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Full Length Article

Assessing the electrochemical performance of a supercapacitor electrode made of copper oxide and activated carbon using liquid phase plasma

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ABSTRACT

Successful modification of surface properties of a nanocomposite electrode is prerequisite to enhancing the overall performance of electrochemical supercapacitors. The present study was designed to describe the microstructural and electrochemical characteristics of a new composite electrode assembled by activated carbon (AC) powder (as a host) and copper precursor (as a guest) using liquid phase plasma. The fabrication processes were conducted by changing plasma discharge time from 30 to 90 min in the presence and absence of (thermal) oxidation. We observed that merging plasma and oxidation treatments raised the content of copper oxide nanoparticles precipitated (evenly) on the AC surface, along with oxygen. A mixed valence state of copper oxides (in the forms of Cu^o, Cu_2O, and CuO) was found in different composites with and without oxidation, where CuO and Cu^o affected a specific capacitance in positive and negative ways, respectively. This led to the difference of electrochemical stability and resistance among the assembled composites. For instance, the best cycling performance was observed in the plasma-treated composite for 90 min with oxidation, whereas that of 60 min without oxidation recorded the lowest resistance. Therefore, a proper balance between the capacitance and resistance appears to be required for effective fabrication of the supercapacitor electrode, specifically in cases involving copper oxides.

1. Introduction

Recently, electrochemical energy storage and conversion devices have claimed intense attention due to their potential for more efficient use of clean, renewable energy sources. Supercapacitors are, in particular, attractive for high power delivery and prolonged lifespan over other electrochemical competitors such as secondary batteries and fuel cells which have a main specialty in high energy density [1–3]. The performance of the supercapacitors is tightly bound to the intrinsic properties of the electrode and associated components such as the electrolyte and current collector. Thus, the properties of those (active and inactive) materials are continuously optimized in a way to achieve both high power and energy density demands.

Transition metal oxides adopted for supercapacitor electrodes are superior to carbon-based materials in terms of energy density. Various metal oxides such as MnO_2 [4], NiO [5], Co_3O_4 [6], and VO_x [7] were extensively studied to compensate for poor specific capacitance and electrochemical stability. However, their performance was not admirable as much as RuO_2 which exhibited the outstanding pseudocapacitive behavior [8]. Despite this remarkable advantage, RuO_2 also suffered from high cost, potentially including poor stability, which restricted its further expansion into current and emerging supercapacitor electrodes. CuO, one other candidate affording various oxidation states (from 0 to +3), was characterized by non-toxic, low cost, and easy control of nanoparticles with respect to size and shape. In our understanding, a few studies have so far examined its applicability to the pseudocapacitor electrodes probably due to rapid capacity loss and poor cycling performance resulted from destruction of the crystal structure [9–12], although extensive tests were conducted for its use in Li-ion battery electrodes [13–16].

A hybrid (nanostructured) composite electrode integrating more than two electrode materials has been recommended as an effective way of alleviating various issues raised for individual candidates [17,18]. For instance, the composite electrode inviting carbon-based materials as a host and metal oxides as a guest

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was found not only to enhance a specific capacitance (owing to carbon-based materials only), but also to maintain a structural integrity during repeated cycling (owing to metal oxides alone) [19]. In addition, liquid phase plasma (LPP) method which took place in aqueous solution by glow discharge allowed much more rapid reaction from a reaction field with a highly excited energy state over conventional method such as chemical reduction method, hydrothermal method, chemical vapor deposition, etc. The composite synthesized by one-step process without any reducing agents is another plus of the LPP method [20–27]. All those advantages taken together, the objectives of this study were, therefore, to assembly a new composite electrode with copper oxide and activated (AC) powder from LPP process and then to characterize its microscopic structure and electrochemical properties in detail.

2. Experimental

2.1. Experimental materials and equipment

Analytical grade chemicals copper(II) chloride dehydrate (CAS Number 10125-13-0) and Cetyltrimethylammonium bromide (CTAB, CAS Number 57-09-0), which was manufactured by Daejung Chemicals & Metals Co., participated as dopant and dispersing materials in assembling a new composite electrode, respectively. The AC powder of YP-50F with total surface area ranging 1500 to 1800 m^2/g, which was commercially available from Kuraray Chemical Co., was used as a host material in trapping derivatives (i.e., copper oxide nanoparticles) from the guest metal precursor using LPP process. An aqueous solution that contained a series of chemical products listed above was prepared with ultrapure water provided by Daejung Chemicals & Metals Co.

