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ARTICLE

Synthesis of Amorphous Hydrous Ruthenium Dioxide for Electrochemical Capacitors

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Abstract: Amorphous hydrous ruthenium dioxide $RuO_2 \cdot xH_2O$ was synthesized by a modified neutralization reaction and heat treatment process, and electrochemical performances of the synthesized product were investigated using the graphite plate with high conductivity as current collector. In the experiment a home-made sprayer and sodium dodecyle sulfate (SDS) were used as an assistant technique and dispersive agent, respectively. Results indicate that amorphous and high performance electrode materials with great specific area of 218 m^2/g and fluffy and heavy black color morphology can be obtained after the precursor of the synthesized product is annealed at 175 ºC. Cyclic voltammetry (CV) results show the prepared product is featured with good average specific capacitance (995 F/g at 1 mV/s) and excellent electrochemical rate. It is further proved by electrochemical impedance spectra (EIS) test that the prepared product has lower equivalent serial resistance of ~25 mΩ and good electrochemical rate performance.

Key words: electrochemical capacitors (ECs); amorphous hydrous RuO_2; modified neutralization reaction; graphite plate current collector; rate performance

Electrochemical capacitors (Ecs, also called Supercapacitors or Ultracapacitor) have attracted worldwide attention because they can store/deliver energy at a very fast speed with much longer service life and ultrahigher charge/discharge efficiency [1-5]. As the governments all over the world have set up clean energy policies, more and more researchers and units put their focuses on ECs. For example, in electric automobile area, ECs have been extensively tested and used in Pure Electric Vehicles (PEVs) and Hybrid Electric Vehicles (HEVs). The milestone event was the Supercapacitor City Buses made from Shanghai Aowei Technology Company which started the first business operation in Shanghai No.11 route on August 28, 2006. Till now, more 3.0 million kilometers has been accomplished and over 10 million people have experienced the new technology. Compared with Li-ion battery and NiMH batteries, ECs exhibit higher coulombic efficiency (more than 95%) and energy efficiency (over 90%), which means less energy loss and heat emission. For dynamic application, such as automobile, these virtues are more important because of safety concerns arising from the public.

As key active materials developed and investigated for ECs, high specific capacitance and low equivalent series resistance (ESR) are quite necessary. Among these materials, activated carbon (AC) was first and extensively investigated [5-9]. Specific capacitances ranging from 200~300 F/g in aqueous system and 100~200 F/g in organic system were achieved [2,4]. However, too big specific area (1000~3000 m^2/g) of AC leads to relatively low material conductivity (10~100 S/m). Electrochemical conductive materials, such as graphite-based particles and carbon black should be added subsequently in the procedure of preparation of the electrodes [10-12]. Other carbon based materials (or their composites), such as carbon fiber, carbon nano tubes (CNTs) and graphene with low Omic resistance

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have been deeply investigated in recent years [12,13-15]. Nevertheless, theses materials suffer either from lower specific capacitance or some electrode fabrication troubles. Conducting polymers materials, such as PAN (Polyaniline) and PPY (Polypyrrole) were considered as alternatives; however, the studies show that the main problems of these materials are that they are quite electrochemically unstable when repeatedly cycling [16,17]. Noble metal oxide materials, particular non-stoichiometric hydrous Ruthenium oxides with general chemical composition of $RuO_x(OH)_y$ (often written as $RuO_2 \cdot xH_2O$) are more competitive and have been widely studied in the past 30 years [1,4,12,18]. It is found that it shares metal-like conductivity (>5000 S/m) and has a fast and reversible electron transfer in bulk together with an electro-adsorption of protons in the surface[19,20]. Electrochemical tests show that it exhibits much higher specific capacitance than carbon-based and conductive polymers. Besides, it also has faster time response which is quite necessary for ECs. In 1995, Zhang J.P and co-workers first reported that the specific capacitance of $RuO_2 \cdot 0.5H_2O$ synthesized by a sol-gel method could reach 720 F/g[21]. Hu, et al. reported a high specific capacitance of 1340 F/g which the authors believed a low barrier to proton exchange and diffusion could contribute[22]. Later, another preparation method by adopting AAO (Anodic Aluminum Oxide) membrane template was also proposed and a specific capacitance of 1300 F/g was achieved[23]. More recently, Kim, et al. reported a nanoporous $RuO_2 \cdot 3.38H_2O$ synthesized with sodium dodecyl sulfate as the template showed better specific capacitance of 870 F/g[24]. However, most investigations for preparing these materials are in relatively low amount (usually less than 1g), e.g. on a lab scale.

