

5,7,12,14-Pentacenetrone as a High-Capacity Organic Positive-Electrode Material for Use in Rechargeable Lithium Batteries

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The performance of 5,7,12,14-pentacenetrone (PT) as an organic active material for rechargeable lithium batteries was investigated. A positive-electrode incorporating PT showed an initial discharge capacity of more than 300 mAh/g_(PT) with an average voltage of 2.1 V vs. Li⁺/Li. The obtained discharge capacity corresponded to a four-electron redox behavior and is more than twice that of a conventional positive-electrode material, lithium cobalt oxide (LiCoO₂). A quantum calculation based on the density functional theory (DFT) was also performed to clarify the mechanism of the electron-transfer in the PT crystal.

Keywords: Organic cathode material, Lithium ion battery, High capacity, Multi-electron redox, DFT calculation

1. INTRODUCTION

Rechargeable lithium batteries consisting of a metal-oxide based positive-electrode and a graphite based negative-electrode are currently common electric sources. As positive-electrode materials, rare metal-free and low-polluting safe materials are recently becoming more desirable, due to concern about their resource scarcity and environmental effects. One of the candidate categories is a series of redox active organic materials that do not contain any scarce metal resources [1–6].

Several types of organic positive-electrode materials have already been proposed. Among them, we have focused our attention on the quinone-based materials, since the quinone skeleton undergoes a two-electron redox reaction [7,8]. The simplest quinone compound, 1,4-benzoquinone, has a high theoretical capacity of up to about 500 mAh/g, although the use of 1,4-benzoquinone itself is practically difficult because it is prone to sublimation. Several scientists have tried to apply the redox of the quinone skeleton to batteries through the synthesis of various polymers [3,9,10]; however,

the desired two-electron redox reaction per quinone skeleton has not been realized in most cases, i.e., the observed capacities of these polymers are much smaller than the theoretical values.

Recently, instead of using high-molecular-weight compounds (e.g., polymers), another approach has been investigated, in which low-molecular-weight crystalline organic compounds are used [7,8,11–14]. In this new approach, each molecule is immobilized by an intermolecular attraction such as van der Waals' force, π - π interaction, and hydrogen bonding. Redox active low-molecular-weight organic compounds reported so far tend to show high utilization ratios during the charge/discharge processes [7,8,11–14]. Anthraquinone (AQ, $C_{14}H_8O_2$), a polycyclic quinone derivative having an anthracene skeleton, also shows a high capacity close to its theoretical value; however, the capacity rapidly decreases upon cycling because the AQ-related molecules leach away from the electrode and dissolve into the electrolyte solution [12]. Based on this result, we consider that the enlargement of the π -system of the quinone derivatives can be an effective way to suppress the dissolution of the quinone derivatives and improve the cycle stability. In the present study, we focused on a larger polycyclic quinone derivative, 5,7,12,14-pentacenetetrone (PT, $C_{22}H_{10}O_4$), as a novel quinone-based active material (Figure 1). PT is a planar molecule and has a highly developed π -system which can induce a strong π - π intermolecular interaction in the crystal. This paper presents the preliminary results of the PT battery performance.

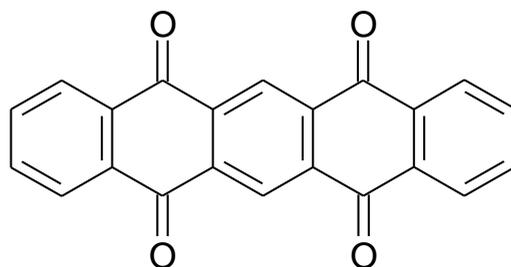


Figure 1. Chemical structures of 5,7,12,14-pentacenetetrone (PT).

2. EXPERIMENTAL

5,7,12,14-Pentacenetetrone (PT) (Tokyo Kasei Corp.) was purchased and used without further purification. The density calculated from the crystallographic data of this compound was 1.48 g/cm^3 [15].

