

Electronic Supplementary Information

Redox equilibrium of a zwitterionic radical polymer in a non-aqueous electrolyte for novel Li⁺ host material in a Li-ion battery

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1. Experimentals

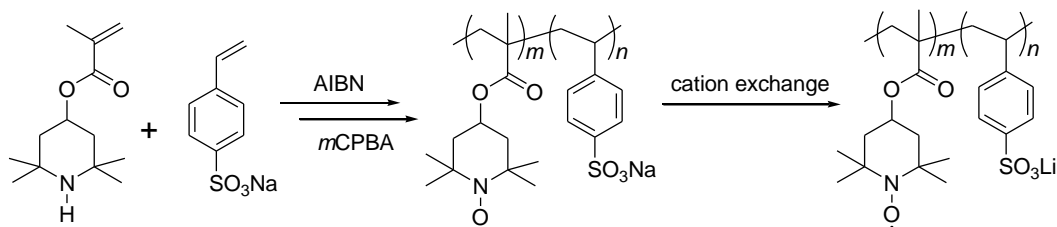
1.1 Materials

2,2,6,6-tetramethylpiperidine-4-yl methacrylate and sodium *p*-styrenesulfonate hydrate was purchased from Tokyo Chemical Industry (TCI) Co., Ltd., 3-chloroperoxybenzoic acid (*m*CPBA), and all solvents were obtained from Kanto Chemical Co. and were used without further purification. Li metal as a anode was purchased from Aldrich. A vapor-grown carbon fiber (VGCF) was obtained from Showa Denko Co. A binder powder, poly(vinylidene fluoride) (PVdF) resin (KF polymer), was purchased from Kureha Chemical Co. The separator film of a coin-cell was cell guard #2400 from Hohsen Co.

1.2 Copolymerization of 1

Copolymerization was carried out at feed molar ratio of 1:1. 2,2,6,6-tetramethylpiperidine-4-yl methacrylate and sodium *p*-styrenesulfonate hydrate as shown in Scheme S1. The total monomer concentrations were 1 mol L⁻¹ in deoxygenated H₂O/MeOH (1/2, v/v) mixture solvent with azobisisobutyronitrile (AIBN, 25 mmol L⁻¹) for 10 hrs at 65 °C. The copolymerizations were stopped by the adding an excess of hexane, and products were obtained as precipitates and were thoroughly dried in vacuum. The product (200 mg) was oxidized by *m*CPBA (323 mg) in THF (5 mL), which was kept stirring for 12h at room temperature. Note that the product of copolymerization was not dissolved in THF. After oxidation, **1** was obtained and filtrated, washed with hexane three times, and thoroughly dried in vacuum. The cation exchange from sodium to lithium was used excess LiCl in DMF.

Figure S1 shows two groups, *i.e.*, styrenesulfonate groups and TEMPO groups have the same diffusion coefficient (red line) in 2D-DOSY (Diffusion Ordered Spectroscopy), indicating two groups exist in the same polymer chain.



Scheme S1. The preparation for poly(TEMPO-substituted methacrylate-co-lithium styrenesulfonate).

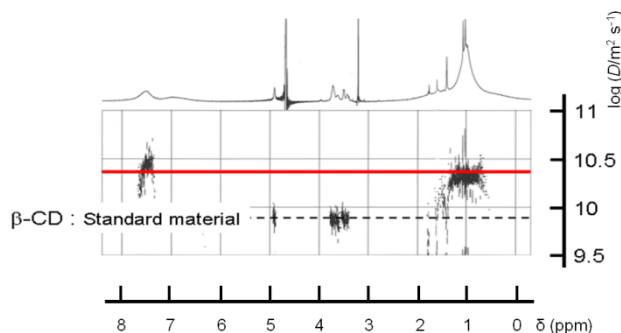


Figure S1. 2D-DOSY for poly(TEMPO-substituted methacrylate-co-lithium styrenesulfonate).

