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Electropolymerization and electrochemical performance of salen-type redox polymer on different carbon supports for supercapacitors

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ABSTRACT

N,N′-ethylenebis(salicylideneaminato) nickel(II), (Ni(salen)), which is the archetype of Schiff base metal complexes, was easily synthesized onto the surface of activated carbon (AC), mesoporous carbon (MC) and multi-walled carbon nanotube (MWCNT) by the route of linear potential sweep, respectively. The microstructure of the poly[Ni(salen)] homogeneously grown on the different carbon supports was evidenced by field emission scanning electron microscopy (FESEM). Growth parameters such as the apparent surface coverage and the doping level were investigated to confirm the effects of supports on the Ni(salen) polymerization. Diffusion coefficient was calculated from the chronoamperometry test to characterize the charge transport ability with the different pore size distributions of the supports, and the result indicates that MWCNT support with abundant macro porous is more active to the growth of the polymer and the charge diffusion. Capacitance performance of the electrodes was discussed by constant charge/discharge and alternating current impedance tests. A 3.79 times capacitance increase of the poly[Ni(salen)] electrode with MWCNT as a support was observed. The exceptional electrochemical properties make the use of MWCNT an attractive support for poly[Ni(salen)] as a supercapacitor material.

1. Introduction

Carbon materials are an essential component in electrochemical energy storage, especially, electric double layer capacitors (EDLC) [1–7]. Although such capacitors have gained commercial success, they fall short of satisfying the need of high capacity for applications such as the next generation all-electric cars [8]. As the demand for new power increases, research interest changes to nano composite materials, with which the combination merits of the two or more materials is expected. Recently, many composites are promoted as new potential materials and exhibit good electrochemical performance for EDLC [9–13]. Furthermore, research aimed at lowering fabrication cost as well as increasing electrochemical capacitance is very necessary. An obvious convenience for composite based on the carbon materials for EDLC is profit from their mature preparation and stability [14–16]. Meanwhile, electro-deposition is a popular method with the advantages of simple, low cost and high efficiency for composite material preparation.

Schiff base metal complexes are a class of compounds that have been studied extensively because of their attractive chemical and physical properties, and their wide-ranging applications in numerous scientific areas [17–19]. Researchers have incorporated Schiff base complexes into polymers, generating new materials with useful mechanical, thermal, chemical, and electronic properties [20]. Metal-containing polymer chemistry is a growing field in which the synthetic materials are anticipated to offer properties unique from their individual organic and inorganic components [20,21]. The development of polymer-modified electrodes is of great interest to researchers not only because Schiff base complexes polymers can be conveniently polymerized by direct electrolysis, but also because of potential applications in electrocatalysts, chemical sensors and electrochromic displays [22,23].

In this article, Ni(salen) was used for electropolymerization to form conductive polymer acting as an electroactive material for supercapacitor by depositing onto the electrode surface with activated carbon (AC), mesoporous carbon (MC) and multi-walled carbon nanotube (MWCNT) as a support, respectively. The polymer film produced by Ni[salen]-type monomers may be combined with the support materials to improve the performance of EDLC capacitors (specific capacitance, energy density, *etc.*). Different properties of microstructure, size distribution among the three kinds of carbon supports are addressed, and the resulting variations

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in electrochemical response of the as-prepared poly[Ni(salen)] are demonstrated and discussed through electrochemical measurement method.

2. Experimental

2.1. Materials

Acetonitrile (AN, >99.9%, A.R. grade) was purchased from Guangdong Xilong Chemical Co., Ltd, while tetrabutylammonium perchlorate (TBAP, >99.9%, C.P. grade) and triethylmethylammonium tetrafluoroborate (Et_3MeNBF_4, >99.9%, C.P. grade), ZhongShengHuaTeng Co., Ltd. They were used as received. The Ni(salen) monomer was synthesized following the procedure in the literature [24] and recrystallized from AN.

The BET surface area of AC was 1683 $m^2 g^{-1}$, and 700 $m^2 g^{-1}$ for MC. The specific surface area of MWCNT increased from 85 $m^2 g^{-1}$ to 195 $m^2 g^{-1}$ under reflux with concentrated HNO_3 and H_2SO_4 (volume ratio = 1/3) treatment. The support electrode was prepared by the homodispersion of the raw support material in N-methyl-2-pyrrolidone (NMP) through sonicating. The slurry was coated on a Ti sheet (current collector) with the coating mass of 0.5 mg. The AC and MC electrodes were made adding 10 wt% super P in order to guarantee the electroconductivity of the electrodes.

2.2. Fabrication and instruments

The surface morphologies of the bare support and poly[Ni(salen)] coated samples were measured by FESEM, using a Zeiss SuprATM^{55} microscope. The electrodeposition of Ni(salen) and electrochemical measurements were carried out on a VMP2 electrochemical workstation with EC-Lab software (version 10.02) made by Princeton.