Coin-type sealed cells for the battery tests were prepared as follows. A positive-electrode composite sheet was first prepared by mixing the PT powder, acetylene black as the conductive additive, and polytetrafluoroethylene as the binder in the weight ratio of 4:5:1 using a mortar and pestle. The sheet was then attached to an aluminum mesh current collector, and the resultant positive-electrode was dried. The amount of active material deposited was approximately 3 mg per electrode. The prepared positive-electrode and a lithium metal negative-electrode were placed in an IEC R2032 coin-type cell case with a glass filter as the separator. After the electrolyte of γ -butyrolactone

containing lithium bis(trifluoromethanesulfonyl)imide (1.0 mol/L) (0.2 mL) was added, the cell case was sealed.

In the charge/discharge cycle-life test, the prepared coin-type cell was galvanostatically discharged at a current density of 20 mA/g_(PT) with a cutoff voltage of 1.5 V vs. Li⁺/Li, and charged at the same current density with a cutoff voltage of 3.0 V vs. Li⁺/Li. The charge/discharge test was performed by a computer-controlled system (ABE System, Electrofield Co., Ltd.) equipped with a thermostatic chamber at 30°C. In this paper, the obtained capacities are described as the value divided by the weights of the active materials.

A quantum chemistry calculation based on the density functional theory (DFT) was performed using the GAUSSIAN 03 program package [16]. A single point calculation using a B3LYP hybrid functional [17,18] with a split valence basis set of 6-31G(d) was carried out on clusters composed of ten PT molecules extracted from the crystallographic coordinates [15].

3. RESULTS AND DISCUSSION

Figure 2 shows the initial discharge curve of the positive-electrode prepared using PT.

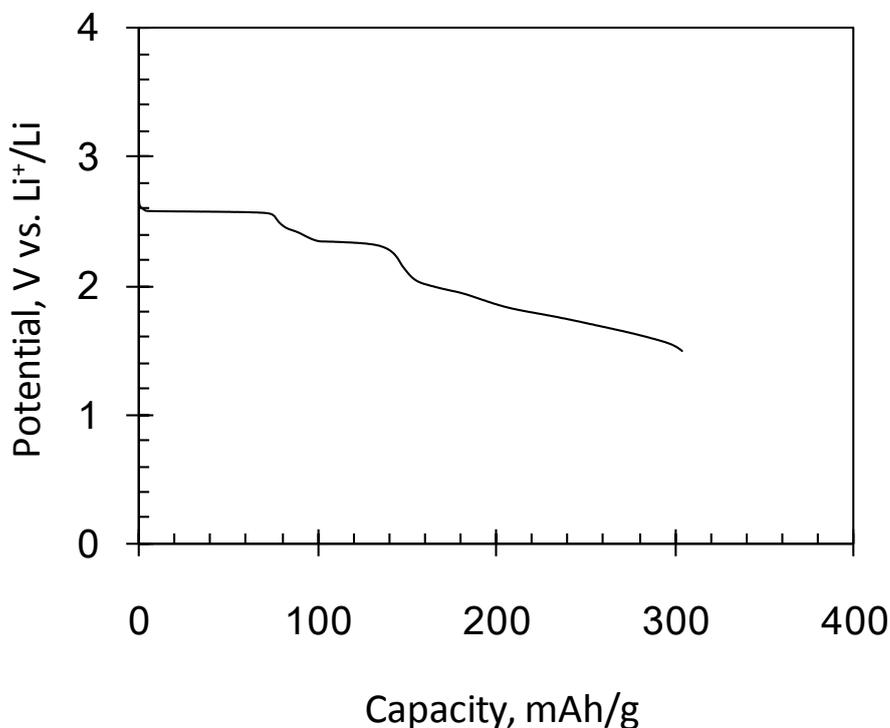


Figure 2. Initial discharge curve of the electrode using PT. (Current density for PT: 20 mA/g, temperature: 30°C)

The electrode showed a characteristic discharge curve consisting of several plateau voltage regions at around 2.6, 2.3, and 1.8 V vs. Li⁺/Li. The observed discharge capacity of 304 mAh/g is

close to the theoretical value of 317 mAh/g based on the assumption of the full four-electron transfer redox reaction of PT (Figure 3). The obtained discharge capacity is more than twice the practical capacity of the conventional LiCoO_2 (~140 mAh/g). In addition, the obtained value is greater than the theoretical capacity of AQ (257 mAh/g). While the average voltage of 2.1 V vs. Li^+/Li is lower than the voltages of conventional positive-electrode materials, such as LiCoO_2 (3.8 V vs. Li^+/Li) and LiFePO_4 (3.4 V vs. Li^+/Li), it is comparable to the voltages of sulfide-based active materials (about 2 V vs. Li^+/Li).

