

Electronic Supplementary Information

Facile preparation method for polymer and exfoliated graphite composites and their application as conduction-promoting materials

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Materials

Expanded graphite (PF-8) was obtained from Toyo Tanso Co., Ltd.; BET specific surface area of 22 m²g⁻¹.

Azodicarbonamide (ADCA; AC#R-K3) was obtained from Eiwa Chemical Ind. Co., Ltd.; a thermal decomposition temperature is 210 °C.

Polypropylene glycol (PPG; GP-3000) was obtained from Sanyokasei Co., Ltd; the number average molecular weight is 3,000.

Polyglycidyl methacrylate (GMA; Marproof G-2050M) was obtained from NOF Corporation; the number average molecular weight is about 200,000; the starting temperature of thermal decomposition is 245 °C.

Ketjen black available in the market (EC300J) was obtained from Lion Corporation.

Polyvinylidene fluoride (PVDF #1100) was obtained from Kishida Chemical Co., Ltd.

LiCoO₂ was obtained from Sigma-Aldrich Corporation.

Instruments

Ultrasonic processing device was carried out with W-113MK2 of Honda Electronics Co., Ltd.

Thermogravimetric analysis (TGA) was carried out with TG/DTA6300 of Hitachi High-Technologies Corporation.

Brunauer–Emmett–Teller analysis (BET) was carried out with ASAP-2000 of Shimadzu Corporation.

X-ray diffraction analysis (XRD) was carried out with Smart Lab of Rigaku Corporation.

IR spectroscopy carried out with FTS2000 of Varian Inc.

Microscopic Raman spectroscopy was carried out with Almega XR of Thermo Fisher Scientific

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Scanning electron microscopy was carried out with S-4300SE/N of Hitachi High-Technologies Corporation.

Powder resistivity was carried out with a prototype of the device from Hioki E.E. Corporation.

Methods

Preparation of P-EExG

Six grams of expanded graphite (PF8) and 12 g of azodicarbonamide (ADCA) are used as a thermal decomposition foaming agent, as well as 120 g of polypropylene glycol (PPG) were mixed with 120 g of tetrahydrofuran (THF). This mixture was exposed to ultrasonic irradiation using an ultrasonic processing device, which was used at 100 W with an oscillating frequency of 28 kHz for 120 min, to absorb PPG in the expanded graphite. The ultrasonically irradiated substance fabricated in such a manner was then shaped using the solvent casting method and maintained under the 20 % of oxygen concentration at 80 °C for 120 min, 110 °C for 60 min, 150 °C for 60 min, and 230 °C for 120 min. The ADCA was thermally decomposed and foamed using this heat treatment process. Finally, the thermal decomposition of the PPG was promoted by maintaining the substance at 450 °C for 30 min was used to fabricate the **P-EExG**.

Preparation of G-EExG

G-EExG: Fifty grams of polyglycidyl methacrylate (GMA) was dissolved in 450 g of THF to derive a solution with 10 wt% of GMA. A mixture was obtained from 2.5 g of PF powder 8F and 5.0 g of ADCA. The other procedure was followed according to that of **P-EExG**.

Fabrication of cathode materials for lithium batteries

Fifteen grams of the THF solution, which was adjusted so that the graphite components in the **G-EExG** having an electrode weight of 5 wt% was mixed with 10 g of LiCoO₂ (Lithium cobalt (III) oxide manufactured by ALDRICH), was used as an active material and adjusted to have an electrode weight of 92 wt%. The mixture was stirred for 60 min at room temperature, and the solid components were collected by filtration. The solid components were dried at 50 °C for 120 min. The baking treatment was performed at 380 °C for 120 min to remove polymer components that were included in the **G-EExG** and to obtain a composite made of **G-EExG** and LiCoO₂. Polyvinylidene fluoride, which was used as a binder resin for this composite, was adjusted to have an electrode weight of 2 wt% and mixed in agate mortar. After mixing, N-methylpyrrolidone was added as needed to dilute

and adjust the viscosity to the level that the substance could be used for coating to fabricate the coating liquid. The fabricated coating liquid was applied on the copper foil with an applicator, which was then dried to fabricate electrode sheets having a thickness of 60 μm . The electrode sheet fabricated in such a manner was dried at 80 $^{\circ}\text{C}$ under reduced pressure for 720 min, and when the temperature was elevated to 110 $^{\circ}\text{C}$, the sheets were dried under reduced pressure for 120 min. A portion of the electrode sheets was punch-formed after drying to create disks with 14 mm diameter to derive cathodes for lithium-ion rechargeable batteries. Furthermore, the remaining electrode sheets were roll pressed under a condition with a temperature of 25 $^{\circ}\text{C}$ by using an ultra-small roll press machine was obtained from Hohsen Corporation, then punch-formed in disks with 14 mm diameter to derive cathodes for lithium-ion rechargeable batteries.

