

Notes

The Possibility of 1,3,4-Oxadiazole Containing Polymer as a New Polymer Electrode in Redox Supercapacitor

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Abstract : Poly(1',4'-phenylene-1'',4''-(2''-(2''''-ethyl-hexyloxy)) phenylene-1'',4''-phenylene-2,5-oxadiazoly) (PPEPPO) was synthesized and its electrochemical characteristics was investigated as electrode material in redox supercapacitor. The cyclic voltammetry (CV) shows there was scarcely a redox reaction and further suggests n-doping is difficult to occur in this system. However, the discharge curve between 3.0 to 0.01 V is continuously decreased like a straight line, similar to the discharge pattern of EDLC. The initial specific discharge capacitance is ~6.4 F/g, while the specific capacitance of 1000th cycle is ~0.1 F/g. The PPEPPO can be used as the electrode of supercapacitor, emissive material, as well as charge-transporting material in polymer LED.

Keywords : 1,3,4-oxadiazole, PPEPPO, polymer electrode, redox, supercapacitor.

Introduction

Supercapacitor provides higher power density than battery, despite of its low operating voltage. It also gives a higher energy density than conventional dielectric capacitors. Recent interest in supercapacitors has been stimulated by their potential applications in an electric vehicle as a power-storage device operating in parallel with the battery. The redox supercapacitor¹ uses metal oxide or conducting polymer as the electrode materials. Conjugated polymers have been regarded as promising pseudo-capacitive materials. There are three types of polymer redox supercapacitors: (I) a symmetric supercapacitor consisted of p-doped polymers on both electrodes; (II) an asymmetric supercapacitor based on two p-doped polymer electrodes by virtue of the difference in potential ranges over which they become p-doped; (III) a symmetric supercapacitor based on p- and n-dopable polymers.² Only the type III supercapacitor is particularly capable of showing 3 V the operating voltage. However, the n-doped polymer is very rare and difficult to

prepare.

On the other hands, many conjugated polymers including poly(p-phenylenevinylene), poly(2-methoxy-5,2'-ethylhexyloxy)-1,4-phenylenevinylene), poly(p-phenylene) derivatives, polyfluorene derivatives, and polythiophene derivatives have been synthesized and investigated as emissive or charge-transporting materials in polymer light-emitting diodes (PLED). The oxadiazole compounds, such as 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole, have also been synthesized and characterized as good electron-injection/hole-blocking materials within multi-layer devices.³⁻⁶ In addition, it was reported that the oxadiazole-containing polymer is possible for n-doping.⁷ Based on these features of oxadiazole-containing compounds, poly(1',4'-phenylene-1'',4''-(2''-(2''''-ethyl-hexyloxy))phenylene-1'',4''-phenylene-2,5-oxadiazoly) (PPEPPO) is worth to be tested as a new 3 V class electrode material in redox supercapacitor. Thus, we synthesized and studied the electrochemical characteristics of the PPEPPO in symmetric (type III) redox supercapacitor.

Experimental

The synthetic methods of PPEPPO has been previously

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reported⁸ detailly. We synthesized *bis*(4-bromobenzoyl) hydrazine, 2,5-*bis*(4-bromophenyl)-1,3,4-oxadiazole, and 2-methoxy-[5-(2'-ethylhexyl)oxy]-1,4-benzene diboronic acid (MEHBBA) monomers. All catalysts and polymerization was handled in a nitrogen atmosphere. 2,5-*bis*(4-bromophenyl)-1,3,4-oxadiazole (0.679 g, 1.786 mmol) in 10 mL THF and 4 mL 2 M K₂CO₃ aqueous solution were added to a stirred solution of 1-methoxy[4-(2'-ethylhexyl)oxy] benzene diboronic acid (0.578 g, 1.786 mmol) with Pd(PPh₃)₄ (8.4 mg, 0.6 mol%) catalyst. The reaction mixture was heated at 80 for 8 h under nitrogen atmosphere. Phenyl boronic acid (0.05 g, 0.41 mmol) and Bromobenzene (0.05 g, 0.318 mmol) were also added consequently with a small amount of catalysts for end-capping. After 2 h, the reaction mixture was poured into methanol (50 mL) and filtered with glass-filter. The residue was dissolved in CHCl₃ and then washed with water. After drying over MgSO₄, precipitation was repeated twice with chloroform/methanol. Bruker AM-500 ¹H-NMR spectrometer was used to identify the polymerization. The chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. UV-visible absorption spectra were also obtained by using Shimadzu UV-3100 spectrophotometer.