1 (ppm): 0.72-0.89 (br, 1×CH₃, methacrylate), 0.94-1.31 (4×CH₃, tetramethylpiperidine), 1.65-2.04 (br, 2×CH₂, tetramethylpiperidine, -CH₂-), 3.18-3.22 (br, 1×CH), 5.02-5.12 (br, 1×-CH-O), 7.42 (br, 2×CH of phenyl)

1.3 Radical Concentration

Magnetic susceptibilities of **1** were determined by SQUID measurements at 0.5 T and various temperatures ranging between 1.95 and 300 K. The Curie constant χT at sufficiently high temperatures (i.e. $2J \ll kT$) corresponded to the value of 0.375 emu K mol⁻¹ calculated for a spin quantum number of $S = 1/2$, which supported the paramagnetic property of the radical polymers. The deviation of χT to lower values at low temperatures indicated a weak antiferromagnetic interaction within the polymers, as typically shown for **1** (Figure S2).

The radical concentration was determined from the $1/\chi$ vs. T plots, based on the Curie-Weiss rule according to $1/\chi_{\text{para}} = T/C - \theta/C$ Where C is a Curie constant defined as $N_e g^2 \mu_B^2 S(S + 1)/(3k)$. The slope of the $1/\chi$ vs. T plots ($1/C$) gave a spin density (N_e) of 2.53×10^{21} spin/g for **1**, which amounted to 96.1% of the TEMPO unit in the polymer.

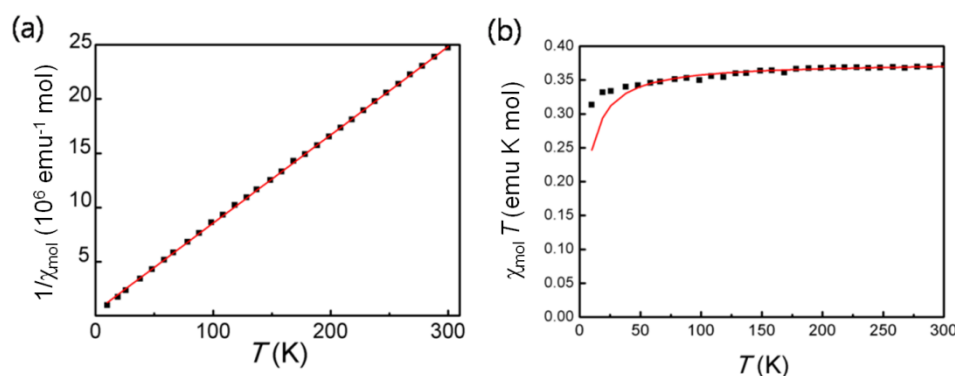


Figure S2. (a) SQUID measurements of **1**. (b) Plots of 1/magnetic susceptibility (18 mg) vs. temperature (Curie-Weiss plots) for **1**.

2. Cyclic voltammograms of PTMA

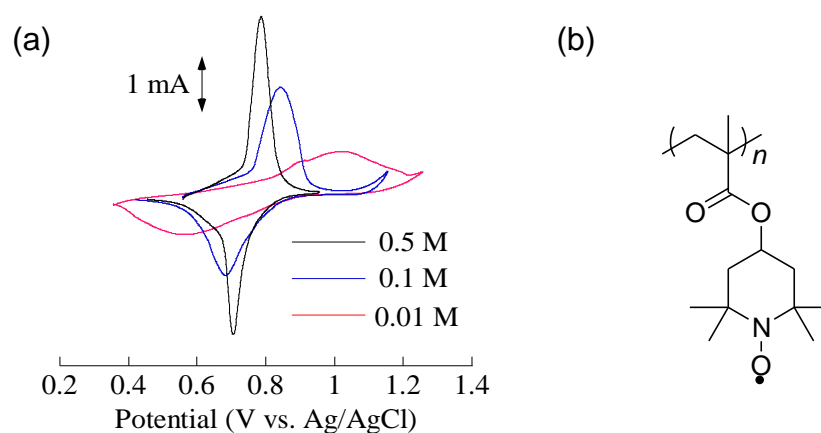


Figure S3. (a) Cyclic voltammograms of PTMA/carbon composite (PTMA-VGCF-PVdF=1/8/1 wt ratio) on ITO substrate at a scan rate of 5 mV s^{-1} in 0.5 M, 0.1 M and 0.01 M LiTFSI in DMF, respectively. (b) A structure of poly(TEMPO-substituted methacrylate), PTMA.

