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Poly(dihydroxybenzoquinone): Its High-density and Robust Charge Storage Capability in Rechargeable Acidic Polymer-air Batteries

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1. Materials and methods

1.1. Preparation of polymer

DHBQ (1 g, 7.14 mmol) was dissolved in acetic acid (70 mL) at 60℃ [39, 40]. The solution was cooled to 25 °C, was added 37% aqueous formaldehyde solution (3 mL, 40.7 mmol) to, and was stirred for 24 h. The reaction mixture was filtered, was washed with a sufficient amount of water, and then was washed with acetone, to yield an orange powder (454 mg, 42%). The polymer was soluble such as in dimethyl sulfoxide (DMSO), methanol, *N*,*N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and tetrahydrofuran (THF), was insoluble in acetonitrile, chloroform, dichloromethane, and water, and was characterized to be PDBM, as follows. ^{13}C-NMR (400 MHz, solid-state, δ): 10–20 (br, CH_2), 104.2 (CH), 114.8 ($\underline{C}$–CH_2), 156 (C–OH), 159.3 (C–OH), 184.3 (C=O). Gel permeation chromatography (DMF eluent, polystyrene standard): $M_n = 1.8 \times 10^3$, $M_w/M_n = 1.1$.

1.2. Estimation of swelling degree

PDBM film was prepared by drop-casting on a glass substrate (MICRO SLIDE GLASS, S1111, MATSUNAMI, 76×26 mm) from the 5 mg/mL PDBM/*N*-methylpyrrolidone solution at 120℃. The PDBM coated sample was placed in water for 24 hours. The sample was subsequently removed from water, and the water droplets on the surface were wiped off. The degree of swelling was estimated from the weight change before and after soaking in water and was 1.26.

1.3. Electrochemical characterization

The electrochemical measurements were performed with aqueous solution at pH 1, adjusted by sulfuric acid, as the electrolyte under nitrogen. A potentiostat system was applied to the cyclic voltammetry. A carbon disk and coiled platinum wire were used as the working and counter electrodes, respectively, and the working potential was measured vs. an Ag/AgCl reference electrode.

A PDBM layer was prepared by drop-casting the NMP solution on a glassy carbon substrate. The PDBM/carbon composite electrodes were prepared by coating the slurry of the polymer, single-walled carbon nanotube (SWNT), polyvinylidene difluoride, and *N*-methylpyrrolidone onto glassy carbon substrates. SWNT prepared by enhanced-direct-injection-pyrolytic-synthesis method were purchased from Meijo Nano Carbon Co.

1.4. Measurements

^{13}C NMR spectra were recorded on a JEOL ECX-400 spectrometer. The molecular weight was estimated by gel permeation chromatography using a TOSOH HLC-8220 instrument. The film thicknesses were estimated using a KLA Tencor P-6 contact stylus profiler.

1.5. Battery evaluation

A tailor-made two-compartment glass cell (Watanabe Kagaku Co.) was employed as the electrochemical cell. Separation of the compartments was accomplished by applying a salt bridge using a fine glass filter in between allowing only the electrolyte to surpass during the measurement. The PDBM/carbon composite electrode was applied as the anode, and an oxygen reduction catalyst composed of 20% Pt on carbon paper (Fuel Cell Earth) was applied as the cathode. The anode room was sealed and filled with a nitrogen-saturated acidic aqueous electrolyte (pH 1) enough to cover the active area of the electrode. Nitrogen was continuously flowed in the anode room during all electrochemical measurements to disable unfavorable redox reactions of oxygen in the anode side. The cathode room was kept at open-air condition and filled with acidic aqueous electrolyte (pH 1) as made to keep the cathode close as possible to ambient air conditions. The voltages obtained by this battery corresponded to the potential of PDBM against that of oxygen.

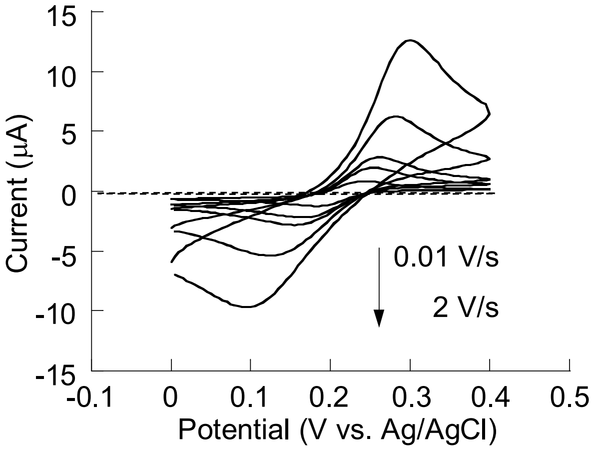

Figure S1. a) Cyclic voltammograms of 1 mM DHBQ in acidic aqueous electrolyte (pH 1) at a scan rate of 10, 50, 100, 500, and 2000 mV/s.

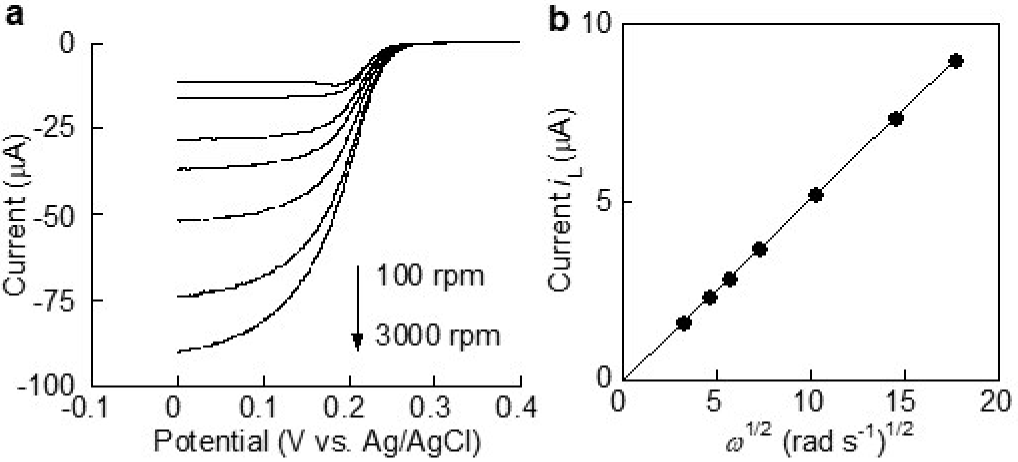

Figure S2. a) Limiting current for 1 mM DHBQ in acidic aqueous electrolyte (pH 1)at a rotating disc GC electrode (RDE) ω = 100, 200, 300, 500, 1000, 2000, and 3000 rpm. b) Levich plots of DHBQ.