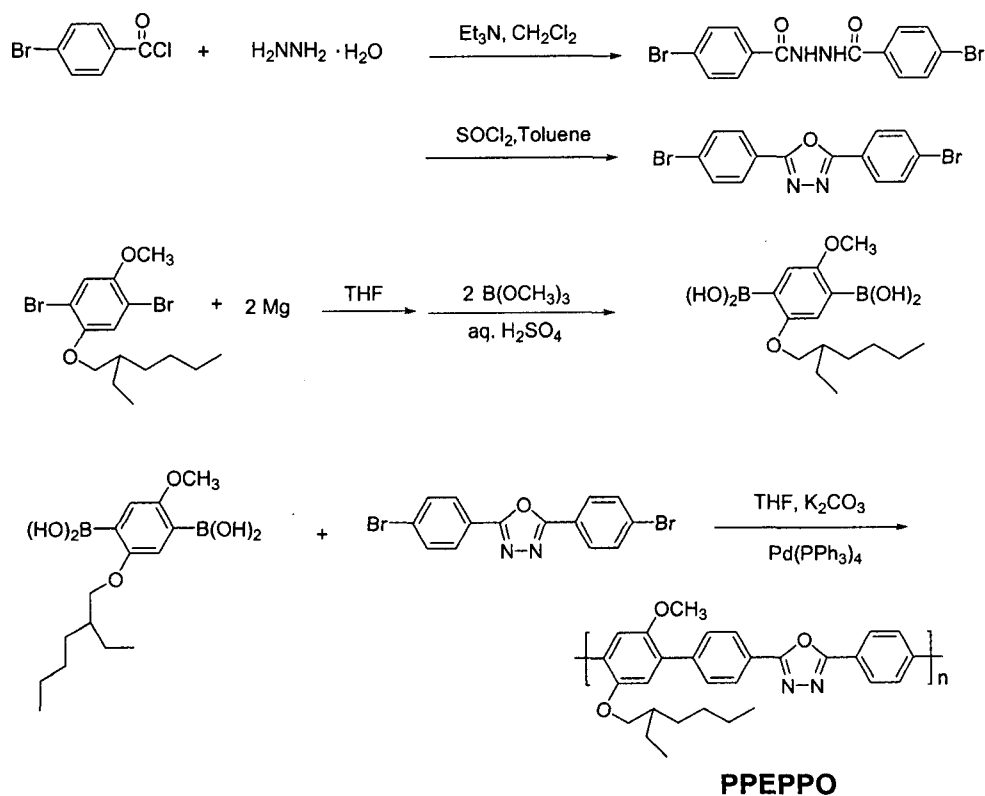
The redox supercapacitor consisted of the PPEPPO powder electrode, porous polypropylene/polyethylene/polypropylene film (Celgard), and 1 M Et₄NBF₄ (Aldrich, 99%) in acetonitrile.

The powder electrode was prepared by mixing the PPEPPO, carbon black (Super P, MMM Carbon Co.), and polytetrafluoroethylene (Aldrich) with the weight ratio of 60:40:10. The charge collector (Al foil), electrode, separator /electrolyte solution, electrode, and charge collector were assembled in sequence as a sandwich and enveloped in a laminated-aluminum pouch in dry room. Cyclic voltammogram was also obtained using a MacPile-II potentiostat system at the constant scan rate of 1 mV/sec in the range of 2.0~2.0 V. The electrochemical impedance spectroscopy was performed by using a Solatron frequency response analyzer 1260 system in the range of 1 MHz~1 Hz. The redox supercapacitor was also tested by using a galvanostatic charge-discharge cyler in the potential range of 3.0~0.01 V with different current densities.