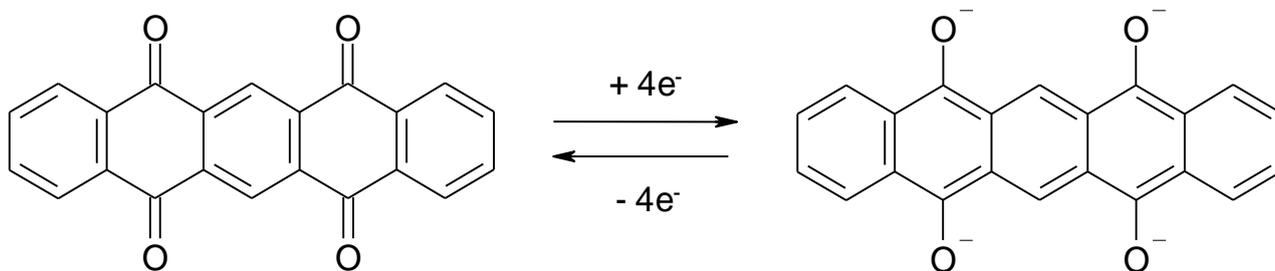


Figure 3. Conceivable four-electron redox reaction in the electrode of PT.

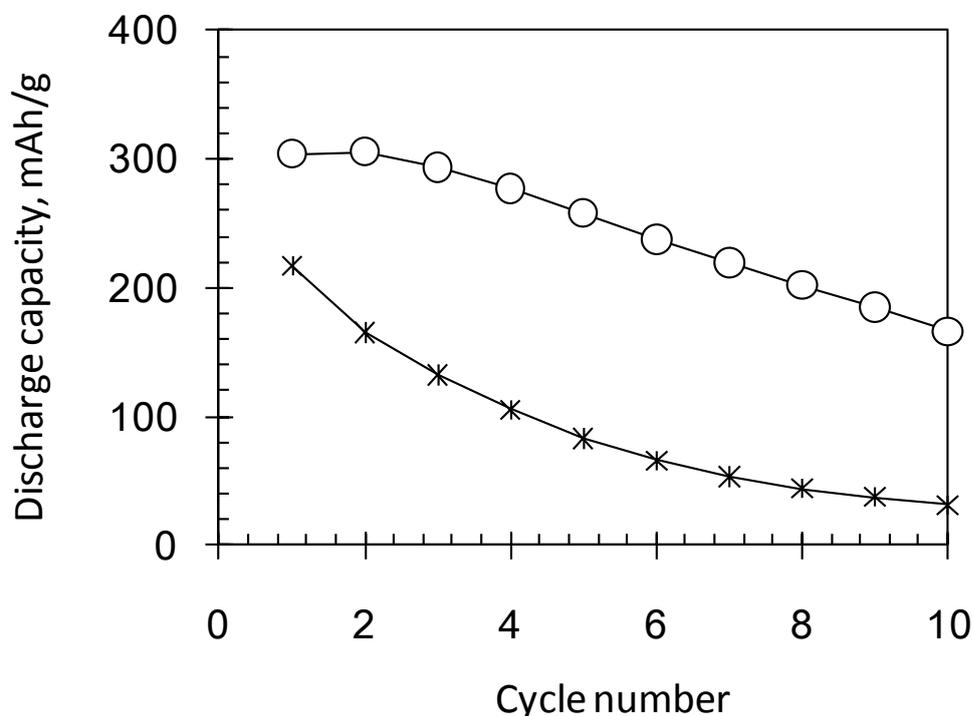


Figure 4. Cycle-life performance of the prepared electrodes (PT: \circ , AQ: $*$). (Current density: 20 mA/g, Potential range: 1.5–3.0 V vs. Li^+/Li).

