Chemically synthesized high molecular weight poly(2,2′-dithiodianiline) (PDTDA) as a cathode material for lithium rechargeable batteries

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Abstract

A high molecular weight poly(2,2′-dithiodianiline) (PDTDA) was chemically synthesized by simple solution polymerization method. The weight average molecular weight ($\bar{M}_w$) was observed to be 420,000 by GPC analysis. The chemical structures of the undoped and the doped PDTDA were characterized by UV-Vis spectroscopy. It was confirmed that the S–S bonds within repeating units could be conserved well after polymerization and doping process by FTIR spectroscopic analysis. The PDTDA powders were found to have granular structure and the average particle size was 1 μm. The charge–discharge behavior of the Li/liquid electrolyte (1 M LiPF$_6$ in EC–PC)/PDTDA cell was also investigated with cycles.
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1. Introduction

Disulfide compounds have been introduced as a new organic/polymer cathode material in lithium batteries [1–5]. A series of compounds having –SH groups within the molecules are being considered as energy storage materials, whereby energy exchange occurs based on the reversible process because the cleavage and recombination of S–S bonds is expected to be easy:

$$2SH- \leftrightarrow -S-S-$$
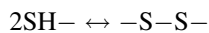
The theoretical capacity and energy density of these materials far exceed those of conventional battery materials as well as those of other candidate materials such as intercalation compounds and current conducting polymers. Among them, poly(2,2′-dithiodianiline) (PDTDA), a new material with polymer chains interconnected with S–S bonds, has been proposed by Naoi et al. They have shown that PDTDA can be synthesized to form an electro-active thin film by cycling potential electropolymerization method at the glassy carbon electrode surface. The discharge capacity and the energy density of the unit cell using the PDTDA as an active material of cathode were 270 Ah/kg and 675 Wh/kg, respectively [6].

In this study, we have tried to obtain high molecular weight PDTDA powders in large quantities using a new and simple chemical synthetic method by oxidation of the monomers, 2,2′-dithiodianiline (DTDA). Also, we have prepared polymeric electrode based on disulfide compound and investigated their electrochemical characteristics.

2. Experimental

2.1. Chemical synthesis of poly(2,2′-dithiodianiline) (PDTDA)

Ammonium persulfate was used as redox initiator. DTDA monomers were dissolved in 1 M HCl (aq.) solution at 80 °C. The initiator solution was slowly added by using a dropping funnel to the reactant solution with vigorous stirring. Then, the reaction mixture was agitated continuously for 12 h under N$_2$ atmosphere at 70 °C. The precipitated particles were filtered and washed with hot distilled water to remove any impurities. The filtered product (HCl doped PDTDA) was dried under vacuum for 48 h. The filtered powder was reduced by excess 0.1 N NH$_4$OH (aq.) solution to prepare undoped PDTDA [7]. The synthesized PDTDA was characterized by GPC, UV-Vis spectroscopy, FTIR spectroscopy, and SEM. The reaction scheme for the synthesis of the HCl doped and undoped PDTDA is given in Fig. 1.

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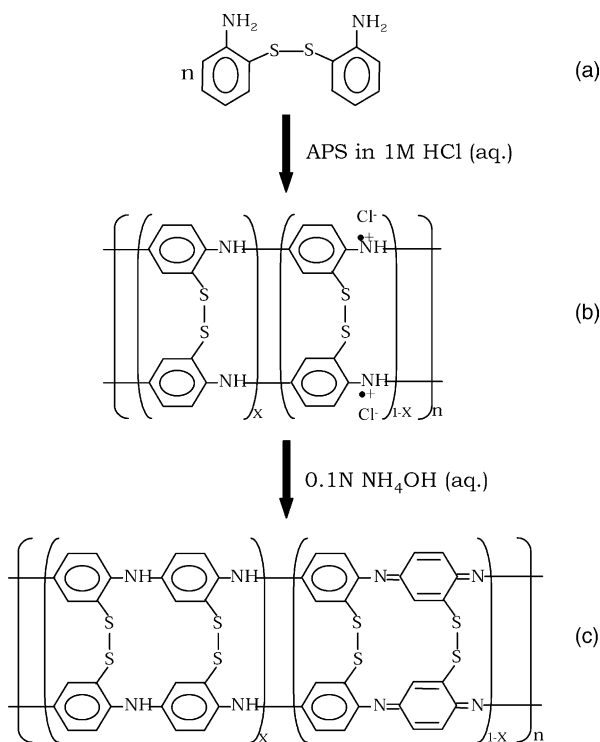*E-mail address:* lyg@etri.re.kr (Y.-G. Lee).