Results and Discussion

Synthesis and Characterization of PPEPPO. The method for preparing monomer and PPEPPO is outlined in Scheme I. Polymer was obtained through the Suzuki reaction of diboronic acid, MEHBBA, dibromide, 2,5-*bis*(4-bromophenyl)-1,3,4-oxadiazole, and following end-capping reaction. MEHBBA and 2,5-*bis*(4-bromophenyl)-1,3,4-oxadiazole were prepared by the following reaction Scheme I.

The polymer structure was consistent with the ¹H-NMR



Scheme I

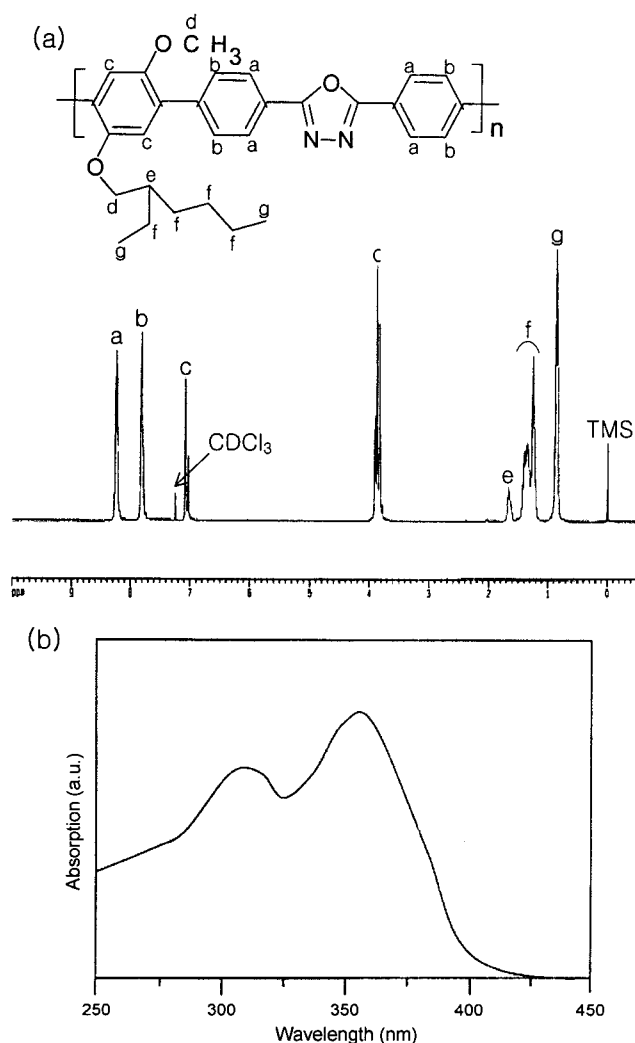


Figure 1. (a) $^1\text{H-NMR}$ spectrum and (b) UV-Visible absorption spectrum of PPEPPO.

spectroscopy result (Figure 1(a)). The polymer was readily soluble in common organic solvents such as THF, toluene, chloroform, chlorobenzene etc. The number of average molecular weight (M_n) of PPEPPO, determined by gel permeation chromatography using polystyrene standard, was 10,000–14,000 with a polydispersity index of 1.3. Figure 1(b) shows the optical absorption spectrum of the polymer in chloroform. The absorption spectrum of the polymer shows the maximum absorption (λ_{max}) and absorption edge at 358 and 425 nm, respectively. The detail analysis of this polymer with other spectroscopy is reported⁸ previously.

