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Research paper

Direct reform of graphite oxide electrodes by using ambient plasma for supercapacitor applications

Ho Jun Kim, Hae Kyung Jeong *

Department of Physics, Institute of Basic Science, Daegu University, Gyeongsan 712-714, Republic of Korea

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ABSTRACT

Ambient plasma is applied to graphite oxide electrodes directly to improve electrochemical properties for supercapacitor applications. Surface morphology of the electrodes after the plasma treatment changes dramatically and amount of oxygen reduced significantly, demonstrating a reduction effect on the graphite oxide electrode by the ambient plasma. Equivalent series resistance of the electrode also reduced from 108 Ω to 84 Ω after the plasma treatment. Corresponding specific capacitance, therefore, increases from 0.45 F cm^{-2} to 0.85 F cm^{-2}, proving that the ambient plasma treatment is very efficient, clean, economic, and environment-friendly method to reform the graphite oxide electrodes directly for the supercapacitor applications.

1. Introduction

Supercapacitor, one of energy storage devices, has attracted much attention recently because of high power density and long cycle-life for alternative energy [1–3]. High performance of the supercapacitor requires high specific surface area, various pore structure, and high electric conductivity of electrodes. Graphene is one of the leading candidates for the supercapacitor electrodes because of its extraordinary properties, such as high surface area, fast electron transport, high mechanical strength, high electric and thermal conductivity [4–6]. Graphene or graphene based supercapacitors, therefore, have been investigated heavily [7–9]. However, it has many drawbacks, such as serious agglomeration of the surface, high cost, and too small scale for industrial production, to overcome for real applications.

Graphite oxide (GO) could be an alternative of graphene due to low cost and possible mass production [10–12]. However, GO also has a drawback which is low electric conductivity. There are many studies to improve the electric conductivity of GO, a reduction of GO, such as chemical reduction [13–16], physical reduction [17,18], electrochemical reduction [19], and optical reduction [20,21], resulting in higher conductivity than that of the precursor GO. However, wettability of the reduced GO is relatively weak, making it difficult to manufacture the supercapacitor electrodes. In other words, the reduced GO or graphite itself is unlikely to stick together or to a collector in a process of the electrode fabrication. Direct reduction of the GO electrode, therefore, is necessary, without pretreatment of the reduction of GO powder before making the electrodes. We applied ambient plasma directly to the GO electrodes and reform the GO electrodes for supercapacitor applications.

Plasma is one of four fundamental states of matter, which consists of electrons, ions, radicals, and neutral atoms [22,23], and it is widely used in industry and many applications, such as metal cutting and welding, plasma spraying (coating), and etching in microelectronics [24,25]. It could be used in material change researches because it has very high reactivity due to free electrons, ions, and radicals. We want to use the ambient plasma to reform the GO electrodes and modify morphology, conductivity, oxygen amount, and reduction level effectively.

In this report, we applied alternating current (AC) plasma, generated by our home-made equipment [22,23], directly onto GO electrodes in ambient condition and investigated changes of chemical and physical properties. The ambient plasma changes surface morphology properties of the GO electrode. Reduction of oxygen content after the plasma treatment is evident, and the plasma treatment finally gives positive effects on the GO electrode for supercapacitor applications. We compared electrochemical properties of precursor graphite, GO, and GO electrodes applied by the ambient plasma.

2. Experimental

Natural graphite (200 mesh, Sigma Aldrich) was purchased from Sigma Aldrich and used without pretreatment. GO was

* Corresponding author.
E-mail address: outron@gmail.com (H.K. Jeong).

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synthesized from the precursor graphite as follows. 1 g of the graphite was ground with 6.5 g of sodium chlorate (99%, Sigma Aldrich) and then stirred in 20 ml of the nitric acid for 24 h followed by vacuum filtration with deionized (DI) water several times as described elsewhere [10,14,18]. Obtained GO was dried in a vacuum oven at 60 °C for overnight. The GO electrode was fabricated as follows. GO was mixed with the conductive carbon black (Super P, TIMCAL Graphite & Carbon) and the binder (poly(sodium 4-styrenesulfonate), Sigma Aldrich) at the weight ratio of 80: 10: 10 in ethanol. An overhead stirrer was used to mix and make the mixture slurry at 600 rpm for 3 h. The obtained slurry was cast onto aluminum foil using a round glass rod as followed by drying in a vacuum oven at 150 °C for 24 h. The GO electrodes were punched into the round electrodes of two diameters, 14 and 10 mm, in order to investigate electrochemical properties in a two-electrode cell. The thickness of the electrodes was about 200 micro meter in which it gave the best performance. Too thick electrode increased resistance and was likely to detach from a collector, and too thick electrode makes pin holes in the collector when the ambient plasma was applied. Fig. 1 shows the schematic of the sample preparation.

Ambient plasma, generated at 25 kHz with the voltage of 7 kV in the Argon gas environment of 25 psi and 25 cc/min [22,23], was then applied directly to the GO electrodes for 2 min, and the obtained GO electrode after the plasma treatment is referred to as P-GO. Fig. 2a shows the GO electrodes before (GO) and after (P-GO) the plasma treatment.

