

## Electronic Supplementary Information (ESI)

### Electrochemical Lithium-ion Insertion/Extraction Reactions of Multilayered Graphene with Random Twist Angles

Satoshi Yamamoto <sup>a</sup>, Ryotaro Sakakibara <sup>b</sup>, Soichi Shima <sup>a</sup>, Shinsuke Matsuura <sup>a</sup>, Takeshi Yajima <sup>a</sup>, Munekazu Motoyama <sup>a, c</sup>, Wataru Norimatsu <sup>b, d</sup>, Yuta Kimura <sup>e</sup>, Koji Amezawa <sup>e</sup>, and Yasutoshi Iriyama

<sup>\*a</sup>

<sup>a</sup> *Department of Materials Design Innovation Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603 Japan*

<sup>b</sup> *Department of Chemical Systems Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi, 464-8603 Japan*

<sup>c</sup> *Kyushu University Platform of Inter-/Transdisciplinary Energy Research, Kyushu University, Kasuga, Fukuoka, 816-8580 Japan*

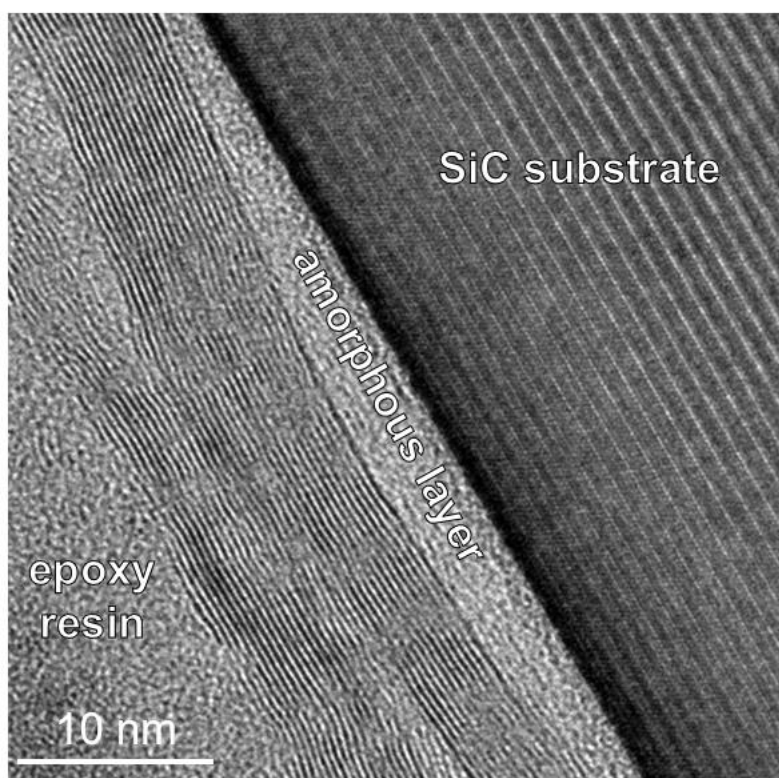
<sup>d</sup> *Faculty of Science and Engineering, Waseda University, Tokyo, 169-8555 Japan*

<sup>e</sup> *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba, Sendai, Miyagi, 980-8579, Japan.*

\* Corresponding author.

E-mail address: [iriyama.yasutoshi@material.nagoya-u.ac.jp](mailto:iriyama.yasutoshi@material.nagoya-u.ac.jp)