Electrochemical performance of PPEPPO. We measured the cyclic voltammetry (CV) and impedance spectroscopy to identify the oxidation/reduction potentials and the cell resistance. Figure 2(a) shows the results of CV for the initial state and the state after 100th charge and discharge process. These curves are different each other, but the CV curve of

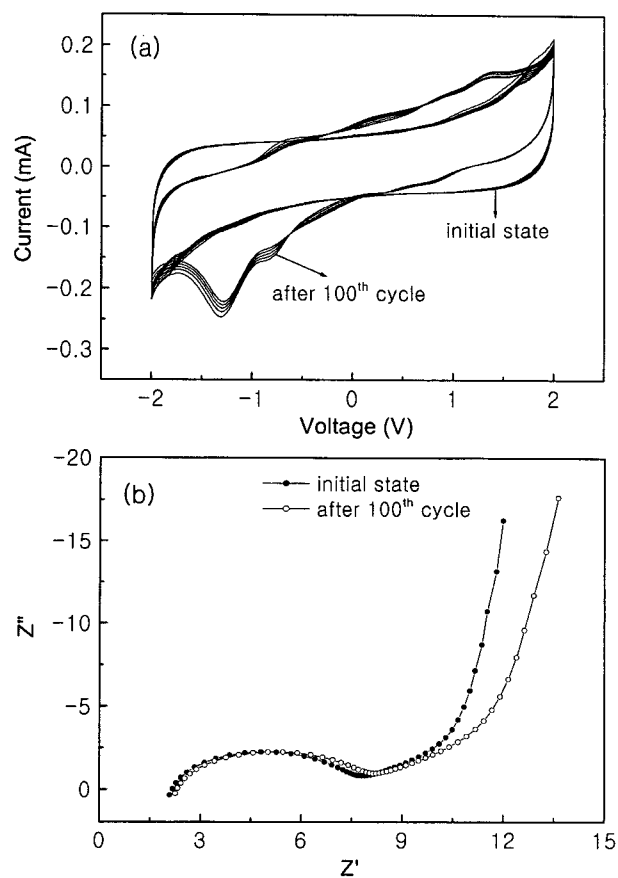


Figure 2. (a) Cyclic voltammetry and (b) electrochemical impedance spectroscopy of PPEPPO/PPEPPO redox supercapacitor.

initial state is very similar to that of typical electrical double layer capacitor (EDLC).⁹ After 100th charge and discharge process, the CV shape is still resemble to that of EDLC although the curve exhibits small oxidation and reduction peaks. This indicates that the redox reaction is almost not occurred in this material and the n-doping is almost not possible in this system. The PPEPPO has the characteristics like electric double layer at initial state and turns into the characteristics of electric double layer and redox with cycling.

As shown in Figure 2(b), interfacial and internal characteristics between electrodes and separator have the internal resistance of $\sim 2.2 \Omega$, the total resistance of $\sim 7.8 \Omega$, and the equivalent series resistance (ESR) of $\sim 8.0 \Omega$ at 1 KHz. These values are relatively larger than those of other conducting polymer systems¹⁰ because the PPEPPO has low electrical conductivity. However, we know that the interfacial and internal resistance is very stable from the impedance curve of initial state and after 100th charge and discharge process.

Figure 3(a) shows 100th discharge curve of redox supercapacitor using PPEPPO electrode with different current den-