Fig. 1. The reaction scheme for chemical synthesis of poly(2,2'-dithiodianiline) (PDTDA): (a) DTDA monomer, (b) HCl doped PDTDA, (c) undoped PDTDA.

2.2. Preparation of unit cell

The coin-type unit cell ($2\,cm^2 \times 3.2\,mm$) was constructed for the charge–discharge test. Lithium foil was used for negative electrode and the HCl doped PDTDA mixed with super-P and PTFE was used for positive electrode. The 1 M $LiPF_6$ in EC/PC (1/1, w/w) was used as electrolyte solution. Cycling test of the unit cell was carried out galvanostatically between 2.5 and 3.8 V with the current density of 0.1 mA/cm^2.

3. Results and discussion

3.1. Optimal condition for chemical synthesis of PDTDA

Yields of synthesized products and various reaction conditions for the synthesis of PDTDA are summarized in Table 1. Trials 2–4 was conducted with various organic solvents at fixed other conditions, however, they are not chemically polymerized well. Trials 11, 12 and 13, 14 also showed no reaction behavior in synthetic medium. These all seem to be due to the poor reactivity and mobility of relatively heavy DTDA monomer in organic medium and at low reaction temperature.

On the other hand, trials 1, 5–9, 15 and 16 succeeded in getting dark and brownish powder showing high yield value (over 75%). In fact, we could observe that as the reaction temperature and time increased the yield increased. For monomer concentration and medium acidity, as the value increased, on the contrary, the yield decreased. From these results, it is found that the trial 1 is an optimal point among various reaction conditions for high yield of the product, PDTDA.

3.2. Molecular weight of the undoped PDTDA

Fig. 2 shows the chromatographic characteristic of a 0.5 wt.% undoped PDTDA (trial 1) solution in DMF. Unlike formerly reported bimodal molecular weight distributions determined in polyaniline (PANI) emeraldine base solutions [8–10], the multimodal distributions were obtained in PDTDA.

Table 1
Various reaction conditions and yields for chemical synthesis of PDTDA

Trial no.	Monomer concentration (wt.%)	Solvent	Medium acidity	Initiator	Reaction temperature (°C)	Reaction time (h)	Yield (%)
1	5	H_2O	1 M HCl	APS	70	24	97
2	5	MeOH	0.5 M $HClO_4$/0.5 M $LiClO_4$	$FeCl_3$	70	24	–
3	5	AN	0.5 M $HClO_4$/0.5 M $LiClO_4$	$FeCl_3$	70	24	–
4	5	NMP	0.5 M $HClO_4$/0.5 M $LiClO_4$	$FeCl_3$	70	24	–
5	5	H_2O	0.1 M HCl	APS	70	24	92
6	5	H_2O	5 M HCl	APS	70	24	97
7	5	H_2O	0.1 M H_2SO_4	APS	70	24	90
8	5	H_2O	1 M H_2SO_4	APS	70	24	80
9	5	H_2O	5 M H_2SO_4	APS	70	24	75
10	1	H_2O	1 M HCl	APS	70	24	45
11	10	H_2O	1 M HCl	APS	70	24	–
12	15	H_2O	1 M HCl	APS	70	24	–
13	5	H_2O	1 M HCl	APS	0	24	–
14	5	H_2O	1 M HCl	APS	25	24	–
15	5	H_2O	1 M HCl	APS	70	6	87
16	5	H_2O	1 M HCl	APS	70	12	96

APS: ammonium persulfate, AN: acetonitrile, MeOH: methanol, NMP: N-methyl pyrrolidone.
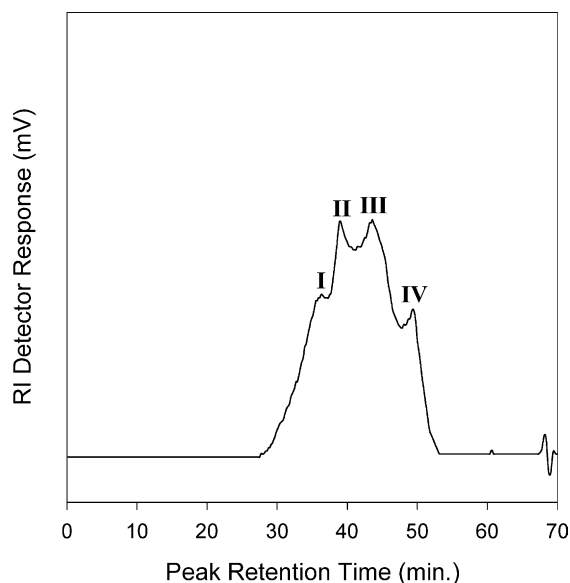
Fig. 2. GPC chromatogram of the undoped PDTDA (trial 1, carrier solvent: DMF, PS standard).

