Contents lists available at ScienceDirect

Electrochemistry Communications

Effect of graphene nanoplatelet edges on the iodide/triiodide redox reaction

Yuta Ohtani, Hajime Hoshi*

Department of Applied Chemistry, Tokyo University of Science, Yamaguchi, 1-1-1 Daigaku-dori, Sanyo-Onoda, Yamaguchi 756-0884, Japan

ARTICLE INFO

ABSTRACT

Carbon electrodes have been extensively studied for the development of Pt-free dye-sensitized solar cells. In this study, the influence of graphene nanoplatelet edges on the activity of an electrolyte reaction was investigated. The reaction activities of graphene nanoplatelet aggregates (GNAs) and graphene nanoplatelets (GNs), which have different surface areas, were evaluated by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). The charge transfer resistances (R_{CT}) of the GNAs and GNs were determined from EIS to be $12\,\Omega$ and $1.4 \times 10^3\,\Omega$, respectively. The coefficient components (A_W) of the diffusion impedance, known as the Warburg impedance, of GNAs and GNs were $63\,\Omega\,Hz^{0.5}$ and $1.2 \times 10^2\,\Omega\,Hz^{0.5}$, respectively. From these results, it was found that the edge plane area of the graphene aggregates affects both the reaction resistance and electrolyte diffusion in the carbon film.

1. Introduction

Carbon materials can be highly conductive, and therefore have been studied for use in electrodes [1]. While platinum has been used extensively as an electrode material for batteries and in catalysts, it is a very expensive material compared with carbon materials. In addition, carbon electrodes have good catalytic activity for electrolyte redox reactions. Dye-sensitized solar cells (DSSCs) have the potential to be produced at a lower cost than silicon-based solar cells, and the energy conversion efficiency (η) of DSSCs is approximately 10% [2–6]. Although platinum is used as an electrode material for DSSCs [7–10], carbon electrodes have also been studied with the aim of developing platinum-free DSSCs [11–17]. The charge transfer resistance (R_{CT}) at the interface of graphite nanofibers (GNFs) and the I^-/I_3^- electrolyte is reported to be $10.3\,\Omega$ [17], whereas R_{CT} at the interface of a platinum electrode and the I^-/I_3^- electrolyte is $16.6\,\Omega$. This difference indicates that carbon materials, such as GNFs, can demonstrate better performance than platinum as counter electrodes in DSSCs.

Graphene is a carbon material with unique properties [18–20]. Graphene materials have been applied in various fields [21], such as conductive switching [22], bioimaging [23], electrochemical sensing [24], catalysis [25,26], and electrochemical energy applications [27–29], and also as electrodes for organic solar cells [30,31] and DSSCs [32–39]. Graphite, which is composed of graphene sheets, has been studied for use in electrodes [40–43]. The reactivities of graphene and graphite vary depending on the location of contact with the reactant [26,41]. For example, graphite contains an edge plane that is

reactive with I^-/I_3^- and a basal plane that is inactive [42,43]. Therefore, the reactivity of graphene with I^-/I_3^- depends on spatial factors.

In previous work, we developed a DSSC using layered graphene as a counter electrode and found that η decreased with decreasing specific surface area [44]. For example, η was 4.26% when using graphene aggregates with a larger specific surface area and 2.49% when using layered graphene with a smaller specific surface area. This reduction in η was due to a decrease in the magnitude of the Faraday current on the carbon electrode surface [44]. However, it was not possible to ascertain the cause of this Faraday current reduction. The Faraday current, which is generated at the electrode, originates from the electrolyte redox reaction through several processes, including (i) the diffusion process of the electrolyte, (ii) the charge transfer process between the electrolyte and the electrode, and (iii) the electron transport process in the electrode.

Therefore, in this work, we evaluated the electrolyte reaction on the surface of graphene aggregates by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), and investigated the influence of graphene nanoplatelet edges on the electrolyte redox reaction.

2. Experimental

2.1. Preparation of graphene electrodes

Commercially available graphene, as shown in Fig. 1, was used in this study. Graphene pastes were prepared by modifying the method

---

* Corresponding author.
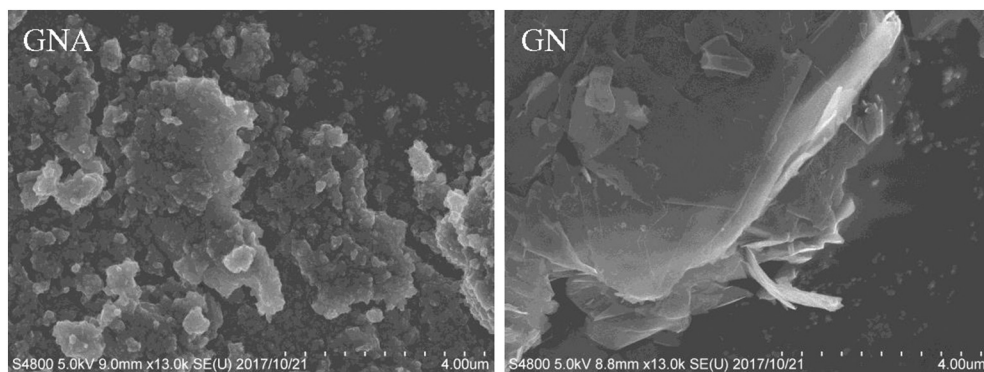 *E-mail address:* hoshi@rs.tusy.ac.jp (H. Hoshi).

