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Potentiostatic activation of as-made graphene electrodes for high-rate performance in supercapacitors

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HIGHLIGHTS

- Expanded graphene oxide electrodes are potentiostatically treated (EGO-PS).
- Significant increase in EDL capacitance with a Faradaic process is observed.
- EGO electrodes treated by other methods do not show enhanced EDL currents.
- Due to the dominance of EDL, EGO-PS shows excellent capacitance at high C/D.
- Unprecedented 230 F g^{-1} at 50 A g^{-1} is obtained with good cyclability.

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ABSTRACT

A thermally expanded graphene oxide (EGO) electrode is electrochemically activated to simultaneously introduce electrolyte-accessible mesopores and oxygen functional groups. The former is produced via O_2 evolution and the latter is incorporated by the intermediate hydroxyl radicals generated during the potentiostatic oxidation of H_2O in 1 M H_2SO_4 at 1.2 V (vs. Ag/AgCl). When applied as a supercapacitor, the potentiostatically treated EGO (EGO-PS) shows significant enhancement in an electric-double layer (EDL) process with a noticeable Faradaic reaction and delivers high capacitance at fast charge/discharge (C/D) rates (334 F g^{-1} at 0.1 A g^{-1} and 230 F g^{-1} at 50 A g^{-1}). In contrast to EGO-PS, EGO that is oxidized potentiodynamically (EGO-PD) shows negligible enhancement in EDL currents. EGO that is subjected to successive potential pulses also shows behaviors similar to EGO-PD, which indicates the importance of hydroxyl radical accumulation via a potentiostatic method for simultaneous functionalization and microstructural control of graphenes. The potentiostatic post-treatment presented here is a convenient post-treatment strategy that could be used to readily increase capacitance and simultaneously improve the high-rate performance of carbon-based electrodes.

1. Introduction

Supercapacitors are electrochemical charge-storage devices, the electrochemical performance of which fills the gap between traditional electrolytic capacitors and state-of-the-art secondary batteries [1]. The conventional method used to accomplish this in a supercapacitor is to implement an electrode material with a high specific surface area, in which the charge-storage occurs via electric-double layer (EDL) formation at the electrolyte/electrode interface. Despite the existence of some controversy [2], the amount of charges stored in an EDL capacitor is expected to be directly proportional to its surface area, so that extensive research has been devoted to the fine control of the microstructure and morphology of electrode materials [3]. In parallel with an EDL capacitor, the electrodes that store charges via a surface-confined redox process (pseudocapacitor) have also been investigated to a great extent [4–13]. In a pseudocapacitor, a significantly high theoretical capacitance compensates for intrinsically slow kinetics

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and relatively low stability due to a Faradaic reaction [7,11,14].

Graphene (one-atom-thick sp^2 carbon sheets) with an incomparably high theoretical surface area (~2600 m^2 g^{-1}) is a fascinating candidate for high-performance EDL capacitors [15–17]. The high electrical conductivity and excellent electrochemical stability of graphenes also makes this notion plausible [18–20]. Despite the theoretical prediction of high capacitance (ca. 550 F g^{-1}) [15], however, the experimentally obtained capacitance in graphene-based EDL capacitors has been limited, which is due mainly to face-to-face restacking between the graphene layers [21–24]. In order to overcome this hurdle, Peng et al. recently introduced holey graphenes with a high surface area of 592 m^2 g^{-1}, but the specific capacitances at relatively high charge/discharge (C/D) rates were far from satisfactory (211 and 170 F g^{-1} at 0.5 and 50 A g^{-1}, respectively), which required further improvements in high-rate performance [25].

Expecting additional capacitance (pseudocapacitance) from functional groups, graphene oxide (GO) has also been studied for use as a supercapacitor. In GO, the reversible Faradaic reaction of the oxygen functional groups ($>C{=}O + H^+ + e- \rightleftarrows >C{-}OH$) in an acidic electrolyte provides pseudocapacitance in addition to EDL capacitance [2,26,27]. Relative to theoretical estimates on the capacitance attainable in GO (ca. 805 F g^{-1} [28]), however, the commonly reported values have been less than 200 F g^{-1} at a moderate C/D rate in most examples [2,29,30]. Such a huge gap is considered to be the result of graphene layers that do not exist as a separate single-layer, which hampers complete electrolyte wetting of the theoretically accessible surfaces. Recently, we addressed the result that the electrolyte-wettability could be improved by intervening spacer molecules between GO layers [27]. This was accomplished via self-assembly of GO and cationic fullerene in an aqueous solution, which resulted in a significant increase in capacitance (314 F g^{-1} at 1.0 A g^{-1}). The hydrothermally reduced graphene, which was subjected to electrochemical oxidation, was also studied for use as a pseudocapacitor [31]. Water oxidation via potential cycling of up to 1.3 V induced oxygen functional groups onto graphenes and led to a specific capacitance of 279 F g^{-1} at 1.0 A g^{-1} without a noticeable increase in EDL behaviors. Utilizing the same potentiodynamic method, the capacitance of thermally expanded graphene oxides (EGO) was inferior at high C/D rates (245 and 114 F g^{-1} at 1.0 and 50 A g^{-1}, respectively).

