

Supporting Information

Efficient charge transport of a radical polyether/SWCNT composite electrode for an organic radical battery with high charge-storage density

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EXPERIMENTAL SECTION

Materials. Pentaerythritol and 3-phenyl-1-propanol were purchased from Tokyo Kasei Co. Phosphazene base, 1,4-butanediol diglycidyl ether, and single-walled carbon nanotube were obtained from Sigma-Aldrich Japan. A vapor-grown carbon fiber (VGCF) was obtained from Showa Denko Co. 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1 in v/v) electrolyte was purchased from Kishida Chemical Co. All other reagents and solvents were purchased from Sigma-Aldrich Japan, Tokyo Kasei Co. or Kanto Chemical Co. All the solvents were used as received. 4-Glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl was synthesized according to our previous report.¹

Measurements. Molecular weight measurements were done by gel permeation chromatography using a TOSOH HLC-8220 instrument with THF as the eluent and the calibration with polystyrene standards. The magnetization and the magnetic susceptibility of the powdery polymer samples were measured by a Quantum Design MPMS SQUID-VSM magnetometer. The magnetic susceptibility was measured from 10.0 to 280 K in a 0.5 T field.

General Procedure for Anionic Ring-Opening Polymerization of 4-Glycidyoxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TGE). TGE (1.14 g, 5.00 mmol) was added to a dry round-bottom flask followed by addition of pentaerythritol (6.80 mg, 50.0 μmol) and DMSO (1.00 mL) under argon atmosphere. 0.8 M Phosphazene base in hexane solution (125 μL, 100 μmol) was added to the mixture and the resulting solution was stirred at room temperature for 24 h. The polymer solution was poured into diethyl ether, and the resulting precipitate was collected by centrifugation. The viscous liquid was dried under vacuum at room temperature to yield the polyTGE (PTGE) as a red solid (80% yield). ¹H NMR (500 MHz, DMSO): δ 3.64-3.26 (Br, Glycidyl group and CH in piperidine), 1.85 (Br, CH₂, 2H), 1.27 (Br, CH₂, 2H), 1.08 (s, (CH₃)₂, 6H), 1.04 (s, (CH₃)₂, 6H) ppm.

Determination of the Radical Content. The radical concentration of CL-PTGE was determined by means of SQUID measurements using the Curie plots and the values for saturated magnetization.

General Procedure for Anionic Ring-Opening Copolymerization of TGE and 1,4-butanediol diglycidyl ether. TGE (1.14 g, 5.00 mmol) was added to a dry round-bottom flask followed by

addition of pentaerythritol (6.80 mg, 50.0 μmol), 1,4-butanediol diglycidyl ether (50.6 mg, 0.250 mmol) and DMSO (1.00 mL) under argon atmosphere. 0.8 M Phosphazene base in hexane solution (125 μL , 100 μmol) was added to the mixture and the resulting solution was stirred at room temperature for 24 h. The resulting gel was rinsed in a large amount of chloroform to remove the reacted residue, unreacted monomers, and phosphazene base. The gel was dried under vacuum at room temperature to yield the cross-linked PTGE (CL-PTGE) as a red solid (98% yield).

General Procedure for Preparation of CL-PTGE/Carbon Composite Electrodes. CL-PTGE (9.00 mg) and a carbon additive (1.00 mg) were dispersed in chloroform (2.00 mL). The mixture was ultrasonicated for 15 min using a probe type sonicator (Sonifier, BRANSON). The obtained dispersion of CL-PTGE/carbon additive was cast-coated on a current collector and dried under vacuum at room temperature.

Preparation of Test Cells. A coin cell was fabricated by sandwiching the electrolyte layer of 1 M LiPF₆ in ethylene carbonate/diethyl carbonate (1/1 in v/v) with the CL-PTGE/carbon composite cathode and the Li anode, using the separator film (cell guard #2400 from Hosen Co.) under strictly anaerobic conditions.

Electrochemical Measurements. Electrochemical analyses were carried out in a conventional cell under argon. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/AgCl immersed in a solution of 0.1 M (*n*-C₄H₉)₄NClO₄ in CH₃CN. The formal potential of the ferrocene/ferrocenium couple was 0.45 V vs Ag/AgCl. The cyclic voltammetry and chronopotentiometry were performed using a normal potentiostat system (BAS Inc. ALS 660D). AC Impedance analyses were performed using a Zahner IM6/ZENNIUM system. In AC impedance measurements, the frequency range was 1.0×10^5 to 5×10^{-4} Hz with an ac amplitude of 10 mV. The DC bias voltage was set at $(E_{\text{pa}} + E_{\text{pc}})/2$ of each cells, at which 50% of the nitroxide radical units polymer were supported to be oxidized to the cationic state (i.e., the oxoammonium cation).