Cyclic voltammograms were obtained from PTMA/carbon composite with different the concentrations of Li^+ in electrolyte in Fig. S3 (a). The increase in half-wave potentials ($E_{1/2}$) to lower logarithm of Li^+ concentrations in electrolyte was observed (cf. Fig. 1-(d))

3. EQCM analysis of 1 electrode

1 solution in water/DMF (1/1 vol. ratio) was drop-casted under the solvent vapor and dried to form a layer with a thickness of c.a. 100 nm on a glassy carbon QCM electrode (the diameter $\phi = 0.5$ cm). Change in the resonant frequency Δf measured simultaneously with the cyclic voltammograms was recorded at a scan rate of 5 mVs^{-1} . The formal potential of the ferrocene/ferrocenium couple was 0.45 V vs this Ag/AgCl electrode. A SEIKO EG&G QCA 922 and an ALS 660B Electrochemical Analyzer was employed to obtain the resonant frequency Δf and the voltammograms, respectively. The increment of the mass Δm accompanied by the reduction of the polymer layer was determined by employing Sauerbrey's Equation.¹²

$$\Delta f = -\frac{2f_0^2}{A(\rho_0\mu_0)^{1/2}} \Delta m$$

Where f_0 , A , ρ_0 , and μ_0 are the fundamental frequency of the QCM (9.1 MHz), the electrode area (0.196 cm^2), the density of quartz (2.65 gcm^{-3}), and the shear modulus of quartz ($2.95 \times 10^{11} \text{ dyncm}^{-2}$), respectively.

4. Charging and discharging curves of 1/carbon composite

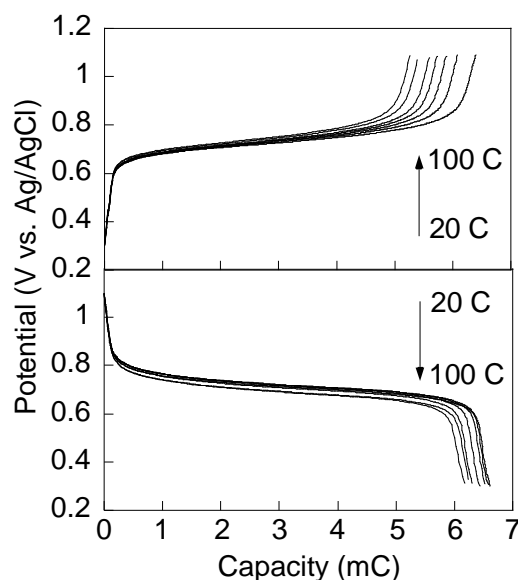


Figure S4. Charging and discharging curves of 1/carbon composite (1-VGCF-PVdF=1/8/1 wt ratio) on ITO substrate in EC/DMF (1/1 v/v) containing 0.5 M LiPF_6 .

