

리튬이차전지 양극재인 유기라디칼 고분자의 산화법에 대한 연구

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Investigation of Oxidation Methods of Organic Radical Polymer for Cathode Material in Lithium Ion Batteries

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초록: 라디칼 고분자화 반응 후 산화법을 이용하여 나이트록실 라디칼 고분자를 제조하였다. 두 가지 방법으로 산화된 라디칼 고분자의 라디칼 농도를 electroparamagnetic resonance spectroscopy(EPR) 법과 UV-visible absorption (UV-vis) 방법을 통하여 측정하고 이를 통해 과산화수소수- Na_2WO_4 법으로 산화하였을 때 라디칼 농도가 97.6% 정도 높게 얻어짐을 확인하였다. 또한 UV-vis 법은 정량적인 분석이 어려우나 대략적인 라디칼 형성 정도를 평가하는데 유용함을 확인하였다. 제조된 유기라디칼 고분을 리튬이온전지 양극재로 적용한 결과 우수한 용량, 초기효율, 높은 속도 특성을 가짐을 알 수 있었다.

Abstract: An organic radical polymer (ORP) was prepared by radical polymerization and following oxidation into nitroxyl radical. Two different oxidation methods were employed and their radical concentrations were measured using electroparamagnetic resonance spectroscopy (EPR) and UV-visible absorption (UV-vis) spectroscopy. From these measurements, H_2O_2 - Na_2WO_4 oxidation method exhibited a complete oxidation, which resulted in 97.6% spin concentration. Also, it was revealed that convenient and cheap UV-vis measurement was useful for preliminary radical concentration comparison. After applied as a cathode material in lithium ion batteries, ORP electrode showed a high initial capacity (110 mAh g^{-1}), a good initial efficiency (96%), a very high rate performance (70% charging during 1.2 min) and stable cycle performance.

Keywords: organic radical polymer, oxidation, nitroxyl radical concentration, cathode, lithium ion batteries.

Introduction

Recently, demands for high power energy source have been increased due to the development of hybrid electric vehicle (HEV), electric vehicle (EV) and wireless charging batteries for mobile phones.^{1,2} Organic radical polymers (ORPs) have been considered as one of the most promising cathode materials for extremely high power lithium ion batteries (LIBs).³⁻⁵ Especially, ORPs are based on the electrochemical reaction of nitroxyl radical with the anion at 3.5 V vs. Li/Li^+ , which produced oxo-ammonium cation.⁴ Because this reaction is very

similar to surface confined pseudocapacitive reaction of metal oxide, an extremely fast charging/discharging performance has been observed in this material (about 70% charging for 1 min).^{4,5} In addition, this charge storage reaction is highly reversible, indicative of very long cycle life. As a typical polymer for ORP, poly(2,2,6,6-tetramethyl-1-piperidinyloxy-4-yl methacrylate) (PTMA) has been widely investigated, which has additional strong merits such as high energy density, non-toxicity, high safety and good fabrication property.^{6,7} Using radical polymerization, especially, PTMA polymer has been prepared. In this method, 2,2,6,6-tetramethylpiperidine-4-yl methacrylate (TMA) monomer was polymerized using initiator, which produced polymerized-TMA (p-TMA).^{3,4} By following catalytic oxidation of p-TMA, PTMA with nitroxyl

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radical was prepared.⁵ In this preparation, oxidation process is very important since the radical concentration of PTMA is determined by this process. In spite of several oxidation methods suggested in the literatures, comparison between proposed methods has been not investigated.^{7,8} Hence, direct comparative study about oxidation methods is highly required. In order to measure the radical concentration, generally, electron paramagnetic resonance (EPR) spectroscopy has been employed, which required an expensive apparatus and delicate sample preparation.^{10,11} Using more convenient measurement method of radical concentration, therefore, comparison of oxidation methods is highly required.

