

研 究 主 論 文 抄 録

論文題目

Graphene Oxide Membranes with Tailored Interlayer Nanospace for Novel All-Carbon Electrochemical Devices

(酸化グラフェン膜層間の機能を用いた新規オールカーボン電気化学デバイスの研究)

熊本大学大学院自然科学研究科 産業創造工学専攻 物質生命化学講座

( 主任指導 栗原 清二 教授 )

論文提出者 上田 盟子

主論文要旨

The rapid development of miniaturized electrochemical devices has increased the demand for compact energy storage. Li-ion batteries (LIBs) generally deliver a high energy density but are limited by their low power density and poor cycling lifetime. In contrast, supercapacitors (SCs) deliver much higher power density and exhibit long cycle stability but suffer from a much lower energy density. Accordingly, a new energy storage device with the combined characteristics of high energy and power densities as well as long cycle life is strongly desired as a solution to bridge the gap between LIBs and SCs. In addition, such energy storage devices should preferably be composed of thin, light-weight, inexpensive, safe, easily acquired materials and be capable of being fabricated through a relatively simple manufacturing process.

Graphene oxide (GO) and reduced GO (rGO) show several key properties that can address emerging energy needs, particularly for the ever growing market of portable and wearable energy conversion and storage devices. GO exhibits excellent properties, including high water permeability, good ion and gas selectivity, and high proton conductivity; these properties arise from the presence of various oxygenated functional groups. Thus, GO can be used as both the separator and electrolyte to simplify the fabrication of the device, because GO is simultaneously a good ionic conductor and an electrical insulator. In comparison, rGO, which exhibits high electrical conductivity and high specific surface area, can be used in various electrodes of electrical devices such as LIBs and SCs. Although most GO-based devices are fabricated either with GO as the electrolyte or with a rGO electrode, a rGO/GO/rGO hybrid structure, which comprises a GO electrolyte/separator and rGO electrodes, is attractive because of the potential to develop an all-carbon energy device. Based on these

considerations, the rGO/GO/rGO structure is expected to perform as an electrical device.

This work aims (1) to explore the new functionalities of interlayer nanospace in multilayered GO and (2) to investigate the electrochemical properties of both an all-carbon supercapacitor (Graphene Oxide Supercapacitor: GOSC) and an all-carbon redox battery (Graphene Oxide Redox Battery: GORB) consisting of rGO/GO/rGO.

This thesis is composed of four chapters.

**Chapter 1** narrates the general background, preparation method, properties, and applications of GO and rGO.

**Chapter 2** presents new functionalities of the interlayer nanospace in multilayered GO for ion diffusion and reactions at the metal/GO (M/GO) interface. Permeation of metal from the surface into GO paper bulk at the M/GO interface was observed at room temperature for metals such as Cu, Ag, Ni, Au, and Pt. Cu, Ag, and Ni quickly permeated GO as ions into the bulk under humid conditions. At first, these metals changed to hydrated ions as a result of redox reactions (with reduction of GO) at the surface, and then permeated the interlayers. Au and Pt were observed to permeate GO as atoms into the GO bulk at room temperature, although the permeation rates were low. These results were considered to be due to the presence of many defects and/or edges with oxygenated groups in the GO paper.

**Chapter 3** presents that development of new all-carbon electrochemical devices—GOSC and GORB. A device with an rGO/GO/rGO structure was fabricated and subsequently observed to function as both a SC and a battery depending on the working voltage. The rGO/GO/rGO device operated as a proton-type SC at working potentials as high as 1.2 V. The charge storage mechanism of GOSC resulted from (1) proton conductivity and (2) polarized/separated water molecules in the interlayer spacing of the nanoscale GO. At potentials greater than 1.5 V, it behaved as a battery that operates on the basis of the redox reactions between the oxygenated functional groups on rGO. We deduced the following two hypotheses for the redox mechanism of the GORB: (1) cathode:  $C=O + H^+ + e^- \leftrightarrow C-OH$ ; anode:  $CH \text{ (defect)} + CO_2 \leftrightarrow 2C=O \text{ (or } C-O) + H^+ + e^-$ ; or (2) cathode:  $4H^+ + 4e^- + O_2 \leftrightarrow H_2O$ ; anode:  $CH \text{ (defect)} + CO_2 \leftrightarrow 2C=O \text{ (or } C-O) + H^+ + e^-$ .

**Chapter 4** gives the general conclusion of the thesis. In this work, we demonstrated (1) new functionalities of interlayer nanospace in multilayered GO for ion diffusion and reaction at the M/GO interface. We also succeeded in the synthesis and operation of (2) new all-carbon electrochemical devices—Graphene Oxide Supercapacitor (GOSC) and Graphene Oxide Redox Battery (GORB)—with tunable SC and battery behavior *via* the working voltage for the first time to our knowledge. The redox reaction at the M/GO interface and ion diffusion behavior based on unique

interlayer nanospace in the GO membrane must be an important aspect of the development of solid GO electrolytes including metal ions for the electrochemical device. Moreover, we believe that an all-carbon electrochemical device, which functions as both a SC and battery, is attractive and will evolve as a next generation electrochemical device.