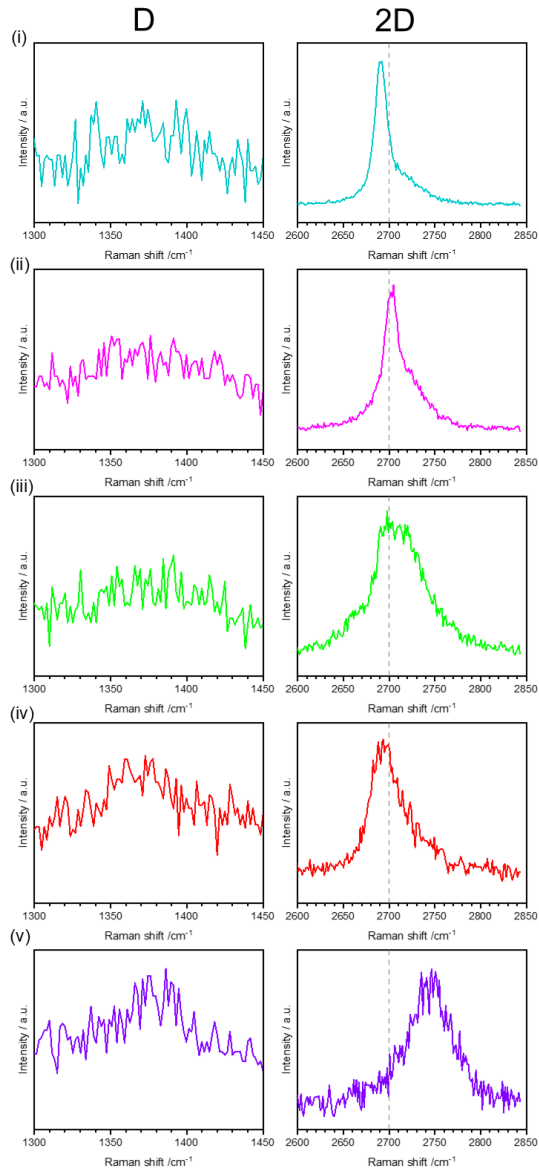
1. TEM image of a TAGr



**Figure S1.** A cross-sectional TEM image of another area of the TAGr shown in Fig. 1

## 2. Raman spectra

D band and 2D band in Raman spectra of **Fig. 2b** are shown in **Fig. S2**. D band is attributed to presence of defect and edge of Gr. Since TAGr is formed from multiple nucleation sites, the Gr edge of the domain boundary will be attributed to the D band. Raman shifts of the 2D band vary at 2690-2740  $\text{cm}^{-1}$  in these five points. It is also observed that some of the 2D bands have shoulder peaks. The cause of these shifts and multiple components in the 2D bands can be attributed to rotation angle, layer number, or distortion <sup>1-5</sup>.

