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Synthesis of manganese oxide/activated carbon composites for supercapacitor application using a liquid phase plasma reduction system

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ABSTRACT

Manganese oxide/carbon composite electrode was synthesized using liquid-phase plasma method, to be applied to supercapacitor. Spherical manganese oxide nanoparticles smaller than 10 nm were dispersed uniformly on the surface of YP-50F. The increase in the amount of manganese oxide precipitated on YP-50F resulted in improved specific capacitance, charge–discharge rate, and Warburg impedance but specific surface area and total pore volume were decreased.

Introduction

The ever worsening energy depletion and global warming issues call for not only urgent development of clean alternative energies and emission control of global warming gases, but also more advanced energy storage and management devices [1]. Electrochemical supercapacitors, which are one of the most promising electrochemical energy storage systems, have attracted considerable attention since they can provide higher power densities and have a longer cycle life than batteries [2,3].

Supercapacitors can be used for a number of applications, such as backup computer power, lightweight electrical fuse, and auxiliary power supply device for electric vehicles [4,5]. There are two kinds of supercapacitors: electric double-layer capacitors (EDLCs) based on ion adsorption and pseudo-capacitance capacitors based on electrical redox reactions. Metal oxides, e.g. ruthenium oxide (RuO_2), manganese dioxide (MnO_2), and nickel oxide (NiO), are used for producing pseudo-capacitance capacitors [6,7].

Among the various metal oxides, ruthenium oxide is widely studied because of its high specific capacitance

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(~720 F g^{-1}) [8,9]. However, the commercial use of RuO_2 is limited because of its high cost. Therefore, alternative and inexpensive electrode materials have been explored. Manganese oxide is cheaper than RuO_2 but its electrical conductivity is lower. In order to improve the electrical conductivity of manganese oxide supercapacitors, composites have been synthesized by adding other transition metal oxides or various carbon materials [10]. One common way of synthesizing a manganese oxide/carbon composite is to deposit manganese oxide film on carbon material surface using film generating techniques, e.g. chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE). These techniques, however, require high temperature processes resulting in low energy efficiency.

Liquid phase plasma (LPP) is reportedly a useful tool to synthesize nanoparticles on supporting materials [11,12]. Nanoparticles can be generated rapidly by the LPP method without adding reducing agents because plasma provides a reaction field with highly excited energy states [13–15]. In the present work, a new strategy of synthesizing manganese oxide/activated carbon composite as dielectric material for capacitor using an LPP reduction system is presented. The effects of plasma discharge conditions are discussed and the resultant products are characterized. The electrochemical capacitance performance of the supercapacitor was evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge test.

Experimental

Materials and experimental equipment

Manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, Daejung Chemical & metals Co. Ltd.) was used as the precursor. Manganese oxide nanoparticles were generated and precipitated in an aqueous solution using the LPP method. Cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N(CH_3)_3Br$, Daejung Chemicals & metals Co., Ltd) was used as a dispersant. Activated carbon powder (YP-50F, Koraray chemical co. ltd.) was used as the carbonaceous material in this study. The particle size and specific surface area of this powder were 5–20 μm and 1500–1800 m^2/g, respectively. Only reagent-grade chemicals and pure water (Daejung Chemicals & metals Co., Ltd) were used in this study.

A schematic diagram of the experimental setup used in this study is shown in Fig. 1. Similar apparatus was used in our previous study to generate nanoparticles dispersed in an aqueous solution using the LPP process [16]. Detailed information of the experimental setup can be found in that paper [16]. Pulsed electric discharge was generated by an electrode system in a double annular tube type reactor (ID 50 mm, OD 80 mm, height 150 mm). Cooling water (30% ethylene glycol, −5 °C) was circulated through the outer channel of the reactor and the cooling circuit. The reactant solution temperature was maintained at 25 °C. A Teflon stirring bar was used in the reactor to maintain the homogeneity of the aqueous solution. The applied voltage, pulse width, and frequency were 250 V, 5 μs, and 30 kHz, respectively. The reactant solution was prepared as follows. CTAB 3 mM was dissolved in 250 mL of ultrapure water and then 2.0 g of YP-50F was added. After stirring, the solution was sonicated for 10 min for uniform dispersion. Reactant solution was completed by adding 6 mM of $MnCl_2 \cdot 4H_2O$ to this solution.

Preparation of composite

Manganese oxide/carbon composite was generated by the LPP process. Liquid plasma is defined as a discharge in aqueous solution, stabilized by the exchange of ions and electrons between gas and liquid phases. This plasma generates a number of high active species, e.g., hydrogen, oxygen, and hydroxyl radicals, in the aqueous solution. The reactants of the desired reaction are added into the solution and they react with the active species at the interface of gas and liquid

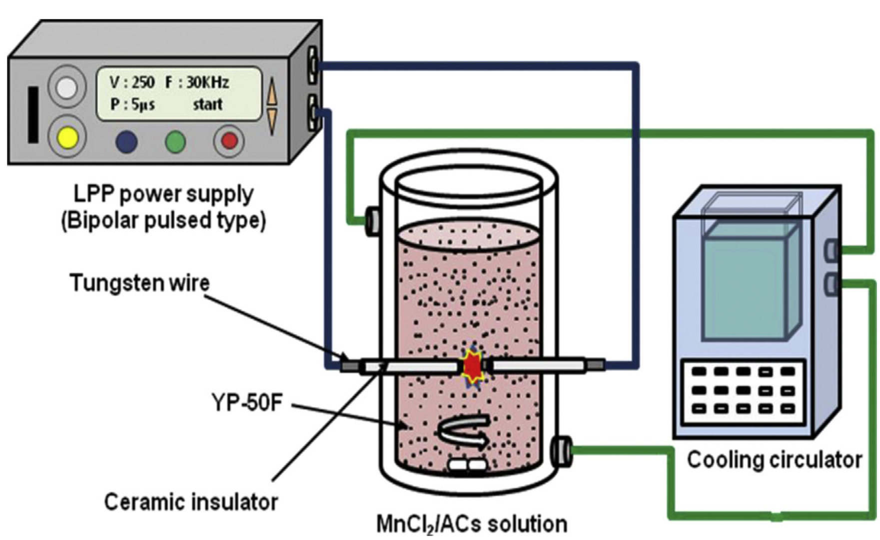

Fig. 1 – Schematic of the experimental system with bipolar pulsed electrical discharge for manganese oxide/carbon composites.