Fig. 3. UV-Vis spectra of the synthesized PDTDA in DMF (trial 1): (a) HCl doped PDTDA, (b) undoped PDTDA, (c) HCl doped PANI.

The chromatogram consists of two major peaks (peaks II and III) having weight average molecular weight ($\bar{M}_w$) on the order of 10^5 and two minor peaks of high molecular weight (peak I) on the order of 10^6 and low molecular weight (peak IV) on the order of 10^4. In peak I, various explanations have been offered for this observation. In general, it is believed that some form of aggregation occurs in the base polymer, accounting for the high molecular weight fraction. The aggregation is believed to be due to interchain interactions such as physical entanglements or hydrogen bonding [11,12]. It is expected that the two major peaks observed (peaks II and III) might be related to different structural characteristics, which could affect on the hydrodynamic volume of the PDTDA polymer chain. Thus, the chromatogram of PDTDA shows a fairly broad distribution (polydispersity index, PDI = 4.9) of molecular weight, with a calculated $\bar{M}_w$ of 420,000.

3.3. Structural characterization of the PDTDA

Fig. 3 shows the UV-Vis spectra of the HCl doped PDTDA (Fig. 3a), undoped PDTDA (Fig. 3b), and PANI emeraldine base (Fig. 3c) as a reference system. These spectra show bands at 305 nm (band I) and 480 nm (band II) for HCl doped PDTDA, 315 nm (band I) and 500 nm (band II) for undoped PDTDA, and 325 nm (band I) and 620 nm (band II) for PANI, respectively.

Generally, band I is attributed to $\pi \rightarrow \pi^*$ transition of the aniline unit and band II arises due to the creation of a localized molecular exciton with the electron on a quinoid moiety and a hole on the two neighboring benzoid moieties based on earlier studies of PANI [13]. A hypsochromic shift was observed for the PDTDA in comparison with that of PANI from 620 nm to shorter wavelength region. It could be
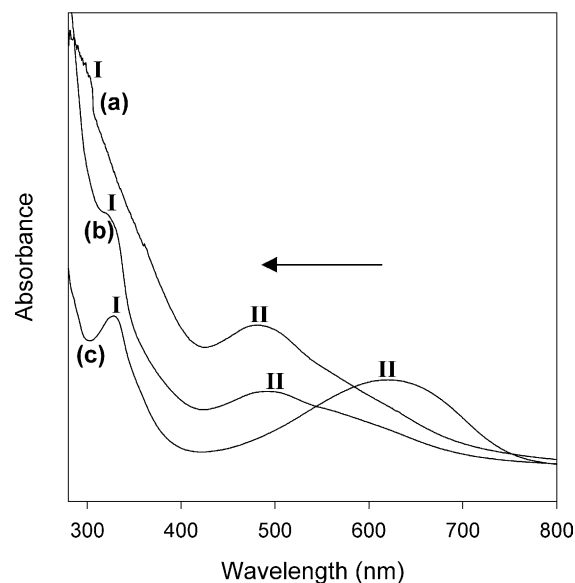
thought that the S–S bonds substituted on the benzene rings can cause an increase in the band gap due to their steric strain increasing the torsional angle between adjacent rings [14].

Fig. 4a–d represents the FTIR spectra of the HCl doped PDTDA, undoped PDTDA, and PANI emeraldine base, and DTDA monomer, respectively. The bands at 3414 and 3326 cm^{-1} as shown in Fig. 4d, which is assigned to the N–H stretching motion of –NH$_2$ in DTDA monomer, disappeared after formation of base polymer. All the polymers
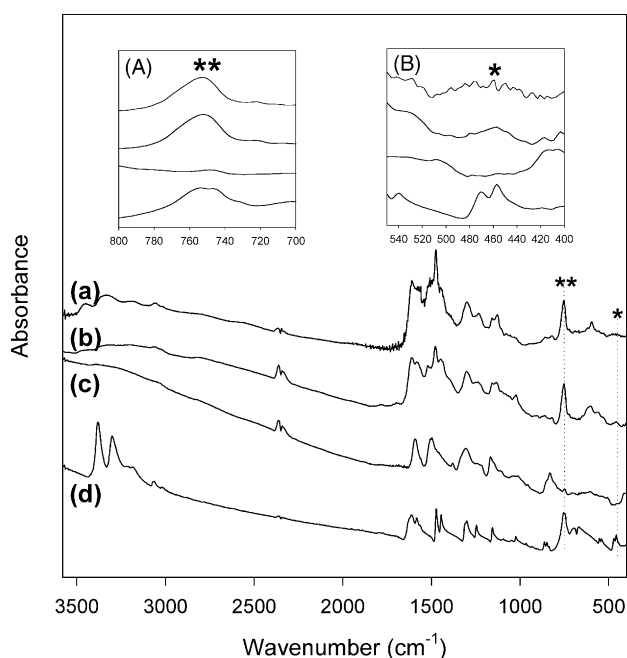