Another problem we must face with is the electrode fabrication technique. Usually, PTFE (Poly Tetra Fluoro Ethylene), CMC (Caboxy Methgt Cellulose) or SBR (Styrene Butadiene Rubber) is added in to ensure good bind properties between the active materials and the current collectors; however, these additives generally have high resistance and some are not very electrochemically stable in acidic media, such as CMC and SBR. In order to further reduce ESR of a hydrous ruthenium oxide based EC device, good conductivity and electrochemical stability acid solution must be considered. Kim, et al. adopted the vapor grown carbon fiber (VGCF) as current collector to test electrochemical performance of $RuO_2 \cdot xH_2O$ and the results showed that the electrode had better rate performances and a partial attribution was supposed to be good conductivity of VGCF[22]. Cheng H M et al proved [12] that hydrous RuO_2 was anchored on graphene sheets by combining sol-gel and low temperature annealing process, and rate capability and electrochemical stability were enhanced. More recently, Msher F El Kady et al. reported a flexible graphene-based electrochemical capacitor prepared by laser scribing. The non current collectors capacitor in 1.0 mol/L H_3PO_4 solution showed very high electrochemical performance and lower time constant (τ=33 ms) [15].

In total, further optimization of $RuO_2 \cdot xH_2O$ preparation method and its electrode fabricating technique are still necessary. The major interest of the present investigation is to optimally prepare $RuO_2 \cdot xH_2O$ material with excellent specific capacitance via a modified neutralization reaction. Reduced ESR between the active material and its current collector is expected by a high conductive graphite plate (8.0×104 S/m).

1 Experiment

15 g $RuCl_3$ of chemical purity was first dissolved into deionized water and then mixed with 3 mL CH_3OH homogeneously under control of a magnetic stirring system. 40 mg sodium dodecyl sulfate (SDS) was subsequently added into the mixture with continuous strong stirring. When small bubbles appeared, 0.5 mol/L $NaHCO_3$ was added into the above solution by a home-made sprayer (Fig.1) till the pH of the solution reached 7.0. The solution was aged overnight, then was filtrated and washed at reduced pressure for 6 times to get the precursor. The final materials were obtained by drying the precursor at 60 ºC, crushed into smaller grains and annealed at different temperatures.

The twin electrodes for electrochemical performance tests in H_2SO_4 solution were fabricated by a brushing method. Details were as follows: 100 mg active materials and 180 mg super P were added in deionized water and mixed homogeneously, and then under the strong stirring condition, 25 mg 60 wt% PTFE emulsion (3F Company, China) was added into the above mixture to form the slurry. A mini hair brush was used to brush the slurry into one surface of the graphite plate (2 mm in thickness). Then the plate at 60 ºC was dried and the above procedure was repeated till the net weight of $RuO_2 \cdot xH_2O$ reached 25 mg on 3 cm×4 cm reactive area of the electrode. The above procedure was repeated to obtain another electrode of the twin electrodes.

X-ray diffraction (XRD) measurement of the material was carried out on a D-8 Advance diffractometer. The surface morphology of the electrodes was observed using Apollo 300 scanning electron microscope. A 2010 transmission electron microscope (TEM) was used to observe the micro structure of the material. The pore characteristics of the $RuO_2 \cdot xH_2O$ was measured by an ASAP 2020 surface and porosity analyzer after degassing at 100 ºC for 4 h. Specific area and mesopore size distributions of the material were determined by Brunauer-Emmett-Telley (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively.

TG experiment was performed at a STA 449C heat analyzer. The sample was heated to 700 ºC at a speed of 3 ºC/min. Another heat experimental method was applied to determine