In our study, TMA is polymerized using radical initiator to obtain p-TMA. The prepared p-TMA is oxidized using two different methods, which produces PTMA polymer with nitroxyl radical. From this comparative study, it can be determined which oxidation method is more effective using our prepared p-TMA. For the purpose of suggestion of more convenient measurement method of radical concentration, as-prepared PTMA is measured by UV-visible absorption and conventional EPR spectroscopy. After comparison of radical concentration, PTMA with higher spin concentration is applied into cathode in lithium ion batteries and the electrochemical performance is investigated.

Experimental

Preparation of Polymerized TMA. 2,2,6,6-Tetramethylpiperidine-4-yl methacrylate (TMA) monomer was polymerized using 2,2'-azobisisobutyronitrile (AIBN) radical. About 1 mol% of AIBN initiator and 5 g of TMA monomer was dissolved in 10 mL of ethanol. The monomer dissolved in ethanol was taken in a polymerization tube and tightly closed with silicone tubes. With N₂ gas purging for 15 m and the polymerization tube was kept oil bath maintained at 75 °C. After 24 h, the reaction mixture was dissolved in diethyl ether and precipitated using hexane solution. The precipitate was dried at 60 °C under vacuum, which produced p-TMA (Yield 90%).⁴

Oxidation Using CPBA. The p-TMA was oxidized using following catalyst such as chloroperoxy benzoic acid (CPBA) and NaWO₄. For oxidation using CPBA, p-TMA dissolved in dichloromethane was taken in 100 mL RB flask. To this, CPBA dissolved in dichloromethane was slowly added. Then the reaction mixture was allowed to stir for overnight. After this, the reaction mixture was precipitate in methanol and dried at 60 °C for 24 h under vacuum (Yield 60%).^{4,5}

Oxidation Using NaWO₄. p-TMA dissolved in ethanol was taken in 100 mL RB flask. To this, 5 mol% of NaWO₄ was added at 60 °C. Then H₂O₂ (50 wt% in water) was slowly added using syringe pump and the reaction mixture was further allowed to stir for 24 h at 60 °C. After evaporation of the obtained liquid, the viscous red polymer was precipitated in hexane. The red precipitate was dried at 60 °C for 24 h under vacuum (Yield 85%).^{8,9}

Materials Characterization. IR spectra were obtained using KBr pellet in Bruker FTIR spectrometer. UV-visible absorption spectra were obtained after dissolution in dichloromethane using Shimadzu UV2100 UV-Vis Spectrophotometer. For nuclear magnetic resonance measurement of TMA and p-TMA, Bruker Avance-700FT-NMR spectrometer was used after dissolving them in DMSO solvent. X-band electron paramagnetic resonance (EPR) spectra were recorded at liquid nitrogen temperature using a JEOL spectrometer (model JES-FA100). As a standard organic radical material, 2,2,6,6-tetramethylpiperidine-1-piperidinyloxy (TEMPO) was used.

Electrode Fabrication and Cathode Application. For the preparation of composite anodes, PTMA were mixed with a conducting agent (Super P) and PVDF (polyvinylidene difluoride) binder with a weight ratio of 8:1:1. The mixture was then dispersed in NMP and spread on Al foil (apparent areas of 1 cm²), followed by pressing and drying at 120 °C for 12 h. The half cell characteristics were analyzed with a coin-type (CR2016) two electrode cell in which lithium foil (Cyprus Co.) was used. The electrolyte was 1.0 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio) (Tomiya Co.). To investigate the cathode performance in a lithium ion battery, a galvanostatic charge-discharge test in a voltage range of 3.0 to 4.3 V vs. Li/Li⁺ was conducted. For the rate performance measurement, the current was varied from 1 to 50 C. The cycle performance for 50 cycles was recorded under 1 C rate at ambient and high temperature (50 °C). All of the electrochemical measurements were made using a WBCS-3000 battery cyler (WonA Tech Co.).^{10,11}

Results and Discussion

In Figure 1, ¹H NMR spectra of TMA and p-TMA are displayed. The chemical shift (δ) at 6.0 and 5.6 in Figure 1(a) corresponded to hydrogen splitting in -C=CH₂ structure in TMA, which disappeared after polymerization in p-TMA as shown in Figure 1(b). Splitting at 5.2 δ was due to -N-H in TMA. Also, several splitting peaks from 2.0 to 1.2 δ was associated with

aliphatic hydrogen in CH_2 and CH_3 groups present in the piperidine moiety in TMA.¹² After polymerization of TMA, chemical shifts associated with -N-H was maintained but those of aliphatic hydrogen were changed due to polymerization effect.