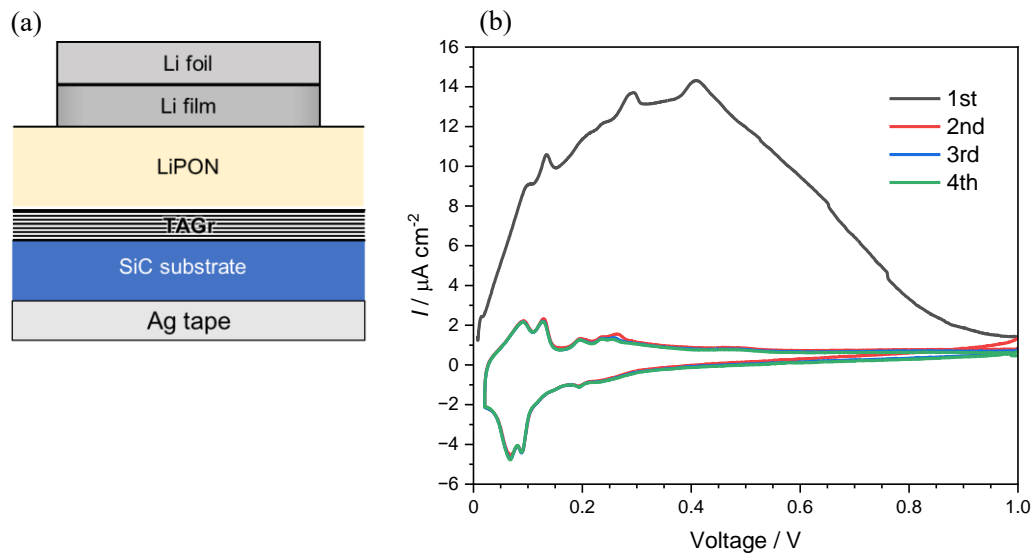


**Figure S2.** Magnified D and 2D band measured at (i)-(v) in Fig. 2(b).

### 3. Electrochemical measurements for a Li/LiPON/TAGr/SiC cell (SE-cell)

The TAGr was formed on the SiC substrate (5 mm square), and the TAGr was completely covered with LiPON film by radio frequency (RF) magnetron sputtering in N<sub>2</sub> atmosphere (4 Pa, 50 W) <sup>6</sup> using a Li<sub>3</sub>PO<sub>4</sub> sintered target. (ca. 8 μm in thickness). Then, Li film (ca. 2-3 μm in thickness, φ 3mm in diameter) was formed around the center of the LiPON film. **Fig. S3a** shows the schematic image of the resultant Li/LiPON/TAGr/SiC stack (SE-cell). Here, Li foil was mounted on the Li film to prevent side reactions between Li film and current collector. The SiC substrate with TAGr were connected with current collector using conductive Ag adhesive tape. Each preparation process was carried out without exposing the samples to the air. Cyclic voltammetry (CV) measurements were conducted at 25°C with a potential sweep rate ( $\nu$ ) of 0.5 mV s<sup>-1</sup>. All the electrochemical measurements were performed using a potentiostat-galvanostat (VMP3, Biologic). During the electrochemical measurements, the SE-cells were stored at 25°C in a glove box with a dew point below -80°C.

**Fig. S3b** shows the CVs (1<sup>st</sup>-4<sup>th</sup> cycles) of the SE-cell. In the first cycle, irreversible oxidation current appeared, which is probably due to Li stripping reaction in addition to Li<sup>+</sup> extraction from TAGr. Similar oxidation currents in the first cycle have been observed in our previous studies using SE-cells <sup>7</sup>.

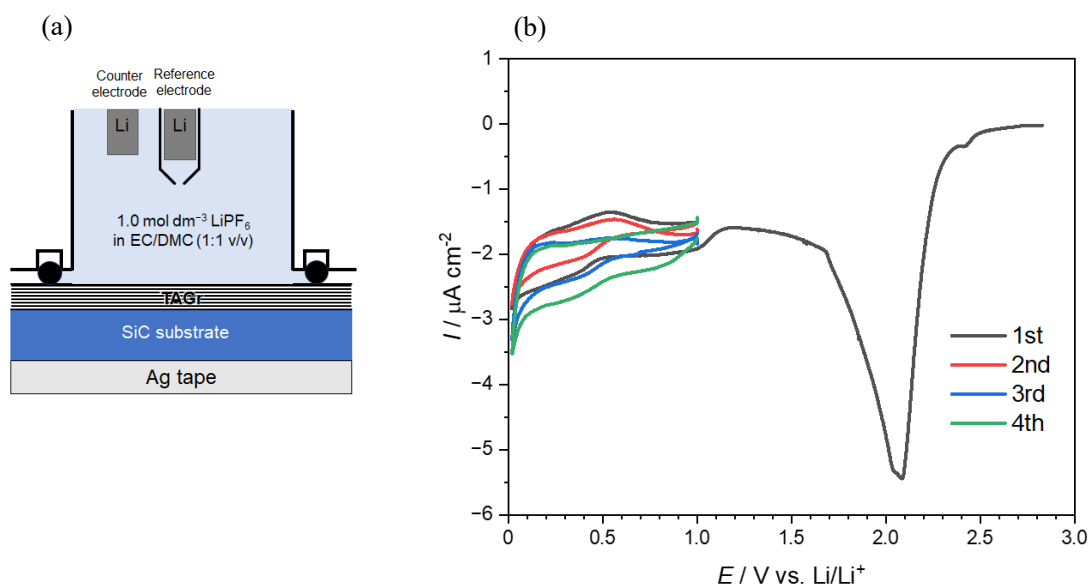


**Figure S3.** (a) Schematic image of the SE-cell. (b) 1<sup>st</sup>-4<sup>th</sup> CV curves for an SE-cell at 25°C.

Scan rate: 0.5 mV s<sup>-1</sup>.

#### 4. Measurements for an organic liquid electrolyte cell (LE-cell)

**Fig. S4a** shows the schematic image of the LE-cell. Working electrode was TAGr film formed on SiC substrate (electrode area immersed with liquid electrolyte was  $0.05 \text{ cm}^2$ ) and both counter and reference electrodes were Li foil. The SiC substrate was connected with current collector using conductive Ag adhesive tape as with the SE-cell. **Fig. S4b** shows the CVs of an LE-cell. The open circuit voltage (OCV) was 2.9 V (vs. Li/Li<sup>+</sup>). A reductive current peak was observed at 2.1 V in the first cycle<sup>8</sup>. Later CVs were repeated at 0.02-1.00 V as with the SE-cell. Several broad redox peaks were observed different from the CV shown in **Fig. 3a**<sup>7</sup>. Also, reductive currents were observed during the CVs. It is suggested that reductive decomposition of liquid electrolyte proceed continuously on TS region. Thus, a stable SEI may not be formed on TS region in this liquid electrolyte.

