Electronic Supporting Information

In-Situ Exfoliation and Modification of Graphite Foil in Supercapacitor Devices: A Facile Strategy to Fabricate High-Performance Supercapacitors

Byungkwon Jang, Han Kim, Si-Woo Park, Minseob Lim, Jimin Lee, Gwang Myeong Go, and Yong-Ho Choa*

Department of Materials Science and Chemical Engineering, Hanyang University, Ansan, Korea

Chemicals and Materials

Expandable graphite (+50 mesh sized), and manganese acetate tetrahydrate ($Mn(OAc)_2 \cdot 4H_2O$, >99 %), and Potassium nitrate (KNO_3, >99.0 %) were purchased from Sigma Aldrich. Polyester single coated tape (silicone adhesive, 3M™ 8993K), and Cellulose separator (Quantitative filter paper, NO.50, 200 μm thickness) was purchased from 3M and Hyundai Micro, respectively.

Fabrication of graphite foil

Expandable graphite (1.5 g) was thermally expanded in a box furnace with a temperature of 950 °C for 3 minutes. After expansion and colling to room temperature, the resulting expanded graphite was pre-formed in 3cm by 12 cm sized-mold and roll-pressed to fabricate graphite foil with a thickness of 100 μm.

GF supercapacitor device fabrication

As-made graphite foil cut into the desired form to apply an electrode of supercapacitor without current collector using a blade. A cut graphite foil electrode was attached to the adhesive side of silicone tape, and 1 M KNO_3 soaked cellulose paper was placed on it. After placing another electrode on them again, the supercapacitor device was assembled using silicone tape and rubbed with a rubber roller to make a highly packed device.

EGF//EGF supercapacitor device fabrication

To get out the gases produced in the assembled device, the silicone tape of the GF supercapacitor device was stripped off as a size of 2 mm x 2 mm during in-situ electrochemical exfoliation. Using a power supply, a voltage was sequentially applied to an electrode at 3.0 V for 30 minutes, 4.0 V for 10 minutes, finally, 5.0 V for 5 minutes in step, and the same voltage sequence was applied to another electrode. After the exfoliation step, the exhaust hole was closed using silicone tape.

EGF//MEGF supercapacitor device fabrication

The fabrication method of the EGF//MEGF supercapacitor device was same to the EGF//EGF supercapacitor fabrication method using 1 M KNO_3 mixed with 10 mM $Mn(OAc)_2$ electrolyte instead of 1 M KNO_3.
As-made graphite foil cut into the desired form to apply an electrode of supercapacitor without current collector using a blade. A cut graphite foil electrode was attached to the adhesive side of silicone tape, and 1 M KNO_3 mixed with 10mM $Mn(OAc)_2$ soaked cellulose paper was placed on it. After placing another electrode on them again, the supercapacitor device was assembled using silicone tape and rubbed with a rubber roller to make a highly packed device. To get out the gases produced in the assembled device, the silicone tape of the GF supercapacitor device was stripped off as a size of 2 mm x 2 mm during in-situ electrochemical exfoliation. Using

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Characterization

  The surface morphology, and corresponding microstructures of the electrodes were analyzed by field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi). Structural characterization of the electrodes was performed using an X-ray diffractometer (XRD, D/MAX-2500/PC, Rigaku) with Cu Kα radiation (1.5406 Å). The surface chemical states were investigated by X-ray photoelectron spectroscopy (XPS, AXIS-Nova, Kratos) with an Al Ka radiation source (1486.8 eV) in an ultrahigh vacuum chamber (7×10^{-9} torr). Cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements were conducted employing an electrochemical workstation (ZIVE MP1, WonATech). The areal capacitances were then calculated using the following equations[1]:

$$C = \frac{1}{S \times v \times \Delta V} \int_{V_0}^{V_0 + \Delta V} I dV \quad \text{(from CV curves)}$$

$$C = \frac{I \times \Delta t}{S \times \Delta V} \quad \text{(from GCD curves)}$$

where C is the areal capacitance (F/cm^2), I is the discharging current density (A), v is the scan rate (V/s), V is the voltage (V), ΔV is the operating voltage window (V), Δt is the discharging time (s), and S is the active area of the electrodes (cm^2). Also, the energy density and power density were calculated by the following relationship[2]:

$$E = \frac{C \times (\Delta V)^2}{2 \times 3,600 \ (s/h)}$$

$$P = \frac{3,600 \ (s/h) \times E}{\Delta t}$$

where E (Wh/cm^2) is the energy density and P (W/cm^2) is the power density, respectively.

Reference

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