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Effects of adding different morphological carbon nanomaterials on supercapacitive performance of sol–gel manganese oxide films

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Abstract

In this study, the supercapacitive performances of manganese oxide films were investigated by adding different carbon nanomaterials, including carbon nanocapsules (CNC), multiwalled carbon nanotubes (MWCNTs) and multi-layered graphene. The manganese oxide films were prepared with manganese acetate precursor by sol–gel method, and the post-treatment effects were also examined. With a heat-treatment above 300 °C, the as-prepared amorphous films transformed to a compound of Mn_3O_4 and Mn_2O_3 phases, and the smooth surface became rough as well. Cyclic voltammogram (CV) tests showed that the manganese oxide film, which was mixed with 0.05 wt% MWCNTs and annealed at 350 °C for 1 h, exhibited the optimized specific capacitance, 339.1 F/g. During 1000CV cycles, the specific capacitances of original manganese oxide film decreased gradually from 198.7 to 149.1 (75%) F/g. After same number of cycle tests, the modified films containing 0.025 wt% CNC, 0.05 wt% MWCNTs and 0.1 wt% graphene retained 201.8 (64.2%), 267.4 (78.9%) and 193.1 (57.4%) F/g respectively. The results indicates that the supercapacitive performance of manganese oxide films were significantly modified by carbon nanomaterials; in addition, the MWCNTs additive could also reduce the decay rate.

Keywords: Supercapacitor; Sol–gel; Manganese oxide; CNTs; Graphene

1. Introduction

Supercapacitor is one modern device for charge storage, so-called electrochemical or ultra-capacitor. Overcoming the disadvantages of conventional dielectric capacitors and secondary batteries, supercapacitors can provide a long cycle life and high power density, and take a high current density while rapid charging as well [1,2].

The storage mechanism of supercapacitor mainly divides into two categories: (i) Electric Double-Layer Capacitor (EDLC): the storage is achieved by the charges separating in the electrolyte, and the electrode does not participate in EDLC reactions directly. Thus, the storage capacity is related to its specific surface area for absorbing. Carbon materials, of high porosity and specific surface area, are good choices for EDLC electrode, such as graphene [3,4], active carbon [5], carbon fiber and nanotubes [6–9]. (ii) Pseudocapacitor: that drives from fast, reversible, and Faradaic redox reactions, occurring within the bulk material of the electrode over an appropriate range of potentials [10]. Electrodes of this category are commonly made of materials with high conductivity and various oxidation states. Conductive polymers, carbon materials and metal oxides are three mainstream electrodes for supercapacitors.

Metal oxides electrodes mostly are composed of transition metals, which could provide more available orbitals for free electrons, and own a wide redox range. Therefore, transition

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metal oxides were generally made into supercapacitor electrodes, including MnO_2, NiO, and RuO_2 [11–15]. Although RuO_2 has the highest specific capacitance value [16], the expensive producing cost and poor anti-corrosion ability to acid electrolytes limit its commercial applications. As to manganese oxides, the advantages of abundant mineral resources, various valence states and high chemical stability make it become a potential candidate for pseudocapacitor. However, manganese oxides also get some drawbacks, like poor conductivity, and manganese ions peeling issue after cyclic voltammogram (CV) tests. In order to overcome the intrinsic limitations, many efforts were devoted to modify manganese oxides, especially by adding carbon nano-materials to improve the capacitor performance and cycle life [3,4]. In addition, the electrode compositions and processes would define their rechargeability, specific capacitance and cycle life as well [17]. Metal oxide electrodes hence were studied by various processes, including chemical co-deposition [18,19], anodic plating [7,20,21], electrophoretic deposition [22], thermal decomposition [23] and sol–gel process [11,24,25]. Among them, sol–gel process can provide a uniform coating onto large scale substrates with relatively low temperature and cost.

In this study, the sol–gel process was used to prepare manganese oxide films onto graphite substrates, and then the as-coated films were modified by adding various carbon nano-materials of selected ratios. The carbon materials would form connection and provide a porous structure. Such porosity could not only expectedly retain the space for electrochemical reactions, but also create a uniform porous structure of high specific surface area to improve the capacitor properties.