Fig. 4. FTIR spectra of the synthesized PDTDA and monomer (trial 1): (a) HCl doped PDTDA, (b) undoped PDTDA, (c) undoped PANI, (d) DTDA monomer.
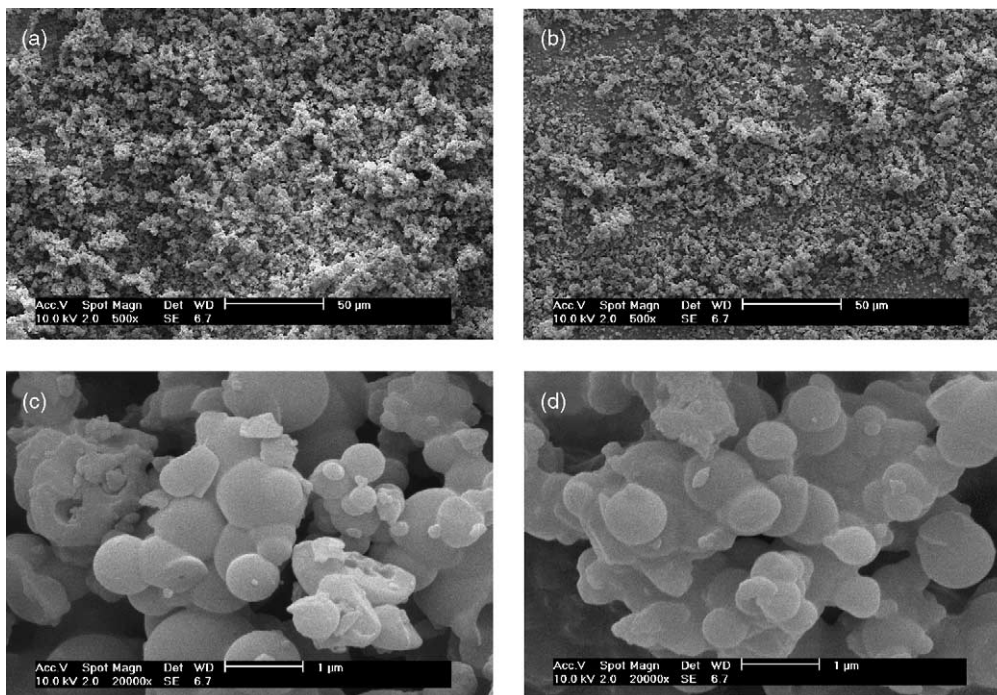
Fig. 5. SEM images of the synthesized PDTDA powders (trial 1): (a) undoped (500×), (b) HCl doped (500×), (c) undoped (20,000×), (d) HCl doped (20,000×).

showed bands characteristics of N–H bending and the symmetric component of the C–C (or C–N) stretching modes in the range 1250–1300 cm^{-1}. The bands at 1155 and 827 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending motion of quinoid and benzoid rings, respectively [15]. Bands at 1474 and 1604 cm^{-1} are assigned to the non-symmetric aromatic ring stretching modes. The higher frequency vibration arises from C=C stretching of quinoid rings while the lower frequency vibration from