Figure 2 shows IR spectra for TMA and p-TMA. In this figure, absorbance peaks appeared at 2924, 2855, 1458 and 1376 cm^{-1} , which corresponded to the aliphatic hydrogen for C-H stretching in $-\text{CH}_3$ and $-\text{CH}_2$ in TMA.¹³ These bands are commonly observed in TMA and p-TMA as shown in Figure 1. Also, the peaks near 1029 and 1300 cm^{-1} were attributed to $-\text{C}-\text{O}$ and $-\text{C}-\text{N}$ vibration in TMA and p-TMA, respectively. The band around 3500 cm^{-1} corresponded to N-H stretching in two molecules.¹³ In IR spectra of p-TMA, particularly, the peak at 1601 cm^{-1} associated with C=C stretching mostly disappeared in p-TMA, indicating that TMA was polymerized. From above NMR and IR measurements, it was confirmed that polymerization using AIBN initiator was well conducted.

Using two oxidants such as CPBA and Na_2WO_4 , the prepared p-TMA was oxidized. During this process, piperidine moiety (-N-H) is converted to nitroxyl radical (-N-O \cdot). After oxidation using these two oxidants, radical concentration was measured using two methods; EPR and UV-vis. method. The

former was based on the paramagnetic property from unpaired electron in nitroxyl radical.¹⁰ Here, TEMPO molecule was used for estimation of relative radical concentration under the assumption that TEMPO contains one nitroxyl radical per molecule. As seen, triplet hyperfine splitting was observed when g is 2.0057, which is due to the oxygen-centered unpaired electron in TEMPO.¹⁴ For $\text{Na}_2\text{WO}_4\text{-H}_2\text{O}_2$ oxidation process, a clear single broad EPR signal was observed, which is ascribed to the local concentration of the unpaired electron within polymer structure. In addition, the peaks broadening in EPR spectra was due to intrachain dipole-dipole interaction within polymer.⁴ However, the peak intensity was very weak for CPBA oxidation method, indicative of low spin concentration. From the double integration of EPR spectra, the spin concentrations of three samples were estimated and compared with TEMPO result as listed in Table 1. Relative spin concentration values for $\text{Na}_2\text{WO}_4\text{-H}_2\text{O}_2$ and CPBA were 97.6 % and 20.5%, respectively. This large difference in spin concentration reflected that the former oxidation method is more efficient under our experimental condition. In the similar equivalent addition of oxidants, it is assumed that H_2O_2 oxidant became more reactive on the surface of Na_2WO_4 catalyst. In the case of CPBA, however, reactivity was possibly limited without such catalyst addition.