Fig. 1. Field emission scanning electron microscopy images of graphene nanoplatelet aggregate (GNA, left) and graphene nanoplatelet (GN, right) powders.
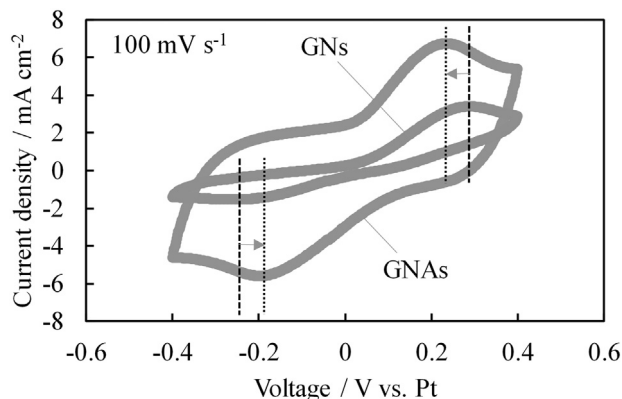

Fig. 2. Cyclic voltammograms of graphene nanoplatelet aggregates (GNAs) and graphene nanoplatelets (GNs) at a scan rate of 100 mV s^{-1} in acetonitrile with 10 mM LiI, 1 mM I$_2$, and 0.1 M LiClO$_4$.

Fig. 4. An equivalent circuit for this system [48].

Table 1
E_{Ox}, E_{Re}, ΔE_P, and $E_{1/2}$ of the GNAs and GNs at a scan rate of 100 mV s^{-1}.

	E_{Ox}/V	E_{Re}/V	ΔE_P/V	$E_{1/2}$/V
GNAs	0.24	−0.20	0.44	0.02
GNs	0.29	−0.26	0.55	0.02

Inc.) were added to the CMC solution, stirred by a magnetic stirrer for 1 h, and treated with ultrasonication for 10 min.

The prepared GN or GNA pastes were dropped on fluorine-doped tin oxide (FTO)-coated glass substrates (Asahi Glass), whose edges were covered by 60 μm thick tape, and spread with a glass rod. The coated area on the FTO glass substrates was 0.2 cm^2. After drying at 40 °C, the GN or GNA films were annealed for 1 h at 180 °C.

2.2. Characterization of GN or GNA electrodes

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out using the same electrochemical cells in a N$_2$-purged acetonitrile solution containing 10 mM LiI, 1 mM I$_2$, and 0.1 M LiClO$_4$ as the supporting electrolyte. A Pt wire was used as the reference electrode, a Pt coil was used as the counter electrode, and the prepared graphene electrodes were used as working electrodes. To investigate the I$^-$/I$_3^-$ reaction, CV was conducted at a scan rate of 100 mV s^{-1} between −0.4 and 0.4 V vs. Pt. EIS was performed using a Compactstat.h instrument (Ivium Technologies) in the frequency range 10^5–10^{-1} Hz with an amplitude of 10 mV under no-bias conditions. The resulting spectra were fitted with an EIS spectrum

reported in previous papers [44,45]. First, 0.03 g of carboxyl methyl-cellulose ammonium (CMC; Wako) as an adhesive was dissolved in a 2 mL water/1 mL ethanol solution, stirred by a magnetic stirrer for 1 h, and treated with ultrasonication for 10 min. Then, 0.25 g of graphene nanoplatelets (GNs; 6–8 nm thick and 5 μm wide, Strem Chemicals Inc.) or graphene nanoplatelet aggregates (GNAs; sub-micrometer particles, surface area = 750 m^2 g^{-1}, Strem Chemicals Inc.) and 0.05 g of acetylene carbon black (average particle size = 42 nm, Strem Chemicals

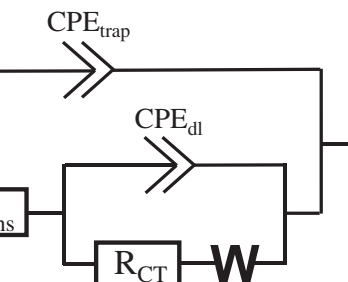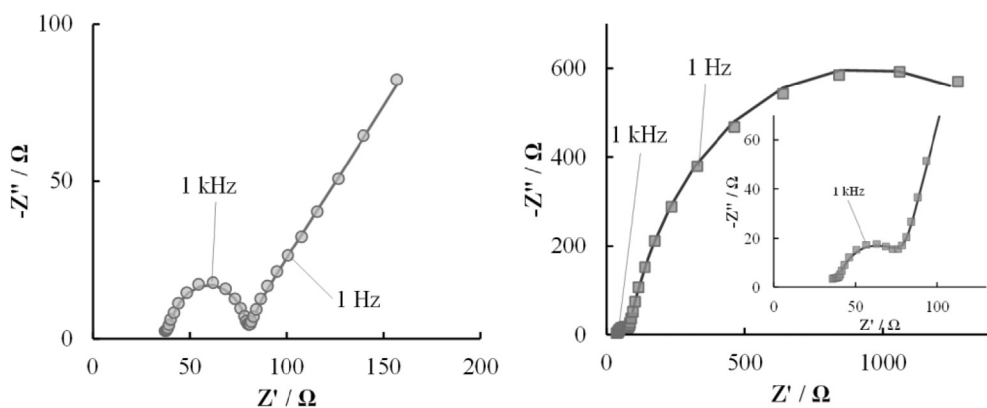**Fig. 3.** Experimental data (symbols) and fitted curves (solid lines) for the electrochemical impedance spectra of graphene nanoplatelet aggregates (GNAs, left) and graphene nanoplatelets (GNs, right) in the frequency range 0.1–10^5 Hz in acetonitrile with 10 mM LiI, 1 mM I$_2$, and 0.1 M LiClO$_4$. The inset shown for GNs (right) is a magnification of the frequency range 15.9–10^5 Hz.