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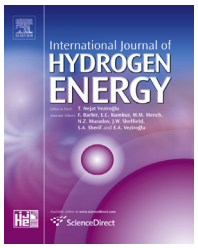

Synthesis of cobalt oxide-manganese oxide on activated carbon electrodes for electrochemical capacitor application using a liquid phase plasma method

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ABSTRACT

An Electrochemical capacitor electrode material was prepared by precipitating cobalt-manganese oxide nanoparticles on the surface of activated carbon powder (ACP) using a liquid phase plasma method. Polycrystalline spherical 100–170 nm-sized metal oxide nanoparticles were precipitated onto the ACP surface with a high degree of uniformity. The initial concentration of precursor influenced the composition of the precipitated nanoparticles. The nanoparticles were bimetallic oxide nanoparticles composed mainly of Co^{2+} and Mn^{3+}. Increases in the amount of metal oxide nanoparticles precipitated on ACP, were accompanied by reduced specific surface area, average pore size, and total pore volume, as well as by increased specific capacitance. The metal oxide nanoparticles improved the cyclic stability of the electrochemical capacitor and reduced equivalent series resistance.

Introduction

Electrochemical capacitors are charge-storage devices with the characteristics of high power density, long cyclic life and low maintenance cost [1–4]. They fill the gap between batteries (high energy density) and electrolytic capacitors (high power density) [5,6]. Such properties make them potentially useful for a wide range of applications such as hybrid vehicles, cordless electric tools, memory back-up, cellular phones, medical devices, as well as a host of additional military and consumer electronics [7]. Electrochemical capacitors can be classified into two types according to their charge storage mechanisms: electric double layer capacitors

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Table 1 – Chemical composition of CMCC obtained with different LPP reaction durations and initial precursor concentrations.

	C		O		Co		Mn	
	Wt%	at%	Wt%	At%	Wt%	At%	Wt%	At%
Bare ACP	96.98	97.71	3.02	2.29	0.00	0.00	0.00	0.00
C5M5-30	96.24	97.40	3.29	2.50	0.36	0.07	0.11	0.02
C5M5-60	95.65	97.09	3.62	2.76	0.49	0.10	0.24	0.05
C5M5-90	94.87	96.63	4.13	3.16	0.62	0.13	0.38	0.08
C1M9-90	95.18	96.74	4.05	3.09	0.28	0.06	0.49	0.11

(EDLC) and redox supercapacitor (or pseudo-capacitors). EDLCs mainly utilize the nonfaradaic charge separation at the electrode/electrolyte interface. Redox supercapacitors make use of a reversible redox reaction in order to store charges [8–10].

Supercapacitor electrodes are usually prepared using carbonaceous materials, conducting polymers, or metal oxides, which have their own specific merits and demerits. Carbonaceous materials with large specific surface areas, e.g. activated carbon, carbon fiber, carbon nanotube, have very high output characteristics due to their storage of store energy in an electric double layer, but the capacity of energy storage devices prepared using these materials is relatively low. Some polymers (e.g. polypyrrole and polyaniline) have conjugated structures that utilize oxidation–reduction reactions, and exhibit higher capacity and better flexibility than carbonaceous materials, but their cycle life characteristics are inferior [11–13]. Metal oxides that use both surface and oxidation–reduction reactions have higher capacitance than carbonaceous materials. However, the capacitance of most metal oxides, e.g. manganese oxide, nickel oxide, and cobalt oxide, is lower than that of conducting polymers, with the exception of ruthenium oxide, which carries a very high cost [14–19]. Therefore, it is of importance to understand the merits and demerits of various materials in order to develop cost-effective supercapacitor electrodes with high capacitance and high output characteristics. In this regard, extensive studies of on composite electrodes composed of multiple materials are being conducte.

Recently, plasmas in the liquid phase have attracted attention due to their applicability to industrial material processing [20]. In particular, glow discharge in the liquid phase is a useful tool for the synthesis of metal nanoparticles [21]. Liquid phase plasma (LPP) can potentially fabricate metal nanoparticles rapidly without the addition of reducing agents because plasma provides a reaction field with highly excited energy states [22–24].

In the present study, cobalt oxide nanoparticles and manganese oxide nanoparticles were simultaneously precipitated onto the surface of activated carbon using the LPP method to generate a composite electrode for supercapacitor applications. The effects of plasma discharge conditions on the properties of the composite electrode were investigated using instrumental analyses. The electrochemical capacitance performance of the supercapacitor was evaluated by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge/discharge testing.

Experimental

Materials and experimental equipment

Activated carbon powder (ACP) YP-50F (Koraray chemical co. Ltd.) was used as the substrate material onto which metal oxide nanoparticles were precipitated. As the precursors of cobalt and manganese, cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Daejung Chemicals & metals Co., Ltd) and manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, Junsei chemical Co. Ltd), respectively, were used. Cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, Daejung Chemicals & metals Co., Ltd) was used to allow for a more uniform dispersion of metal oxide nanoparticles formed from the LPP process. Only reagent-grade chemicals and ultrapure water (Daejung Chemical & metals Co. Ltd.) were used in the reactant solution. An LPP apparatus equipped with a high frequency bipolar pulse-type power supply was used to precipitate metal oxide nanoparticles in the reactant solution onto the ACP surface. A similar apparatus was used in our previous study to generate nanoparticles dispersed in an aqua solution [25], and detailed information of the experimental setup can be found in that paper.

Preparation of composite

$CoCl_2 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ with predefined ratios were dissolved in 250 mL of ultrapure water. CTAB with a 50% molar ratio with respect to total precursor quantity (5.0 mM) was added. After adding 0.5 g of ACP in the reactant solution, the mixture was stirred for 1 h for sufficient mixing. The reactant solution was than introduced into the LPP reactor. Cobalt-manganese oxide nanoparticles on activated carbon composite (CMCC) materials were produced in the solution after operation of the system for various predefined durations (30–90 min). When the LPP process was completed, unreacted cobalt, manganese and CTAB were removed from the solution through centrifugation (4000 rpm) and repeated washing. Filtered CMCC was than dried in a vacuum at 353 K for 48 h. The dried CMCC was than oxidized by supplying O_2 gas for 2 h at 423 K.

Electrochemical test

A coin cell battery was produced to evaluate the electrochemical properties of the synthesized CMCC. The mass ratio of active material (CMCC), conducting agent, and binder was 83:10:7 wt%. Super-P conductive carbon black (TIMCAL graphite & carbon com.) was used as the conducting agent in this study. A mixture of styrene-butadiene rubber and carboxymethyl cellulose was used as the binder. 6 M KOH solution was used as the electrolyte. 150 μm glass felt was used as the separator. The cyclic voltammetry measurement was conducted using an the actuation voltage of 0.1–0.8 V, current density of 0.001 A/cm^2, and scan rate of 10 mV/s. Impedance was measured using an alternating-current impedance analyzer within the frequency range of 0.1 hz–300 kHz. A potentiostat (VSP, Princeton Applied Research)