Graphene-tin oxide hydrid supercapacitor electrode by electron beam irradiation

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1. Introduction

Supercapacitor have highly potential in energy storage system due to large capacitance, rapid charging/discharging rate, high power density and long life cycle [1,2]. Supercapacitors have electrodes of two types according to charging methods; the electric double layer capacitor (EDLC) and pseudocapacitor are typical supercapacitor electrodes. EDLC which stores energy through physical adsorption and desorption have unique advantages such as high power density and long life cycle. However, EDLC electrodes have a big issue that it has poor energy density. On the other hand, pesudocapacitor electrodes show the better energy densities than EDLC electrodes. But, that electrodes have still some issues such as low power densities, low charging/discharging rates and poor life cycle.

Recently, a hybrid composite supercapacitor electrodes which combine EDLC and pseudocapacitor, has attracted to researchers, since hybrid composite electrodes improve not only capacitances but also stabilities. Moreover, hybrid composite electrodes can overcome the disadvantages of each electrodes. In this study, the hybrid composite electrode is prepared using graphene which is typical EDLC ingredients and tin oxide which is pseudocapcitor materials. Furthermore, electron beam irradiation is performed on hybrid composite electrode to enhance the binding strength between graphene and tin oxide, resulting in increment of specific capacitance of electrode.

Electron beam irradiation induces the scissioning and crosslinking of graphene [3], after that some chains between graphene and tin oxide are produced. It improves the binding strength, then electrical conductivity and specific capacitance increase. Moreover, electron beam irradiation is eco-friendly process because it doesn't require complicated process and hazard materials. In this study, vertically-aligned graphene (VAG) is used at EDLC electrodes and 50 keV electron beam is used at fabrication of hybrid composite electrodes.

2. Methods

2.1 Fabrication of VAG electrodes

VAG electrodes are prepared by anodization of graphite foil. Graphite foil (t: 3 mm) was cut into 1*1cm² and washed in ethanol for 3 min. Graphite foil

as working electrode and platinum foil as counter electrode are placed in 0.1M NH₄F aqueous solution. Constant voltage of +10V is applied to two electrodes for 60 min. After anodization process, graphite foil was washed in deionized water for several times and dried in vacuum oven for 1 hr.

2.2 Fabrication of VAG-tin oxide hybrid composite electrodes

VAG-tin oxide hybrid composite is produced by sonication assisted chemical bath deposition (S-CBD) method. VAG electrodes are sequentially immersed in a 0.05 M SnCl₂·2H₂O aqueous solution and 1% H₂O₂ aqueous solution for 20 s, respectively. Excessive ions are rinsed in deionized water. All process was performed with sonication process. After that, composite electrodes are annealed in 300°C for 2 hrs.



Fig. 1. Image of fabricated MOs-graphene hybrid electrode

2.3 Electron beam irradiation on hybrid electrodes

In this study, Electron beam device of 50 keV fabricated in this lab is utilized. The hybrid composite electrode is placed in the center of beam devices and internal device is evacuated. The pressure of device are kept at 10^{-6} Torr. The electron beam irradiated to the hybrid composite electrode by controlling the current densities and irradiating time (Fig. 1).

2.4 Characterization of hybrid composite electrodes

The characteristics of hybrid composite electrode are measured by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectrometer (EDS).

Electrochemical features of hybrid composite electrode are observed through cyclic voltammetry and galvanostatic charge-discharge method using SP-200 instrument (Biologic, France) (Fig.2).



Fig. 2. Electrochemical measurement instruments to evaluate the hybrid composite electrodes (SP-200, biologic, France)

3. Results and discussion

3.1 Fabrication of VAG-tin oxide hybrid electrodes

S-CBD process was performed on the VAG electrodes for 4 times (VAG–SnO2-4). FE-SEM images show the morphology of hybrid electrodes. A large number of SnO₂ nanoparticles are decorated on the VAG edges and inside of VAG surface (Fig.3). Especially, numerous tin oxide particles are observed at edges of VAG. It is assumed that tin oxide nano-particles are connected to VAG edges including oxygen functional groups.



Fig. 3. SEM images of a) edges and b) inside of VAG-SnO₂-4.

Atomic ratio of tin oxide decorated on the VAG are evaluated using EDS (Fig. 4). In the EDS, atomic ratio of Sn and O are measured to be 30.34 at.% and 68.19 at.%, respectively. It means that the nano-particles formed on the surface of the VAG electrode are SnO₂.



Fig. 4. EDS results of tin oxide on VAG electrodes

4. Conclusions

Hybrid composite supercapacitors have attracted for energy storage industries due to their large capacitance and stabilities. This study suggested a simple method to fabricate hybrid composite electrodes using anodization process and electron beam irradiation.

The VAG-tinoxide hybrid electrode was successfully synthesized through the S-CBD method. Electron beam irradiation improve the binding strength between VAGs and tin oxide then specific capacitance can increase. It is expected that this study would suggest the application of electron beam irradiation technology in energy storage fields.

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