2. Experimental procedures

The manganese oxide films were prepared by using sol–gel process, and then modified by decorating various carbon nanomaterials. The procedures include the pre-treatment of graphite substrate, sol–gel manganese oxide coating and post heat-treatments. Firstly, graphite substrates (EDM-200, Poco) used as the electrode base for manganese oxide films were cut into $1 \times 1 \times 0.6\ cm^3$ plates. After grinding, cleaning and baking, the graphite plates were ready for coating. The sol–gel precursor was a mixture of citric acid ($C_6H_8O_7$), n-propanol ($CH_3CH_2CH_2OH$) manganese acetate (Mn $(CH_3COO)_2$), and ammonium hydroxide (NH_4OH). Then, carbon nanomaterials were individually added at 45 °C and kept a pH value around 9.5 ± 0.2 to obtain the modified precursors. The adding amounts of carbon materials, including carbon nanocapsules (CNC), multiwalled carbon nanotubes (CTube 100, CNT Co., Ltd., Korea) and multi-layered graphene, were ranging from 0.0125 wt% to 0.2 wt%. Finally, the drop coating process was used to coat the manganese oxide films on graphite substrates, and then dried at room temperature for 24 h. To further verify the heating effects on those oxide electrodes, the dry manganese oxide electrodes were annealed at 250, 300, 350 and 400 °C in ambient air for 1 h, respectively.

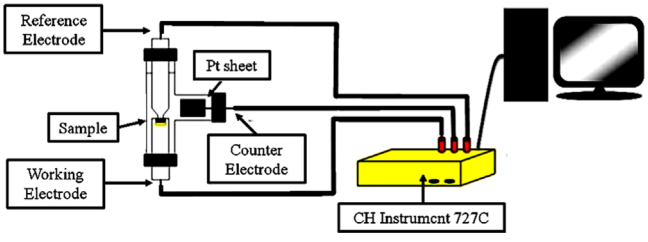

Fig. 1. Schematic drawing of electrochemistry measuring system.

The phase transformation temperatures and thermal stability were examined by a thermal gravity analyzer (TGA, MDSC29, TA Instrument). X-ray diffractometer (XRD, PW 3040/60, Philips), scanning electron microscopy (SEM, HITACHI S4800) and transmission electron microscopy (TEM, JEOL JEM-2010) were used to identify the structures and chemical compositions. The battery properties of metal oxide electrodes were further measured by using cyclic voltammetry (CV, Model 737C Series, CH Instruments, USA). Fig. 1 is the illustration of electrochemistry measuring system. The scanning range is within 0 to 0.9 V (vs. Ag/AgCl) and the scanning rate is 25 mV/s. After recording the variation of currents, the

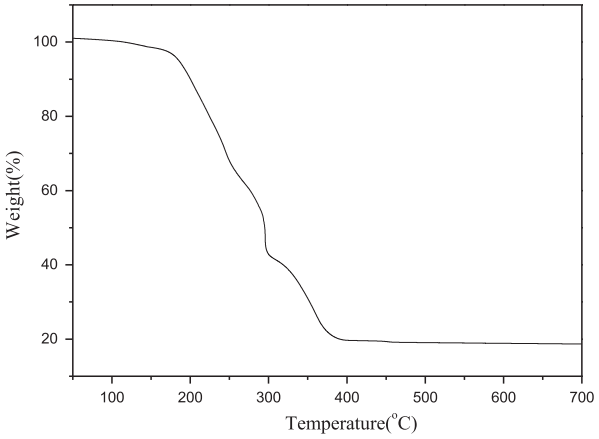

Fig. 2. TGA result of as-coated manganese oxide film.

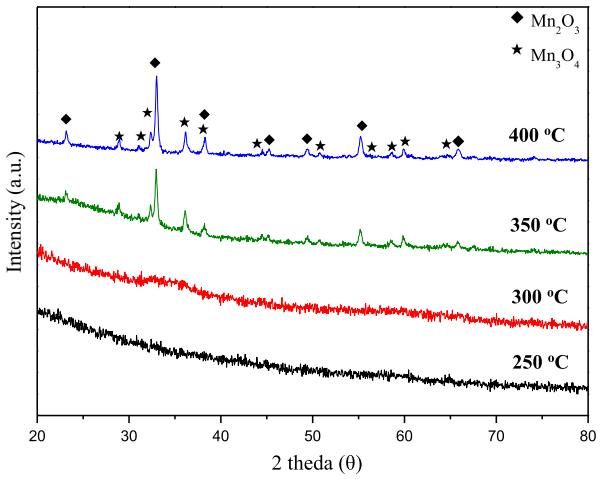

Fig. 3. XRD results of manganese oxides after annealed at 250, 300, 350 and 400 °C respectively.