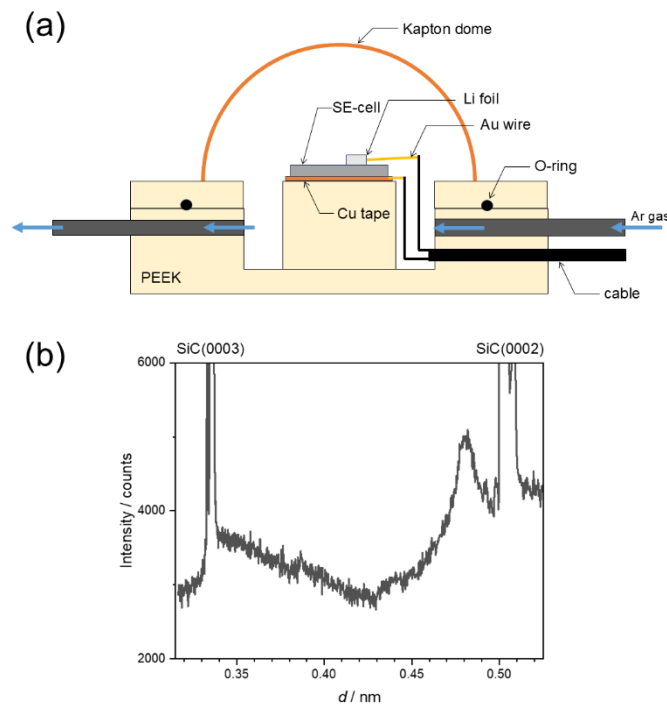


**Figure S4.** (a) Schematic image of the LE-cell using an organic liquid electrolyte ( $1.0 \text{ mol dm}^{-3}$  LiPF<sub>6</sub> dissolved in EC/DMC (1:1 v/v)). (b) CV curves of a TAGr electrode at 25°C in the LE-cell. Scan rate:  $0.5 \text{ mV s}^{-1}$ .

## 5. *In-situ* XRD measurement for a SE-cell

The *in-situ* X-ray diffraction (XRD) measurements were carried out at BL19B2 in SPring-8, Japan. The X-ray energy was 15 keV, and the measurements were performed at room temperature. **Fig. S5a** shows the schematic image of *in-situ* XRD measurement holder<sup>9</sup>. Kapton (polyimide) dome was bonded to a PEEK substrate to realize a gas tight holder. Both electrochemical cables and gas in- and out-let lines were assembled to the substrate holder. The SE-cell (thickness of LiPON was reduced to 2  $\mu\text{m}$ ) was mounted inside the dome and Li foil (ca. 0.5 mm in thickness) was mounted around the edge of Li anode film as an electrochemical connection part. This *in-situ* X-ray measurement holder was constructed in an Ar-filled glove box (dew point <  $-70^\circ\text{C}$ ). During the XRD measurements, Ar gas was continuously flowed in the holder. The voltage of the SE-cell was swept by CV with a  $\nu$  of  $1.0 \text{ mV s}^{-1}$  to a given voltage using a potentiostat-galvanostat (SP-150, Biologic) and was held for 10 minutes before each XRD measurement. The XRD measurements were carried out by  $\theta$ - $2\theta$  ( $4.5 < \theta < 7.5$ ) with step-scan mode ( $0.0075^\circ / \text{step}$ ), where X-ray radiation area was  $1 \text{ mm} \times 4 \text{ mm}$  as a slit.

**Fig. S5b** shows the XRD pattern of the SE-cell measured at 1.0 V in Fig. 4 a. Two sharp peaks appeared at  $d=0.336 \text{ nm}$  and  $d=0.505 \text{ nm}$ . Since  $4\text{H-SiC}(0004)$  has  $d=0.252120 \text{ nm}$ <sup>10</sup>, the two peaks are assigned to  $\text{SiC}(0003)$  and  $\text{SiC}(0002)$ . Usually, these peaks do not appear because they are forbidden reflections. However, the N-doped SiC substrate used in this study is thought to have disrupted the structure, causing the peaks to appear.



**Figure S5.** (a) Schematic image of the electrochemical cell for *in-situ* XRD. (b) *In-situ* XRD pattern at 1.0 V of the SE-cell in **Fig. 4a**.

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