

폴리퀴놀린 제조 및 전기화학적 특성

최경린, 이완진*

전남대학교 공과대학 응용화학공학과

(wjlee@chonnam.ac.kr*)

Preparation and Electrochemical Characteristics of Polyquinoline

Gyoung-Rin Choi, Wan-Jin Lee*

Faculty of Applied Chemical Engineering, Chonnam National University

(wjlee@chonnam.ac.kr*)

1. Introduction

Polyquinolines (PQ) in the conjugated polymers is an attractive material for an application of polymer battery, fuel cell and supercapacitor owing to good electrical conductivity and good thermal stability [1,2]. Even if rigid and highly crystalline, PQ is soluble in THF, m-cresol, chloroform and so on [3,4]. Furthermore, the electrical conductivity of PQ can be enhanced by doping materials such as using poly(sodium 4-styrenesulfonate). In this study, PQ was synthesized by a dehydrogenative polycondensation, a direct route to synthesize the non-substituted quinoline oligomers, of 1,2,3,4-tetrahydroquinoline (THQ) by using ruthenium sulfide precursor [5]. The electrochemical property of PQ was studied.

2. Experimental

2.1 Preparation of ruthenium sulfide catalyst precursors.

A three-neck round-bottom flask equipped with a condenser and an inert gas bubbler was charged with lithium sulfide and absolute ethanol, and the ammonium hexachlororuthenate(IV) was added to the above flask. This mixture was stirred at 40 °C in the nitrogen carrier gas for 12h. The suspension were filtered, washed repeatedly with ethanol, and dried to give black solids of ruthenium sulfides.

2.2 Preparation of rigid-rod polyquinoline

PQ was prepared by a dehydrogenative polycondensation of 1,2,3,4-tetrahydroquinoline (THQ) by using ruthenium sulfide precursor. This method is a direct route to synthesize the non-substituted quinoline oligomers. A three-neck round-bottom flask equipped with a condenser and an inert gas bubbler was charged with a solution of 1,2,3,4-tetrahydroquinoline, which was thoroughly mixed with a 3 wt.% ruthenium sulfides. The suspended mixture was maintained in an argon carrier gas at atmospheric pressure and heated at 210 °C for 4 h and then at 270 °C for 1 day. After that, the dark solid was obtained by cooling at room temperature. The dark solid was changed as the suspension form by stirring for overnight at room temperature in a solution mixture of diethylether-hexane(1:5). The resulting insoluble solid was filtered and washed over several times by using a new solution mixture of diethylether-hexane(1:5). The solid was divided into the low molecular weight quinoline oligomers and the high molecular weight ones (PQ) by the methylene chloride extraction.

2.3 Preparation of doped polyquinoline

The high molecular weight PQ was doped with poly(sodium 4-styrenesulfonate) in THF for 18 h, and then dried in vacuum oven for 7 h. This method is n-type doping. Lewis acids, such as arsenic pentafluoride and iodine, are poor oxidants for polyquinoline, probably as a result of Lewis salt formation with the nitrogen lone pair making it even more difficult to remove an electron from the quinoline ring.

2.4 Preparation of PQ electrode

The cell was consisted as a system, Al mesh collector/(PQ + PVDF)//1M LiPF₆ + EC/DMC//Li metal/Ni mesh collector. The cathode material was prepared as follows. At first, PQ was dissolved in THF, and then mixed PVDF solution and carbon conductor. Carbon black (Super-P, MMM Carbon Co.) was used as a conducting agent and PVDF was used as a binder. Al mesh was used as a cathode collector, and Ni mesh was used as an anode collector. The slurry solution cast on Al mesh, dried solvent on the vacuum oven, and then the dried electrode was used to do hot pressing at 70 °C. The ratio of PQ, binder and conducting agent was 80: 10: 10 by wt.% Li metal on Ni mesh was used as an anode, and the porous polypropylene film was used as a separator, and 1 M LiPF₆ dissolved in EC/DMC was used as the organic liquid electrolyte. In order to test charge-discharge properties, two electrodes were assembled as a sandwich type and enveloped in a laminated-aluminum pouch in glove box. The half cell was consisted as three electrodes, WE, CE (Li) and RE (Li), to obtain cyclic voltammograms.

3. Results and discussion

The electrical conductivity of PQ was measured by the four probes method. PQ was doped by poly(sodium 4-styrenesulfonate). The electrical conductivities of doped PQ was approximately 10 S/cm. Fig. 1 is 300MHz 2D homonuclear-corrected ^1H NMR spectrum (Varian Co. Unity Plus-300) of quinoline oligomers in CDCl_3 . It can be seen that the structure of quinoline oligomers was formed as the ratio of 2,3-quinoline to 2,6-quinoline was 1 : 9. Fig. 2 shows the images of scanning electron microscopy (SEM) for the doped PQ. The PQ particles are shown as small spherical granules with well-developed micro porosity as well as three-dimensional network. This formation might be the relationship with the enhancement of electrical conductivity and electrochemical characteristics. Fig. 3 shows the impedance spectra by the Nyquist plots in the range of 1 Hz to 1 MHz for PQ electrode. The shape of the semicircle in the higher frequency region represents the charge-transfer process of the cathode originating in doping and de-doping of the dopant, while the inclined line in the lower frequency region represents the mass transfer of the dopant in cathode. Fig. 4 is the cyclic voltammograms of PQ electrode at scan rate of 20 mV/S in the range of 0 to 4V. The oxidation and reduction peak are observed at about 1.2 and 1.5 V, respectively. The current range changed slightly with number of cycles as shown at the typical conducting polymer. Taken as a whole, the cyclibility was stable. In addition, it can be guessed that PQ is the good candidate as the electrode material.