Evaluation of fabricated lithium batteries

The performance evaluation of the fabricated lithium batteries was carried out using as follows: The cathode of the lithium-ion rechargeable batteries was dried at 110 $^{\circ}\text{C}$ for 240 min in vacuum. These cathodes were used to fabricate lithium-ion rechargeable batteries for the experiment, inside a glove box with atomised argon gas. An anode cell, a battery separator, and an electrode guide were installed between the anode body and cathode body, starting from the anode body in that order. The cathode body prepared in the method described above was layered with an electrode support and a spring. A lithium metal piece of 16 mm diameter was used as the anode. Furthermore, the resin film was obtained from Sekisui Chemical Co., Ltd., (product name: ESFINO) was used as the battery separator, and 1 mol L^{-1} of LiBF_4 (EC : DEC of 1 : 1 v/v%), obtained from Kishida Chemical Co., Ltd., was used as the battery electrode.

Cycling performance of charge-discharge process in lithium batteries fabricated with **G-EExG** and Ketjen black. The Li battery was initially charged to 3.1 V and then kept for 60 min. The first to 5th charging processes were carried out by charging from 3.1 to 4.25 V with 0.05C rate and keeping for 120 min. The 6th, 7th and 8th to 20th charging processes were carried out with 0.1, 0.2 and 0.5C rates, respectively. Similarly, the first to 5th, 6th, 7th and 8th to 20th discharging processes were carried out by discharging from 4.25 to 3.1 V with 0.05, 0.1, 0.2 and 0.5C rates, respectively.

Table S1 Preparation condition of **P-EExG** and **G-EExG**

Composite ratio			Baking condition		
PF8	PPA	GMA	ADCA	O ₂	time
(g)	(g)	(g)	(g)	(%)	(min)
1	20	0	2	20	30
1	20	0	2	5	30
1	20	0	2	7.5	30
1	20	0	2	10	30
1	20	0	2	20	20
1	20	0	2	20	25
1	20	0	2	20	35
1	20	0	2	20	40
1	0	20	2	20	30
1	0	5	2	20	30
1	0	10	2	20	30
1	0	15	2	20	30
1	0	20	0.5	20	30
1	0	20	1	20	30
1	0	20	3	20	30
1	0	20	2	5	30
1	0	20	2	7.5	30
1	0	20	2	10	30