Crystalline structure of the samples was investigated by using X-ray diffraction system (XRD, D/MAX-2500/PC, Rigaku, Japan) with Cu K_α radiation ($\lambda = 1.54$ Å), and the surface morphology was examined by field emission scanning microscopy (FE-SEM, S-4300, Hitachi) with the energy dispersive X-ray spectroscopy (EDS) to analyze elemental composition. The specific surface area of samples was measured at 77 K by Brunauer Emmett Teller (BET, ASAP 2420, USA) measurement. X-ray photoelectron spectroscopy (XPS, Thermo scientific, USA) with Al K_α of X-ray source was performed for chemical states of the samples, and Raman spectroscopy (Horiba Scientific Ltd., Japan) was used to determine defect ratios of the samples.

The punched two electrodes are assembled for the two-electrode cell as described elsewhere [23] and characterized the electrochemical properties by using Potentiostat/Galvanostat with impedance spectroscopy (Bio-Logic SAS, SP-200) in 1 M KOH electrolyte. The cyclic voltammetry (CV) was performed with the scan rate of 5, 10, and 50 mV s^{-1}, and frequency from 100 mHz to 100 kHz were applied for the electrochemical impedance spectroscopy (EIS).

3. Results and discussion

Fig. 2a shows photos of the electrodes before (GO) and after (P-GO) the plasma treatment. Initial color of GO was brown, but P-GO color is black after the treatment, implying that GO reduced

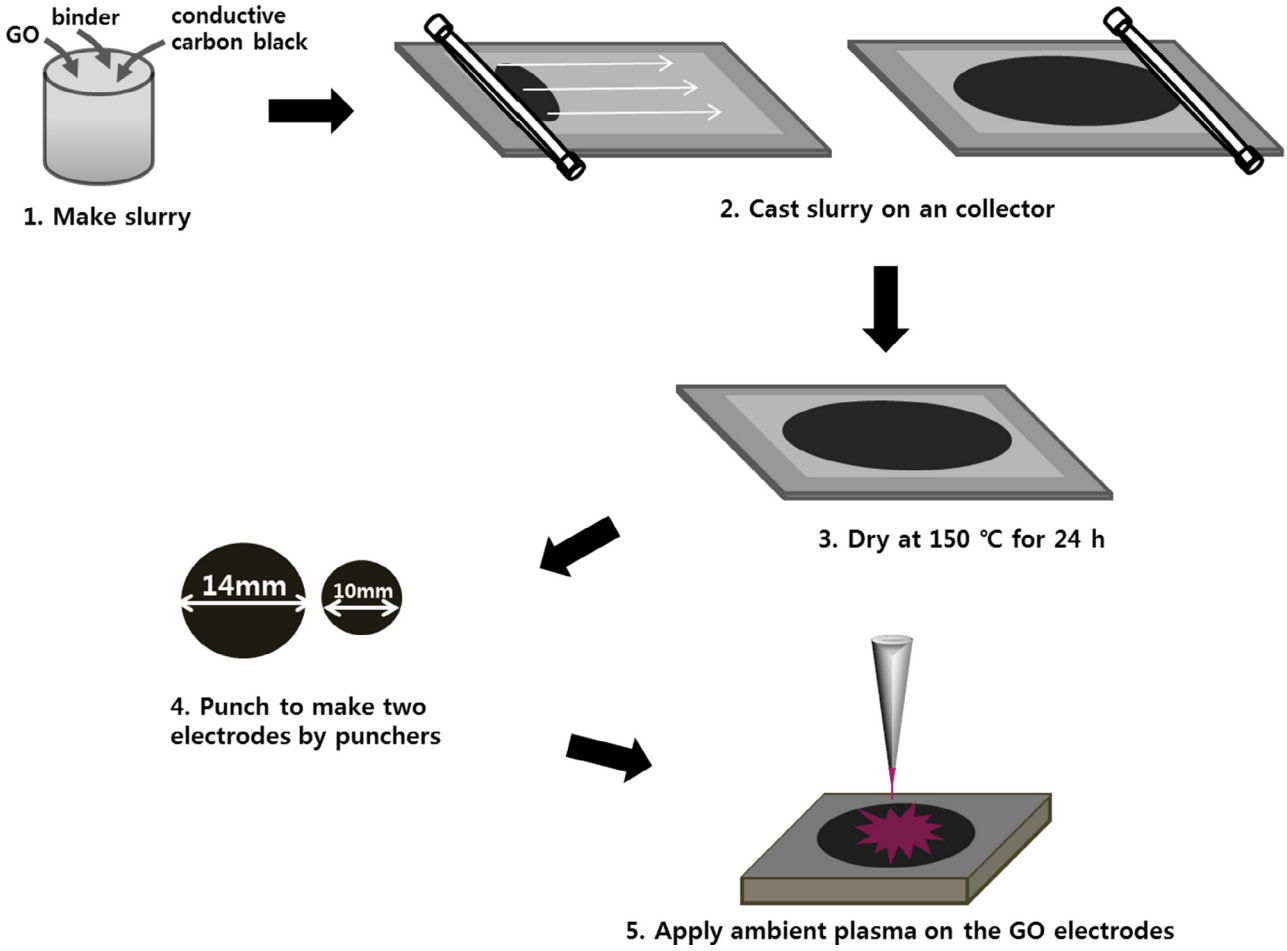

Fig. 1. Schematics of the samples preparation.