4. Conclusions

PQ was prepared by a dehydrogenative polycondensation of 1,2,3,4-tetrahydroquinoline (THQ) by using ruthenium sulfide precursor. The structure of quinoline oligomers was formed as the ratio of 2,3'-quinoline to 2,6-quinoline was 1 : 9. PQ was doped by poly(sodium 4-styrenesulfonate). The electrical conductivities of doped PQ was about 10 S/cm. The cyclibility of the doped PQ stable.

Acknowledgement

Support for this work was provided by KOSEF under Grant number R01-2003-000-10100-0.

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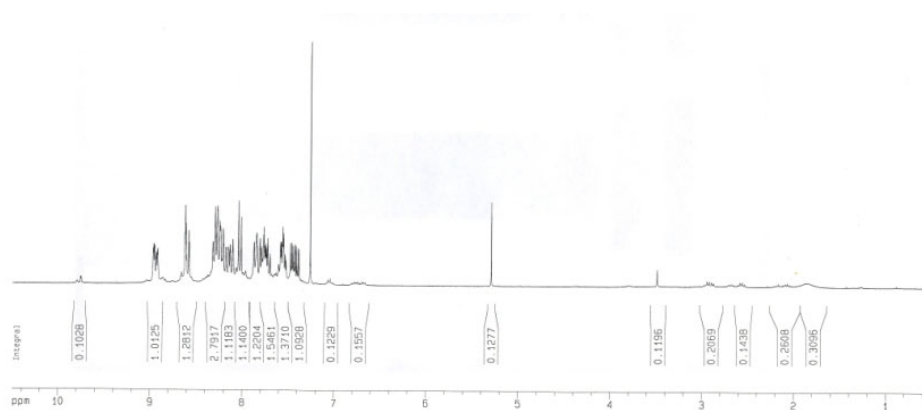


Fig. 1. 300MHz 2D homonuclear-corrected ^1H NMR spectrum of quinoline oligomers in CDCl_3

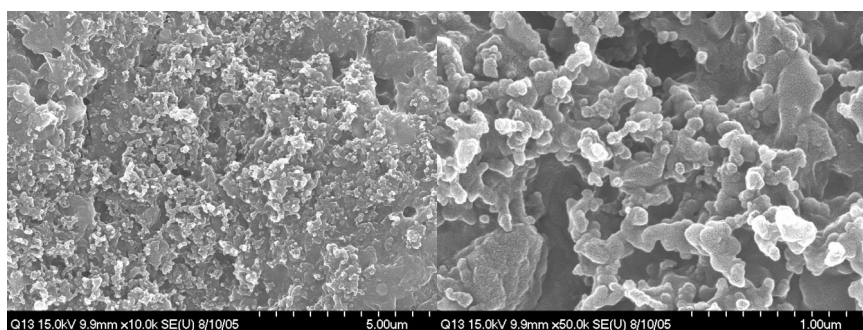


Fig. 2. The SEM images of PQ

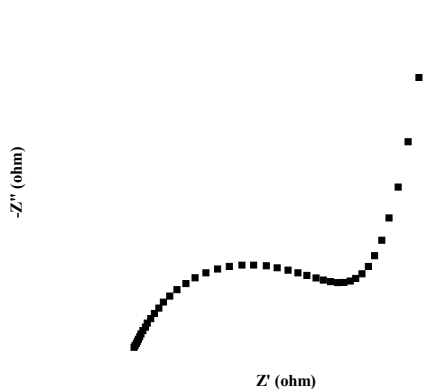


Fig. 3. The impedance spectra of PQ electrode

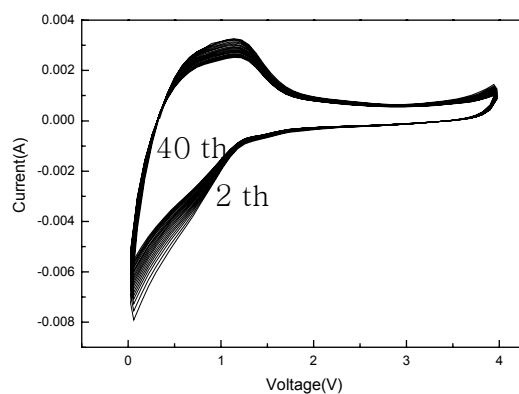


Fig. 4. The cyclic voltammograms of PQ electrode at a scan rate of 20mV/S