Fig. 1 illustrates the experimental system which is adopted not only to yield copper oxide nanoparticles in the aqueous solution, but also to deposit them on the AC powder surface using LPP process. The apparatus was made up of three independent components, a reaction chamber (located in the middle of the figure), power supply (on the right side), and circulating bath (in the bottom-left corner). The reaction chamber was constructed with double tubes of 40 mm in internal diameter and 800 mm in height, in which the inner tube occupied by the aqueous solution was completely separated from the outer tube filled with an insulation material. The chamber had two parallel holes to mount high purity tungsten electrodes of 2 mm in diameter (TTM Korea Co.) which was also covered with insulator. The insulated electrodes were coupled to the power supply operated at a voltage of 250 V, a frequency of 30 kHz, and a pulse width of 5 μs to activate (electrical discharge) plasma in the aqueous solution. Specifically, the power supply which was capable of the bipolar pulsed operation with high frequency mode was used to increase the efficiency of nanoparticle generation loaded on top of the AC powder. Finally, the solution temperature in the chamber was constantly kept at 293 K using the (cooling) circulating bath to avoid any thermal influences during the fabrication.

2.2. Preparing a composite electrode with copper oxide and AC powder

Given below is a detailed methodology to synthesize a new composite electrode using LPP process. Initially, 250 mL of ultrapure water was used to dissolve 6 mM of copper(II) chloride dehydrate. 3 mM of CTAB was then added to the precursor solution (above) under vigorous stirring, which was again mixed with 0.5 g of the AC powder. The mixture was subject to ultrasonication treatment for 5 min and kept stirring for another 1 h to form a reactant solution.

The reactant solution, once loaded to the chamber, was exposed to the plasma (i.e., LPP process) operated at specified time intervals, 30, 60, and 90 min, to successfully produce different amounts of copper oxide nanoparticles. The residues suspended in the reactant solution, such as non-reactive chemicals including CTAB, was centrifuged at 4000 rpm and washed with ultrapure water five

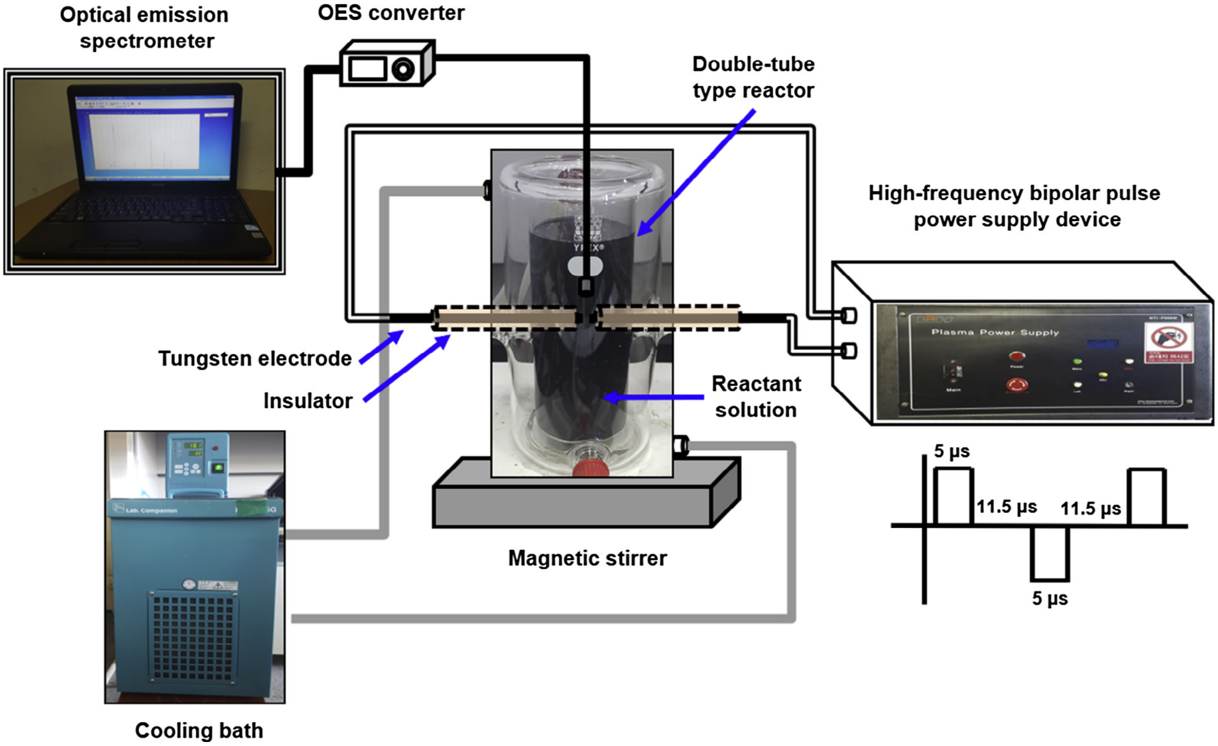

Fig. 1. Experimental setup for the fabrication of copper oxide-loaded AC composites using LPP method.

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