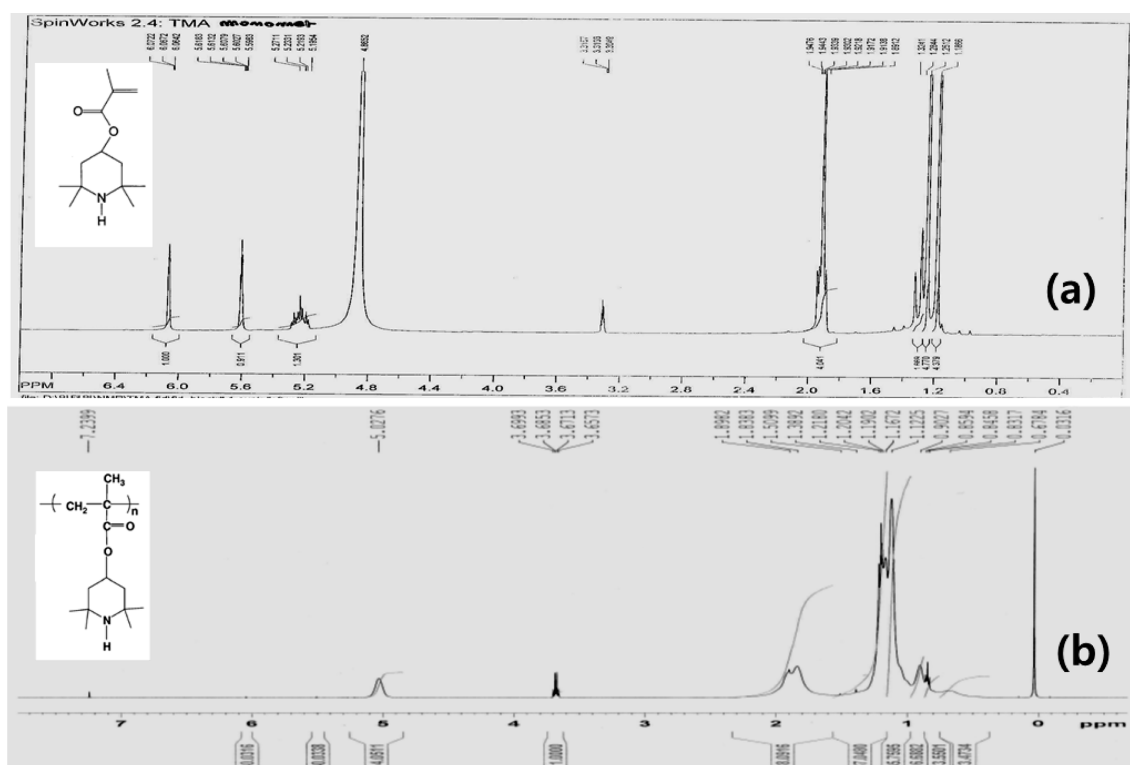


Figure 1. NMR spectra of TMA (a); p-TMA (b).

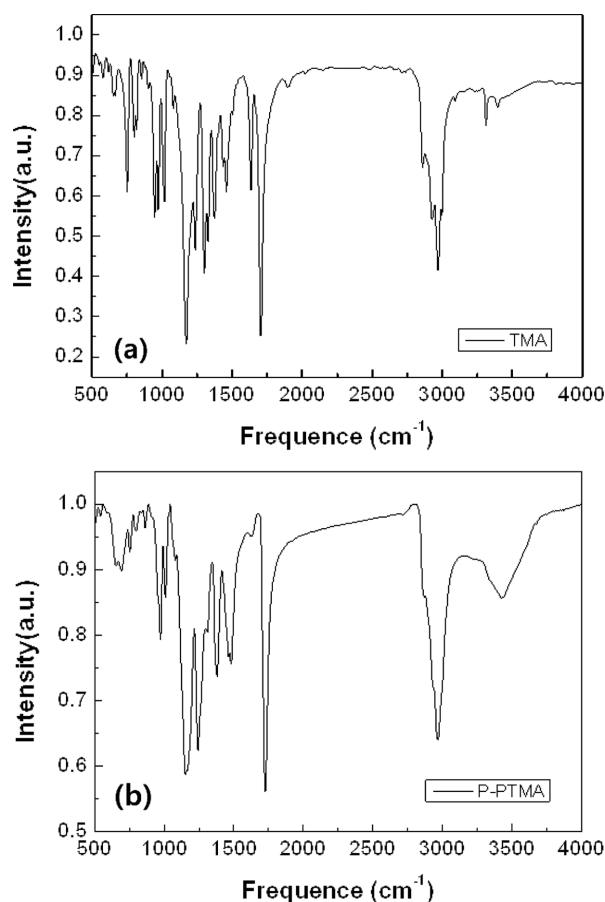


Figure 2. FTIR spectra of TMA (a); p-TMA (b).