5. Cycle performances of 1/carbon composite

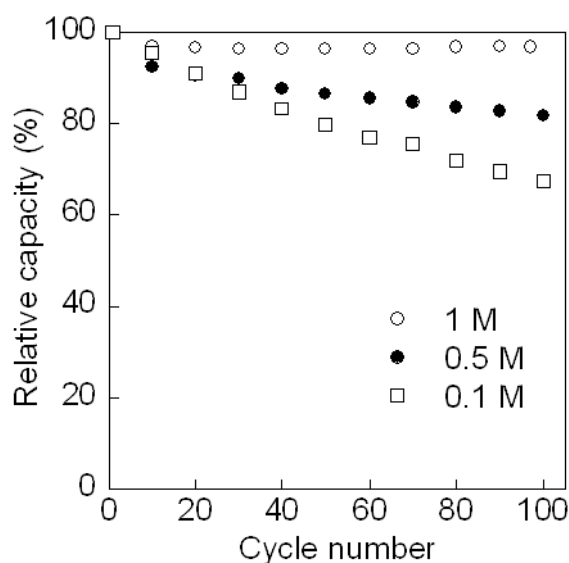


Figure S5. Cycle performances of 1/carbon composite (1-VGCF-PVdF=1/8/1 wt ratio) on ITO substrate in EC/DMF (1/1 v/v) containing 1M, 0.5 M and 0.1 M LiPF₆ at current density 20 C. Relative capacity was calculated on the basis of observed capacity.

6. Preparation of 1/Carbon Composite Electrodes and coin-cells

The copolymer **1** (5.0 mg) was mixed with VGCF (40.0 mg) and PVdF (5.0 mg) in N-methyl-2-pyrrolidone (NMP). The mixture was pasted on a glassy carbon substrate and dried under vacuum at 40 °C for 10 h to give the composite electrode with a composition of 1/VGCF/PVdF=1/8/1 (w/w/w). A Coin cell was fabricated with 1/carbon composite electrodes, separator and Li metal, under anaerobic conditions.

7. Cyclic voltammograms of coin-cells

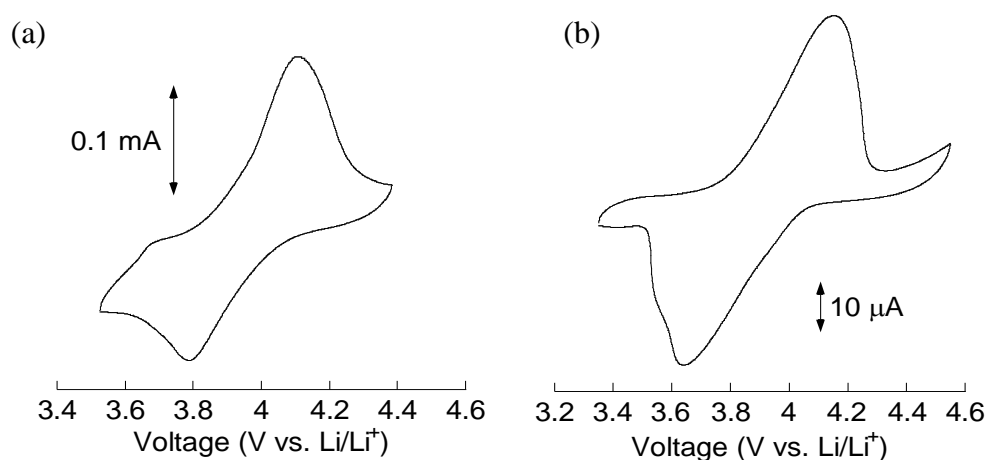


Figure S5. Cyclic voltammograms of coin-cell with (a) 0.1 M and (b) 0.05 M LiPF₆ in DMF/EC (1/1 v/v) solution at a scan rate of 1 mV s⁻¹, respectively.

A half-wave potential ($E_{1/2}$) of coin-cell with both 0.1 M and 0.05 M lithium cation in electrolyte was observed the constant value, 3.94 V (vs. Li/Li⁺).

7. Measurements

¹H spectra were recorded on a Bruker AVANCE 600 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Molecular weight measurements were done by gel permeation chromatography using a TOSOH HLC8220 instrument with DMF as the eluent. Calibration was done with polystyrene standards. Elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 multi-DOSIMAT. ESR spectra were recorded using a JEOL JES-TE200 spectrometer with a 100 kHz field modulation frequency and a 0.1mT width. The magnetization and the magnetic susceptibility of the powdery polymer samples were measured by a Quantum Design MPMS-7 SQUID magnetometer. The magnetic susceptibility was measured from 1.95 to 300K in a 0.5 T field. Cyclic voltammetry was performed using a normal potentiostat system (BAS Inc. ALS660B). A Hokuto Denko charge–discharge analytical instrument (HJ1001SM8) was used to measure the electrical charge–discharge characteristics of the test cell.