Table S1 Anionic Ring-Opening Polymerization of TGE

Entry	Alcohol	[OH]/[<i>t</i> -BuP ₄]	[Cross-linker]/[M]	Yield (%)	M_n (10^3 g/mol)		PDI ^c
					Theo. ^b	GPC ^c	
1	3-phenyl-1-propanol	2.0	-	4	23	2.2	1.27
2	3-phenyl-1-propanol	1.0	-	72	23	9.6	1.51
3	3-phenyl-1-propanol	1.0	0.05	77	-	-	-
4	Pentaerythritol	2.0	-	80	23	9.3	1.57
5	Pentaerythritol	1.0	-	90	23	5.8	1.76
6	Pentaerythritol	2.0	0.02	70	-	-	-
7	Pentaerythritol	2.0	0.05	98	-	-	-

^aConditions: [Monomer]₀/[initiator]₀ = 100 in DMSO; 1,4-butanediol diglycidyl ether as cross-linker; RT; 24 h. ^bEstimated by [Monomer]₀/[initiator]₀. ^cEstimated by GPC with THF eluent calibrated on polystyrene standards.

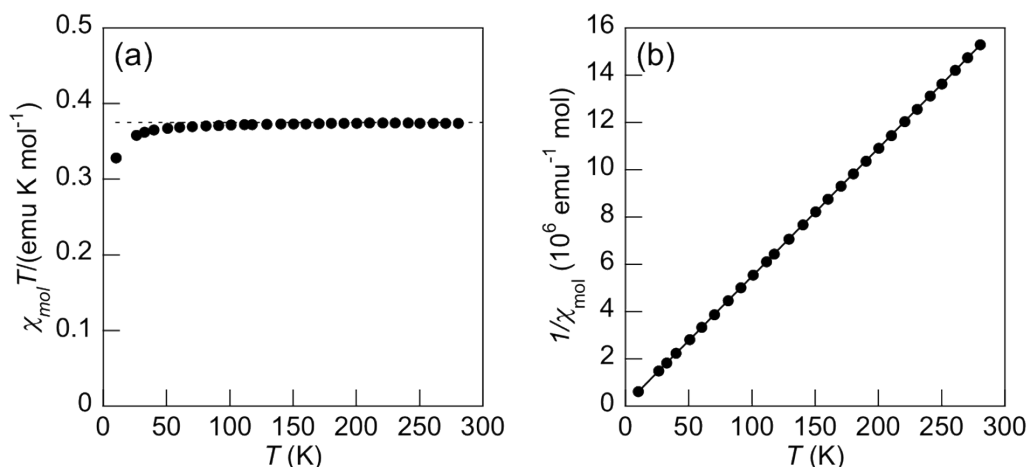


Fig. S1 Plots for (a) $\chi_{mol}T$ vs T and (b) $1/\chi_{mol}$ vs T with Curie-Weiss fitting for the CL-PTGE (13.8 mg) obtained by SQUID measurement, where χ_{mol} (molar magnetic susceptibility) was based on per mol of the radical. Dashed line in (a) represents the theoretical value of $\chi_{mol}T$ for $S = 1/2$.

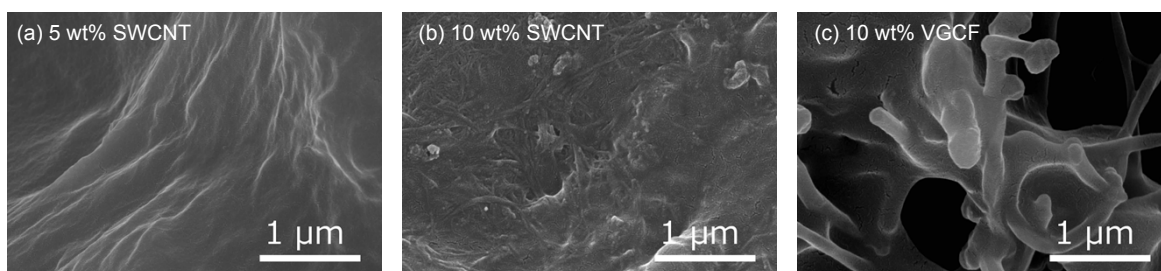


Fig. S2 SEM images of the CL-PTGE composite electrodes containing (a) 5 wt SWCNT, (b) 10 wt% SWCNT, and (c) 10 wt% VGCF.