benzoid ring units. In addition, the band at 1604 cm^{-1} can be assigned to the C=N stretching of the quinoid ring, which is overlapped with C=C stretching of the quinoid ring. The occurrence of these two bands clearly shows that these polymers are composed of amine and imine units. For the PDTDA, a band at 750 cm^{-1} corresponding to C–S bending (enlarged region A) and a weak band at 459 cm^{-1} for S–S bending (enlarged region B) are additionally present [16]. It can be noticed that the S–S linkages in DTDA monomers are
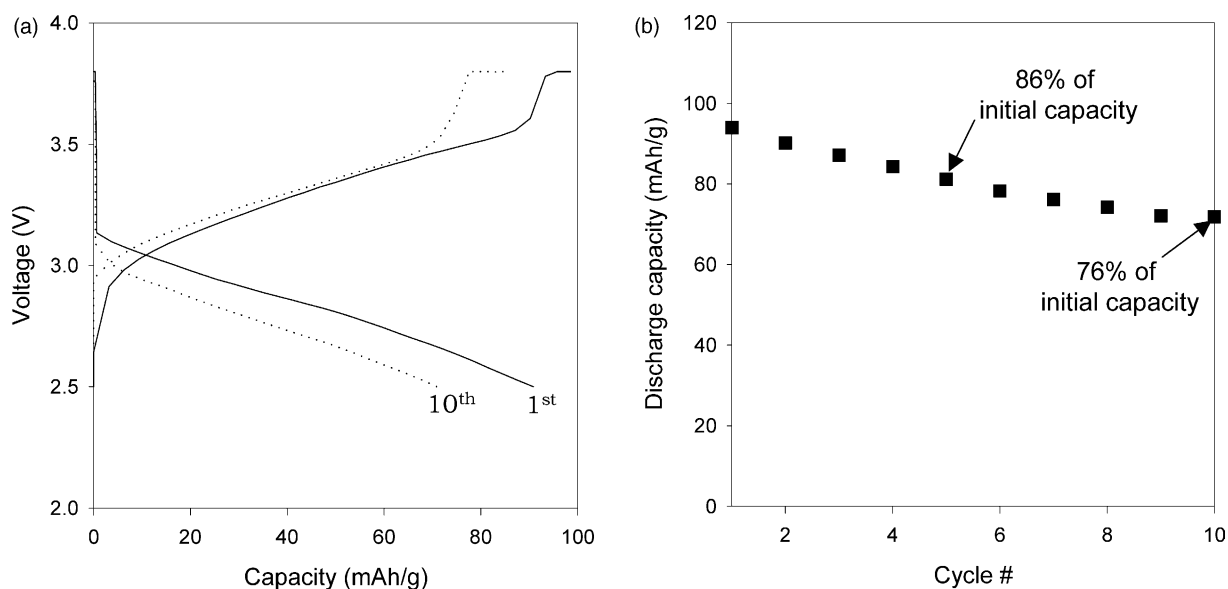

Fig. 6. Li/1M LiPF$_6$ in EC–PC/PDTDA unit cell (coin-type, 2 cm^2 × 3.2 mm, current density: 0.1 mA/cm^2): (a) charge–discharge curves of the unit cell, (b) discharge capacities as a function of cycle number.

well preserved after polymerization and doping process under such a severe reaction condition, acidic medium.

Fig. 5 is the scanning electron micrographs of the undoped ((a) and (c)) and HCl doped PDTDA powder ((b) and (d)). Both HCl doped and undoped PDTDA powder has granular structure and the average particle size was 1 μm.

3.4. Charge–discharge characteristics of the unit cell using the PDTDA as a cathode material

Fig. 6a shows the voltage profiles for the charge–discharge of the unit cell, Li/1M LiPF$_6$ in EC–PC/PDTDA. Cycling test of the unit cell (coin-type, $2\,cm^2 \times 3.2\,mm$) was carried out galvanostatically between 2.8 and 3.8 V with the current density of 0.1 mA/cm^2. The specific discharge capacities of the unit cell are plotted as a function of cycle number in Fig. 6b. The initial discharge capacity is 94 mAh/g and it falls to 82 mAh/g at 5 cycles and 71 mAh/g at 10 cycles. At 10 cycles, the discharge capacity is 76% of the initial value. It is required to enhance the slow reaction rate of disulfide bonds (cleavage and recombination), increase electrical conductivity of the PDTDA electrode, and reduce the internal resistance of the unit cell.

4. Conclusion

The high molecular weight PDTDA was easily synthesized by chemical method and the weight average molecular weight ($\bar{M}_w$) showed 420,000. A little different spectroscopic characteristic has been shown in UV-Vis and FTIR spectra from PANI and disulfide bonds (S–S) were still conserved after polymerization and doping process within PDTDA. The PDTDA powders were found to have granular structure and the average particle size was 1 μm. The initial

discharge capacity of Li/1 M LiPF$_6$ in EC–PC/PDTDA unit cell was 94 mAh/g.

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