In this work, we describe simultaneous increases of the EDL and pseudocapacitive behaviors of EGO via the potentiostatic treatment of as-made electrodes. The potentiostatic oxidation of as-made EGO electrodes induces the electrochemical functionalization of hydroxyl groups and the enhancement of meso-porosity. This is contrasted with potentiodynamically activated EGO, wherein an increase in EDL capacitances is not observed. Reflecting the characteristics of an EDL process, the high capacitance values at slow C/D are retained at fast C/D for the EGO-PS (334 F g^{-1} at 0.1 A g^{-1} and 230 F g^{-1} at 50 A g^{-1}).

2. Experimental section

Synthetic graphite (KS6L, C-NERGY™) was purchased from TIMCAL, Switzerland. A carbon-cloth current collector was obtained from Fuel Cell ETC., USA. All other chemicals were from Sigma-Aldrich and used without further purification. GO was synthesized from graphite powder via a modification of Hummer's method [32,33]. To prepare the EGO, the dried GO (50 mg) was placed in a muffle furnace that was preheated at 300 °C for 10 s. Brownish GO was turned to black and the volume was expanded by ca. 10-fold.

The morphology of the graphene electrodes was examined via field emission scanning electron microscopy (FESEM, JEOL JSM-7100F). The oxygen content of the EGO electrodes was analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Scientific, USA) with K_α X-rays. X-ray powder diffraction (XRD) patterns were recorded using a Rigaku ULTIMA 4, equipped with Cu K_α radiation ($\lambda = 1.5406$ Å) at a scan rate of 0.5°min^{-1}. The high-resolution transmission electron microscopy (HRTEM) investigations were performed on a TEM JEOL 2100 instrument with an accelerating voltage of 200 kV. Raman spectra were recorded with a micro-Raman system (Alpha 300 s, WITec GmbH) using a 532 nm laser line with a 1 μm beam diameter. N_2 adsorption/desorption isotherms of EGO and EGO-PS were measured using a BELSORP-max (BEL Japan, Inc.) by a standard volumetric technique at 77 K. In order to determine the surface area, the Brunauer-Emmet-Teller (BET) equation was applied to the N_2-adsorption isotherm in the P/P_0 range of 0.01–0.3. The non-localized density functional theory (NLDFT) with a cylindrical pore model was used to evaluate the pore size distributions. For the characterizations, samples were recovered from the electrodes after thorough washing with distilled water and drying at room temperature.

The composition of working electrodes was a mixture of 85 wt% active material (EGO or GO), 10 wt% acetylene black (AB), and 5 wt% polyvinylidene fluoride (PVdF). A slurry in N-methyl-2-pyrrolidone was pasted over a clean carbon-cloth current collector (1 cm × 1 cm) and dried in a convection oven at 100 °C for 12 h. EGO electrodes were electrochemically treated in 1.0 M H_2SO_4 via various methods. The electrodes activated by a potentiostatic method at various potentials will be designated as EGO-PS, EGO-1.4, EGO-1.6, EGO-1.8, and EGO-2.0, indicating the potential applied for 1 h (EGO-PS indicates an electrode subjected to +1.2 V for 1 h). EGO electrodes were also treated via a potentiodynamic method between −0.2 and + 1.2 V (20 mV s^{-1}, 20 cycles), which will be denoted as EGO-PD. For comparison, EGO electrodes were activated via multiple double-potential pulses between −0.2 and + 1.2 V with different durations of time per single step, but with identical total-residence times at +1.2 V (For example, a single double-potential step was comprised of potential applications of +1.2 and −1.2 V for a certain period at each potential. For multiple double-potential experiments, single potential steps were repeated for 2 h). GO electrodes were subjected to the same potentiostatic and potentiodynamic procedure and will be denoted as GO-PS and GO-PD, respectively. The electrochemical oxidation of H_2O in 1.0 M H_2SO_4 produces hydroxyl radicals, which can functionalize graphene layers and/or can generate O_2 molecules via subsequent oxidation of H_2O_2 (formed via coupling between 2 hydroxyl radicals) (Fig. S1). The latter process is believed to contribute to the change of porosity of as-prepared electrodes, relying on potential application programs and electrode materials.

For capacitance measurements, cyclic voltammetry and galvanostatic C/D were performed within a potential window of −0.2 and + 0.8 V. The specific capacitance obtained from cyclic voltammograms was calculated using the following equation:

$$C = \frac{\int idV}{2 \times \nu \times m \times \Delta V}$$

where i, ν, m and ΔV are the current (A), the scan rate ($V{\cdot}s^{-1}$), the mass of the active material (g), and the potential range (V), respectively. The specific capacitance was also calculated from galvanostatic C/D curves using the following equation:

$$C = \frac{i \times \Delta t}{\Delta V \times m}$$

where i, Δt, ΔV, and m are the current (A), the discharge time (s),