Table 1. Results of Double Integration from EPR Spectra and Estimation of Relative Spin Concentration

	Area per weight /g ⁻¹	Area per mol /mol ⁻¹	Relative spin concentration/%
TEMPO	2198.9	12.7	100
PTMA-Na ₂ WO ₄	3000.0	12.4	97.6
PTMA-CPBA	629.4	2.61	20.5

For comparison with EPR method, spin concentration was measured using UV-vis method. In this method, TEMPO or as-prepared PTMA polymers were dissolved in dichloromethane solution. Typically, it is well-known that nitroxyl radical can absorb light at 460 nm wavelength. In Figure 3(b), absorption spectra of UV-vis were plotted as change of wavelength. As seen, almost identical spectra were observed in both PTMA polymer oxidized by Na₂WO₄-H₂O₂ and TEMPO, indicative of similar radical concentration. However, the peak intensity of PTMA by CPBA is very weak, reflecting low radical concentration. While spin concentration can be quantitatively estimated from EPR spectra, it seems hard to calculate spin

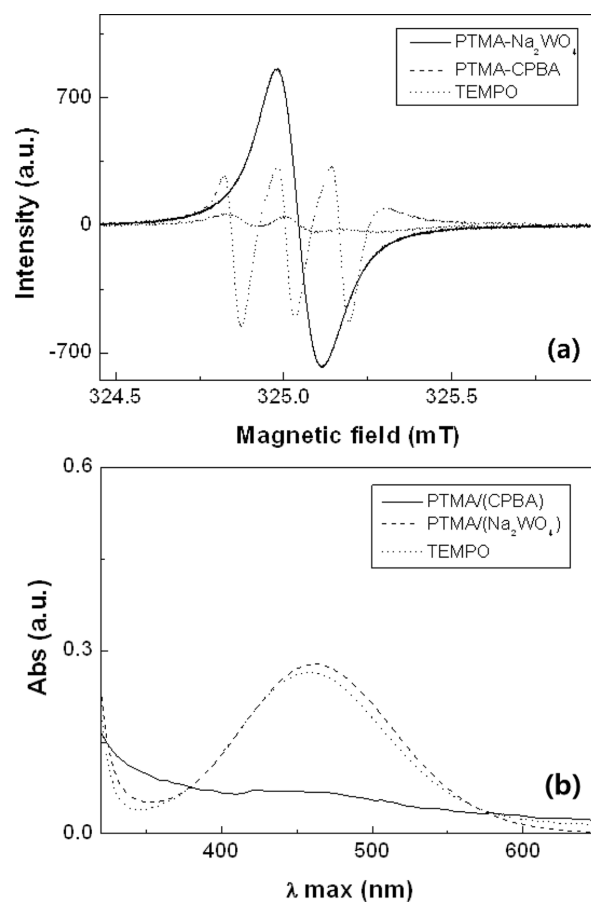


Figure 3. (a) EPR; (b) UV-vis results of TEMPO (dot line), PTMA-CPBA (dash line) and PTMA-Na₂WO₄ (solid line).

concentration from UV-vis spectra, which is ascribed to large peak broadening and increase of background absorption intensity according to decrease of wavelength. However, UV-vis method is inexpensive and convenient when compared with EPR method because the latter required a highly delicate and expensive apparatus. Hence, UV-vis measurement of nitroxyl radical in PTMA can be utilized for preliminary comparison of nitroxyl radical concentration.