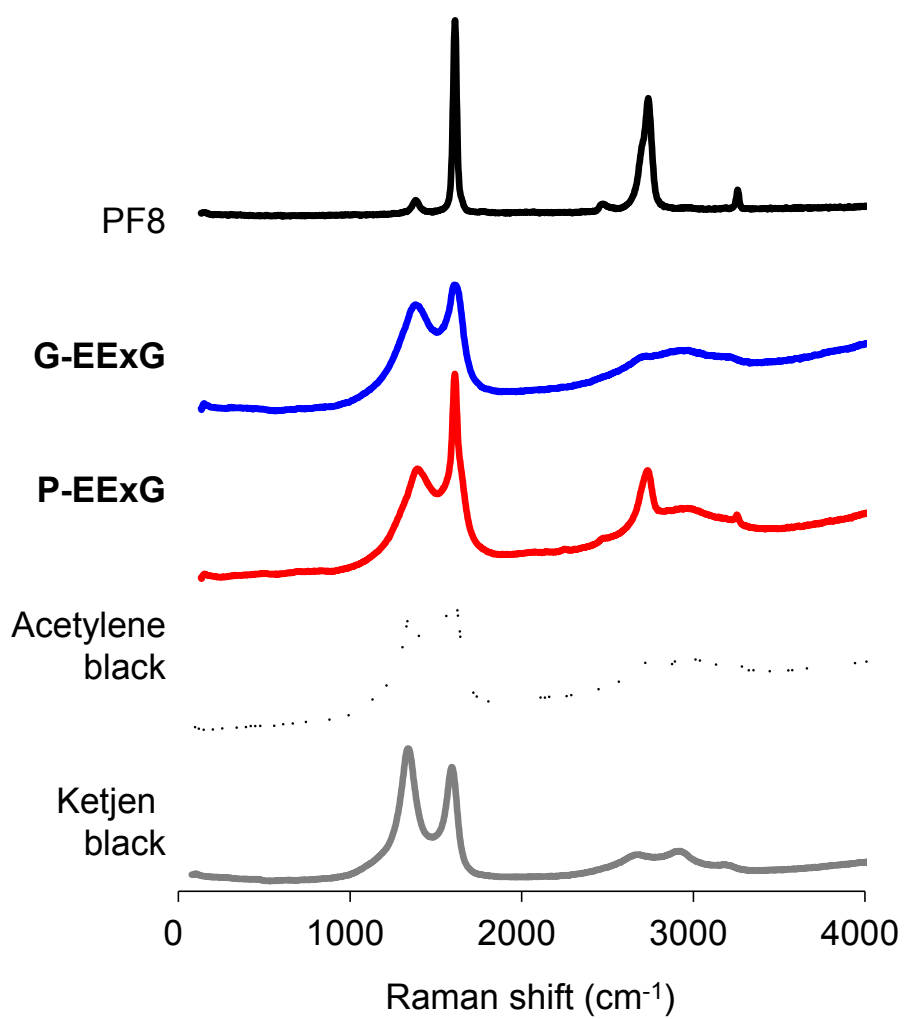


Fig. S1 Raman spectra of PF8, GMA, **G-EExG**, PPG and **P-EExG**.