The electropolymerization was conducted in a closed three-electrode compartment cell. The electrodeposition of Ni(salen) on the resulting electrode (1 cm × 1 cm) was performed in AN solution which containing 1.0 mmol L^{-1} Ni(salen) complex monomer and 0.1 mol L^{-1} TBAP by potentiodynamic electrodeposition between 0.0 and 1.2 V using an activated carbon sheet (1.5 cm × 2.5 cm) and a capillary Ag/AgCl wire as the auxiliary and reference electrodes, respectively, and the scan rate was 20 mV s^{-1}. The poly[Ni(salen)] electrodes were then washed in acetonitrile in order to remove any soluble species from the film and were tested in a monomer-free solution of 1 mol L^{-1} Et_3MeNBF_4 in acetonitrile. Cyclic voltammetry (CV), chronoamperometry (CA), galvanostatic charge/discharge test, and electrochemical impedance spectroscopy (EIS) were measured with the same counter and reference electrodes. All potentials in this article are given *vs.* Ag|AgCl [25]. The ferrocene/ferrocenium couple (Fc/Fc^+) was used as internal standard: under the experiment conditions used, $E_{1/2}$ for the couple was 0.47 V in AN.

3. Results and discussion

3.1. Pore size distribution of supports

The pore size distributions of AC, MC and MWCNT are shown in Fig. 1, and widen in the order MC, AC, and MWCNT. The pores of MWCNT have the widest pore size distribution with majority of pore diameter about 29.98 nm, and 4.59 nm, 1.78 nm for MC and AC, respectively. Abundant of macro pores in supports not only provide a large surface to afford the growth of large amount of poly[Ni(salen)], but also is favorable for the diffusion of monomer and other ions. MWCNT with adequate pores of large diameter meets the requirements both the polymerization growth of Ni(salen) and the diffusion in the support. For this reason, MWCNT could play a positive role in the poly[Ni(salen)] film growth and ensure high electrochemical activity of as-grown poly[Ni(salen)].

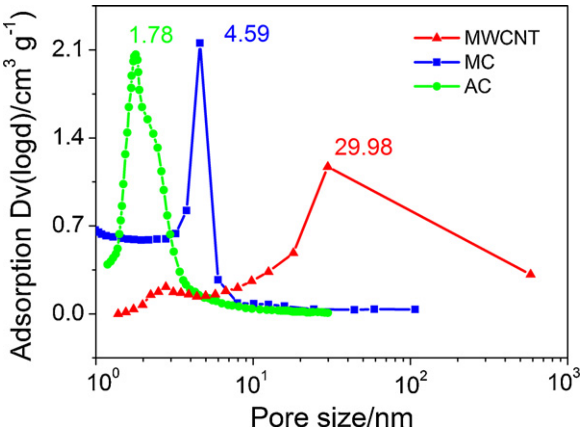

Fig. 1. Pore size distributions of AC, MC and MWCNT.

3.2. Film growth

Cyclic voltammograms illustrating the general scanning procedure for anodic polymerization are shown in Fig. 2 for Ni(salen). The increase in current with repetitive scanning is due to film growth on the electrode surface. However, the peak current decreases after a certain scanning, in accompany with the increase of the anodic–cathodic peak potential separation (ΔE) and even the disappearance of the oxide peak. This indicates the increase of the difficulty of Ni(salen) polymerization and the decrease of electrochemical activity of the as-prepared poly[Ni(salen)]. The film growth rate on the electrode can be represented by the plot of the apparent surface coverage (Γ, $\mu mol\ cm^{-2}$) *vs.* the scan number in Fig. 3. The apparent surface coverage is a growth parameter to give an estimate for the actual surface coverage, which was calculated using the equation $\Gamma = \Delta Q/nFA$, where n is the number of transferred electrons, F is the Faraday's constant, A is the area of electrode in cm^2, and ΔQ is the charge (area) difference under the cyclic voltammetric anodic oxidation wave of the poly[Ni(salen)] coated electrodes and bare support electrodes at 20 mV s^{-1}.

The dependence of the apparent surface coverage on the scan number can be divided into two parts. For all the three kinds of carbon materials, the apparent surface coverage of Ni(salen) increases linearly for the first several scans (almost 40 scans), followed by a

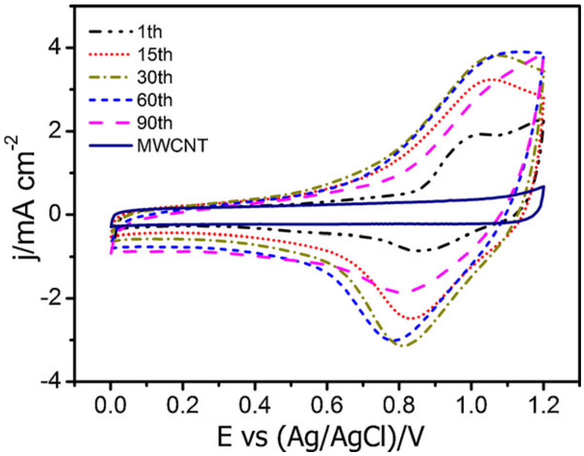

Fig. 2. CV plots for anodic polymerization of Ni(salen) on MWCNT.