Table S2 Material properties for CL-PTGE electrodes

Electrode	Conductivity (mS/cm) ^a	Charge transfer resistance (Ω/cm^2) ^b
CL-PTGE	-	44
5 wt% SWCNT composite	14	60
10 wt% SWCNT composite	42	41
10 wt% VGCF composite	2.3	52

^aDetermined by four probe method. ^bDetermined by AC impedance spectroscopy.

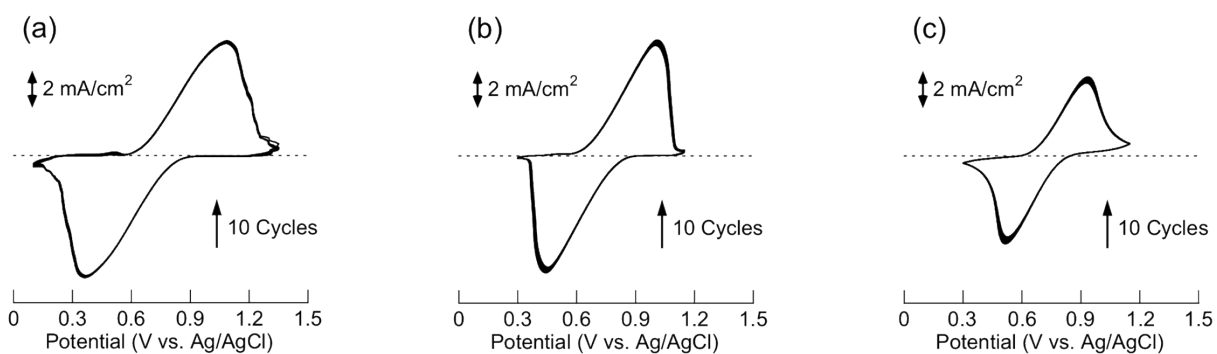


Fig. S3 Cyclic voltammograms obtained for the CL-PTGE composite electrodes containing (a) 5 wt% SWCNT, (b) 10 wt% SWCNT, and (c) 10 wt% VGCF at a scan rate of 5 mV/s. The electrolyte was a solution of 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in CH_3CN .

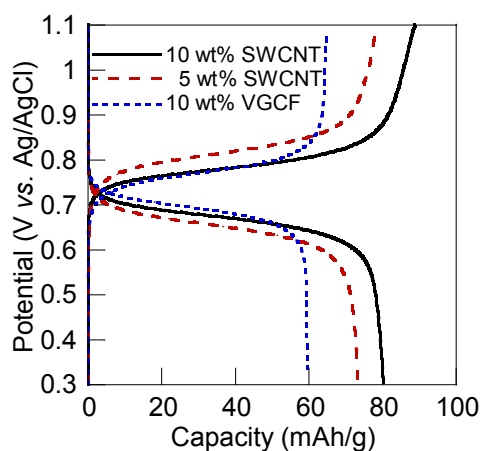


Fig. S4 Charging/discharging curves obtained for the CL-PTGE composite electrodes containing (a) 5 wt% SWCNT, (b) 10 wt% SWCNT, and (c) 10 wt% VGCF at a 10 C rate. The electrolyte was a solution of 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in CH_3CN .

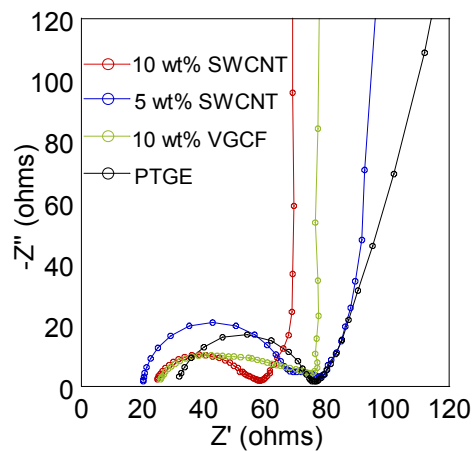


Fig. S5 AC Impedance spectra for the CL-PTGE composite electrodes containing 5 wt% SWCNT, 10 wt% SWCNT, and 10 wt% VGCF, and the CL-PTGE electrode at 0.73 vs Ag/AgCl. The electrolyte was a solution of 0.1 M $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$ in CH_3CN .

Reference

- 1) T. Suga, K. Yoshimura, and H. Nishide, *Macromol. Symp.*, 2006, **245-246**, 416-422.