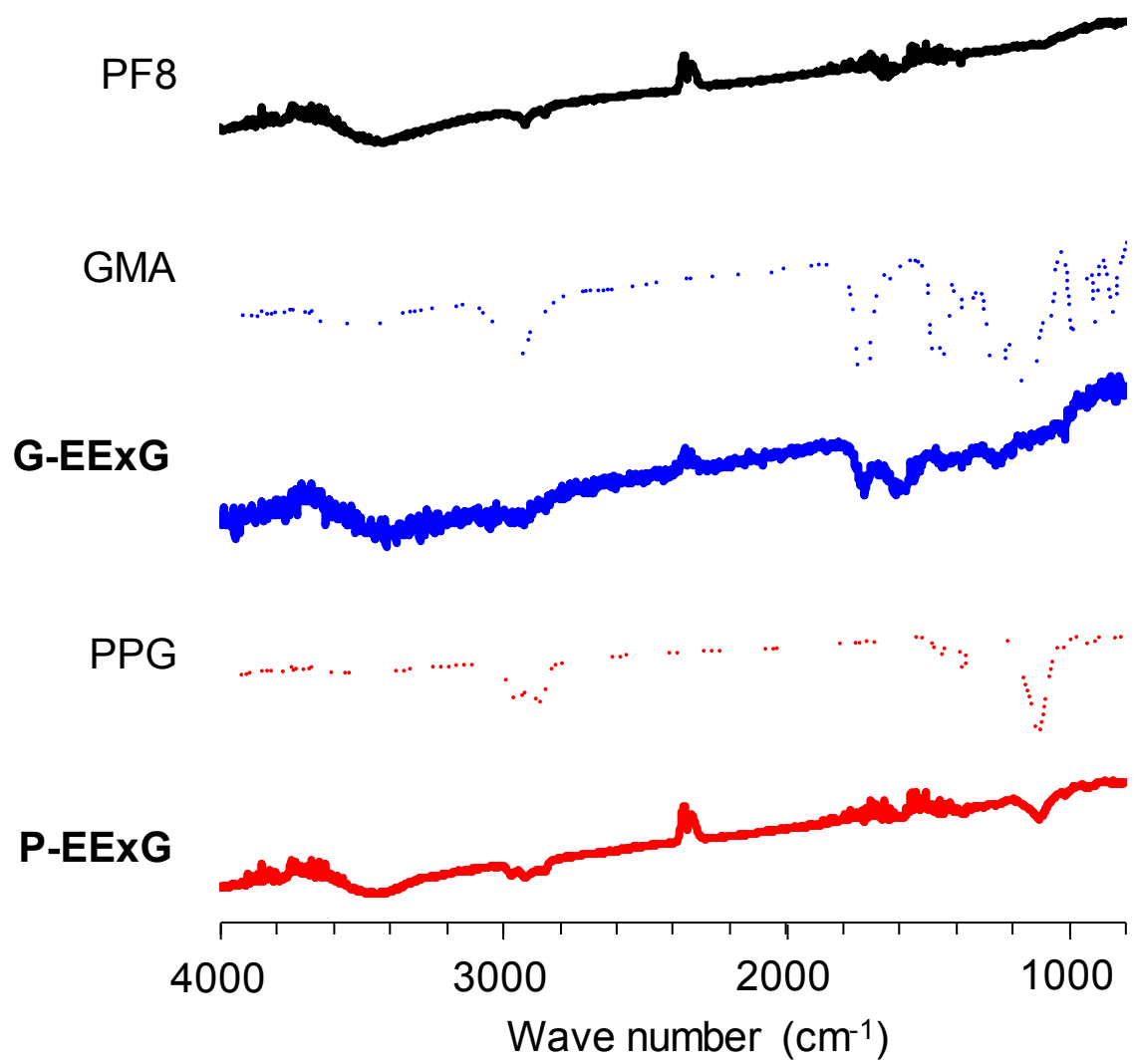


Fig. S2 FT-IR spectra of PF8, GMA, P-EEExG, PPG, G-EEExG.

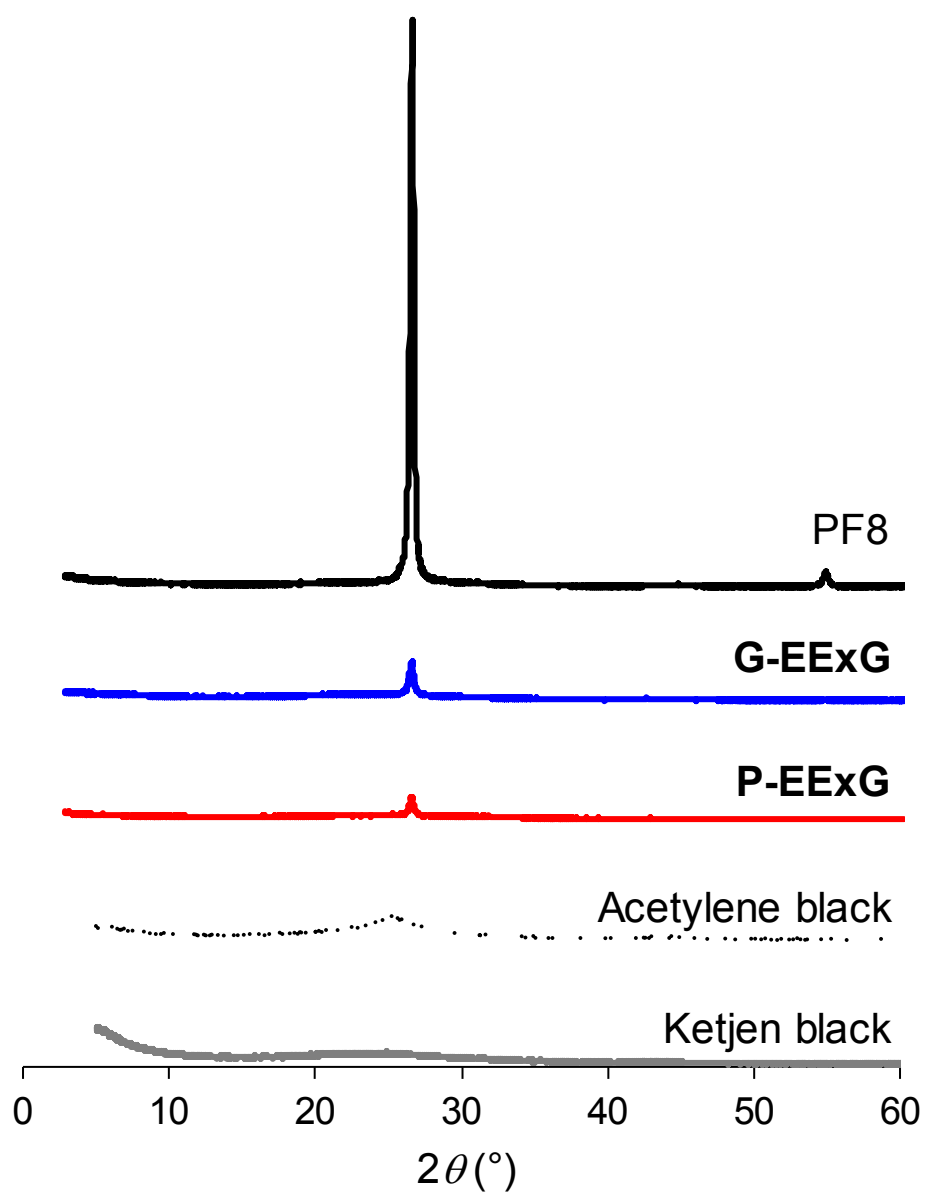


Fig. S3 X-ray diffraction patterns of PF8, P-EExG, G-EExG, Acetylene black and Ketjen black.