The dissertation is structured as following chapters.

Chapter 1 describes the research background and principles of EDLCs, the current research status of WIS electrolyte and porous carbon electrodes, and the research purposes of this dissertation.

In chapter 2, sulfonated resorcinol-formaldehyde microspheres were novelly synthesized by introducing the sulfonic acid group into the RF microspheres during polycondensation of RF. The hydrophilicity of the sulfonated RF allowed activation agent KOH to infiltrate inside the microspheres. In the subsequent activation process, a large number of mesopores were developed in addition to micropores and macropores. The surface area of these porous carbon derived from sulfonated RF microspheres exceeds 2000 m^2/g. The specific capacitance of the porous carbon in 6 M KOH electrolyte exceeded 240 F/g at a current density of 0.2 A/g, with high retention over 70% at 10 A/g. The introduction of hydrophilic sulfonic acid into RF was an effective way of making porous carbon with high surface area and unique pore distribution.

In chapter 3, the mesoporous carbon was applied as the electrode of $NaClO_4$ WIS electrolyte-based high-voltage SC because the large pores allow fast ion motions in the WIS electrolyte. Three different current collectors including Pt, stainless steel and graphite were compared. The ESWs of 17 m $NaClO_4$ using Pt, stainless still and graphite electrodes were found to be 2.08 V, 2.68 V and 2.64 V. When Pt or graphite was used as current collector, the mesoporous carbon microspheres exhibited very high specific capacitance of 170 F/g at a current density of 0.5 A/g, which decreased gradually with increasing current density. The mesoporous carbon/Pt symmetric cell was operated at 2.0 V; whereas the symmetric mesoporous carbon/graphite cell could operate at 2.5 V. Accordingly, the mesoporous carbon/graphite exhibited a high energy density of 43 Wh/kg at a power density of 0.25 kW/kg, 32 Wh/kg and 25 Wh/kg at a power density of 1.25 kW/kg and 6.25 kW/kg, respectively, which were significantly higher than those of C/Pt and C/stainless. If stainless-steel was used as collectors, the mesoporous carbon/stainless had much lower capacitance due to the high resistance of the carbon/stainless interface.

In chapter 4, exfoliated graphene oxides (MEGOs) were fabricated by rapid microwave irradiation of graphene oxide films. With microwave irradiation, the temperature of GO rose so rapidly that the eruption of gases due to the sudden vaporization of water and decomposition of functional group caused the exfoliation of graphene layers, accompanied by mass loss of approximately 50%. The highly porous fluffy MEGOs consisted of crumpled and curved graphene layers stacked loosely, which had good wettability to 17 m $NaClO_4$ because there were still more than 10% oxygen in MEGOs. It was found that the specific capacitance of the MEGOs increased with higher operating voltage to 2.5 V, which might involve the rearrangement of ions in the hydrated ion clusters under a high electric field. The environmentally friendly supercapacitor using aqueous 17 m $NaClO_4$ electrolyte could operate at 2.5 V and had high energy density 22 Wh/kg at a power density of 12.5 kW/kg.

Chapter 5 summarizes the above research results.