The cathode performance of the PTMA polymer oxidized by Na₂WO₄-H₂O₂ was investigated. In Figure 4(a), the galvanostatic charge-discharge patterns are displayed. At a current rate of 1 C, a characteristic plateau associated with faradaic reaction of the nitroxyl radicals was observed at 3.6 V vs. Li/Li⁺. During this reaction, nitroxyl radical is oxidized into oxoammonium cation with electron loss.^{3,4} Also, the PTMA polymer electrode exhibited a high initial efficiency of 96% with discharge capacity of 110 mAh g⁻¹ at 1 C rate. Because theoretical capacity of PTMA is 111 mAh g⁻¹, this high discharge capacity of PTMA reflects that PTMA was completely oxidized, which

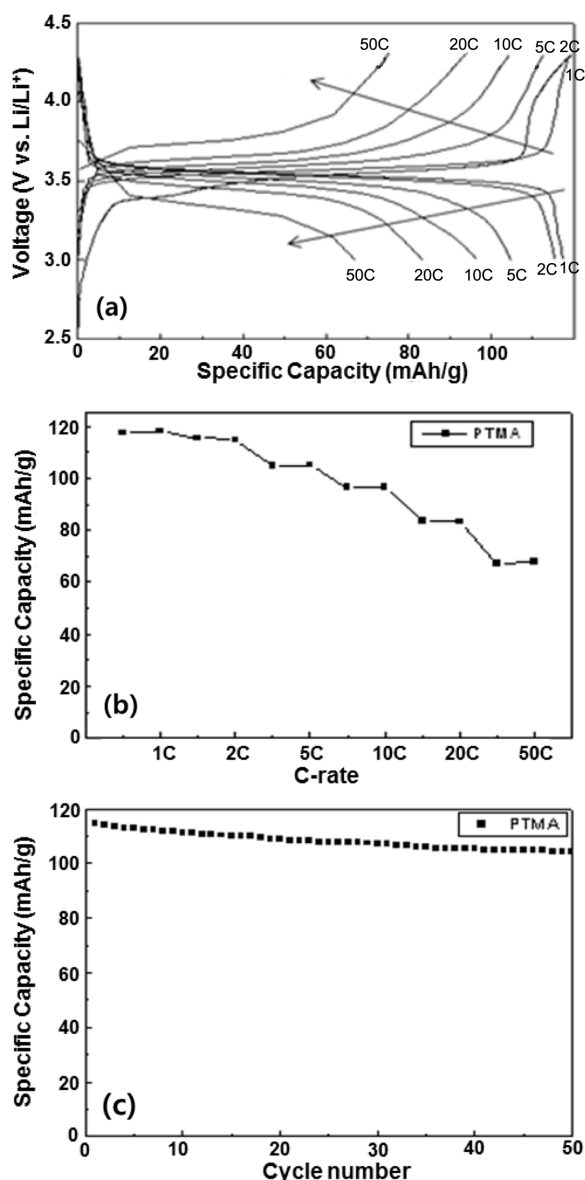


Figure 4. (a) Galvanostatic charge-discharge patterns of PTMA- Na_2WO_4 cathode according to increase of C-rate; (b) Change of discharge capacity against C-rate change; (c) Cycle performance under 1 C rate until 50 cycles.

corresponded spin concentration comparison in Figure 3.¹⁰ In Figure 4(a), furthermore, the rate capability patterns of PTMA were plotted. The characteristic plateau at 3.6 V was maintained until 10 C rate and afterward a slight voltage deviation from this plateau was observed. However capacity retention under 50 C rate was about 67%, which indicated that the about 70% capacity can be charged and discharged within 1.2 min. This extremely fast charging/discharging property is characteristic for PTMA polymer cathode. In Figure 4(c), the capacity retention was plotted against cycle number. The capacity

retention was as high as 90% after 50 cycles at room temperature. This stable cycle performance is due to well-developed polymer structure and non-destructive charge/discharge reaction of nitroxyl radical with Li^+ .¹⁵

Conclusions

TMA monomer was polymerized using radical polymerization. This polymer was oxidized using $\text{Na}_2\text{WO}_4\text{-H}_2\text{O}_2$ and CPBA oxidant in order to obtain PTMA. From EPR and UV-vis radical measurement method, the former oxidation method produced complete oxidation of PTMA with high radical concentration. As cathode material, PTMA by $\text{Na}_2\text{WO}_4\text{-H}_2\text{O}_2$ produced a high capacity, good initial efficiency, extremely high rate performance and stable cycle performance.

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