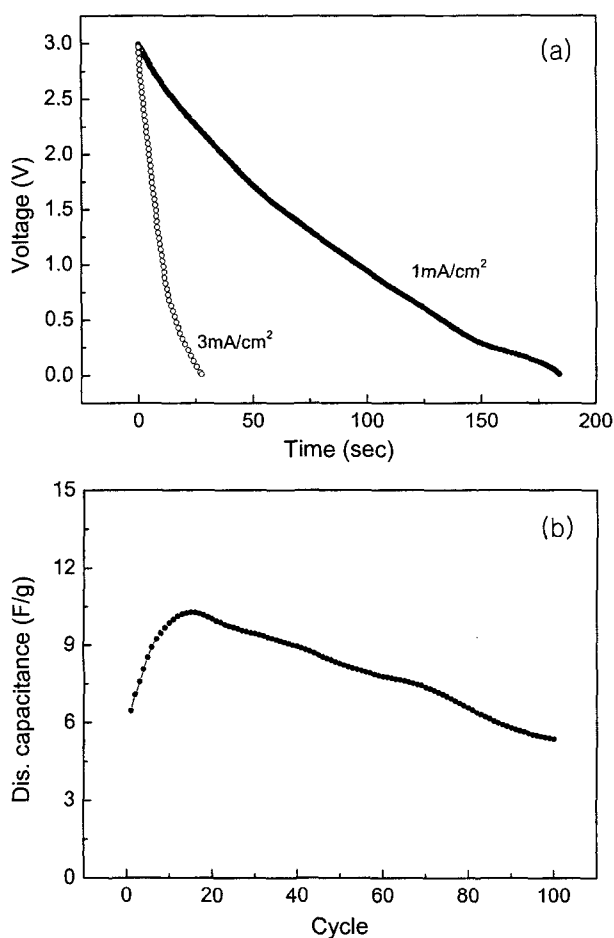


Figure 3. (a) 100th discharge curve and (b) cyclic capacitance (current density = 3 mA/cm²) of PPEPPO// PPEPPO redox supercapacitor.

sities before CV measurements. As the applied current density is increased both the voltage and the discharge time are rapidly decreased. The discharge curve between 3.0 to 0.01 V is continuously decreased like a straight line, which is the characteristic of the discharge pattern of EDLC. If the n-doping is occurred in PPEPPO, the discharge profile deviates from the straight line. Figure 3(b) shows discharge capacity during 100 cycling. The initial specific discharge capacity is ~6.4 F/g, while the specific capacity after 100 cycles is ~5.7 F/g. The specific discharge capacity increases up to ~17th cycle and then tend to decrease. This initial increase may be due to the unstable system, which is often founded in polymer system. The initial specific discharge capacity and the specific capacity after 100 cycles is almost the same. This is in good accordance with the results of CV. The initial area of CV and that of after 100 cycles is almost same although the curve exhibits small oxidation and

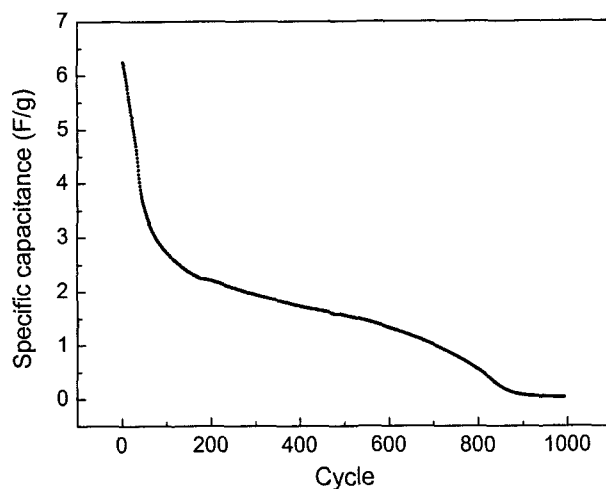


Figure 4. Cyclic capacitance of PPEPPO//PPEPPO redox supercapacitor after CV measurements (current density = 3 mA/cm²).

reduction peaks in CV after 100 cycles.

Figure 4 shows the cycle life of redox supercapacitor using PPEPPO electrode after CV measurements (current density 3 mA/cm², cut-off range 3.0~0.01 V). The initial specific discharge capacitance is ~6.3 F/g, while the specific capacitance at 1000th cycle is ~0.1 F/g. The discharge capacitance is abruptly decreased as the cycle repeated. Though the cyclic property is not good compared with other conducting polymer, it appears that the PPEPPO can be used as the electrode of supercapacitor, emissive material, as well as charge-transporting material in polymer LED.

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