A cycle-life test was also carried out using the prepared PT positive electrode (Figure 4). As a comparison, the cycle-life performance of an AQ-based electrode was also examined under the same conditions. Whereas the capacity of the electrode containing AQ dropped from 220 to 30 mAh/g after

ten cycles, the PT electrode retained more than half of its initial capacity under the same conditions, i.e., from 300 to 170 mAh/g. Similar to the AQ electrode, a poor cycle life performance of the electrodes composed of other low molecular weight compounds has been reported [8,12,13]. One of the reasons for these decreases in capacities is the dissolution of the redox active molecules into the electrolyte solutions. PT has a lower solubility in common organic solvents than AQ, which is considered to partially contribute to the better cycle-life performance of the PT electrode. Although the cycle performance of the PT electrode is still far from the practical application, the obtained result implies a favorable effect of the large π -system on the cycle-life stability of the organic electrodes. We expect further improvements in the cycle-life performance by using redox active molecules with larger π -systems.

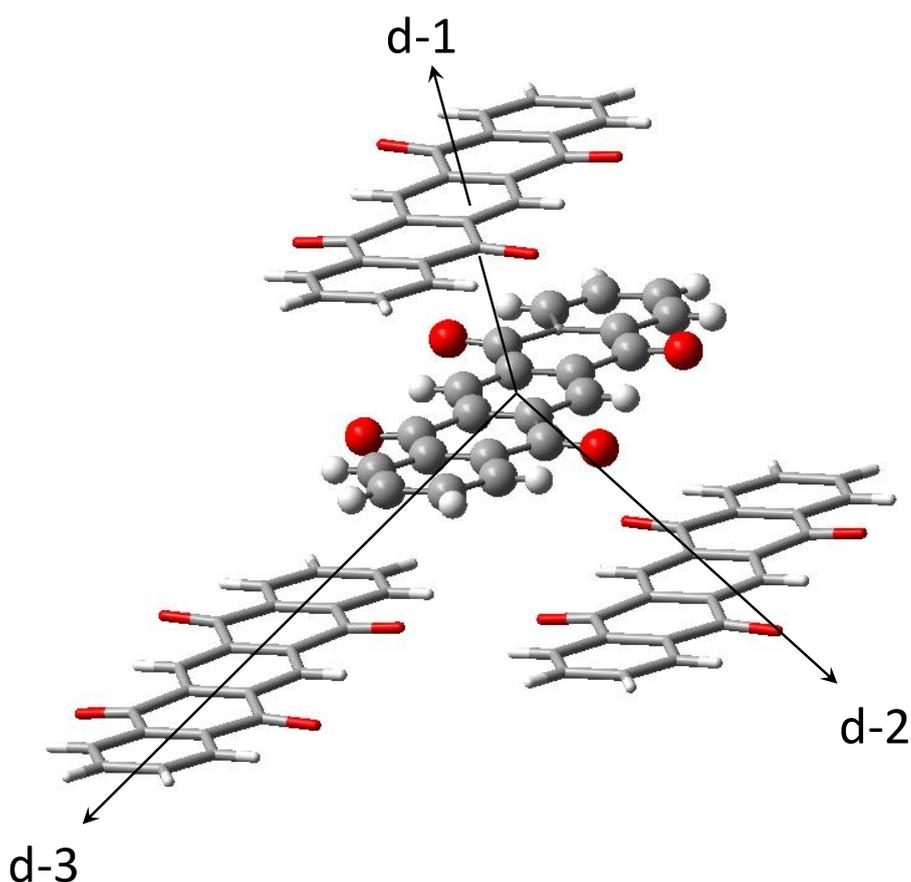


Figure 5. One-dimensionally aligned PT in the crystal [15]. The coordinates, d-1, d-2, and d-3, indicate the directions along which the clusters were formed in order to calculate the electronic structure.

A DFT calculation was performed to obtain theoretical insight into the electronic conduction mechanism of the PT crystalline state. In the crystal, the unit cell contains one PT molecule, and the PT molecules align periodically as shown in Figure 5 [15]. In this figure, some directions are described as d-1, d-2, and d-3. Along the d-1 direction (a -axis), the PT molecule forms a π -stacked column structure. In the column, the mean intermolecular distance is 3.38 Å, which is close to the

interlayer distance of graphite (3.35 Å). The calculation of the electronic state was performed along each of the three directions, d-1, d-2, and d-3, indicated in Figure 5 using clusters composed of ten molecular units.

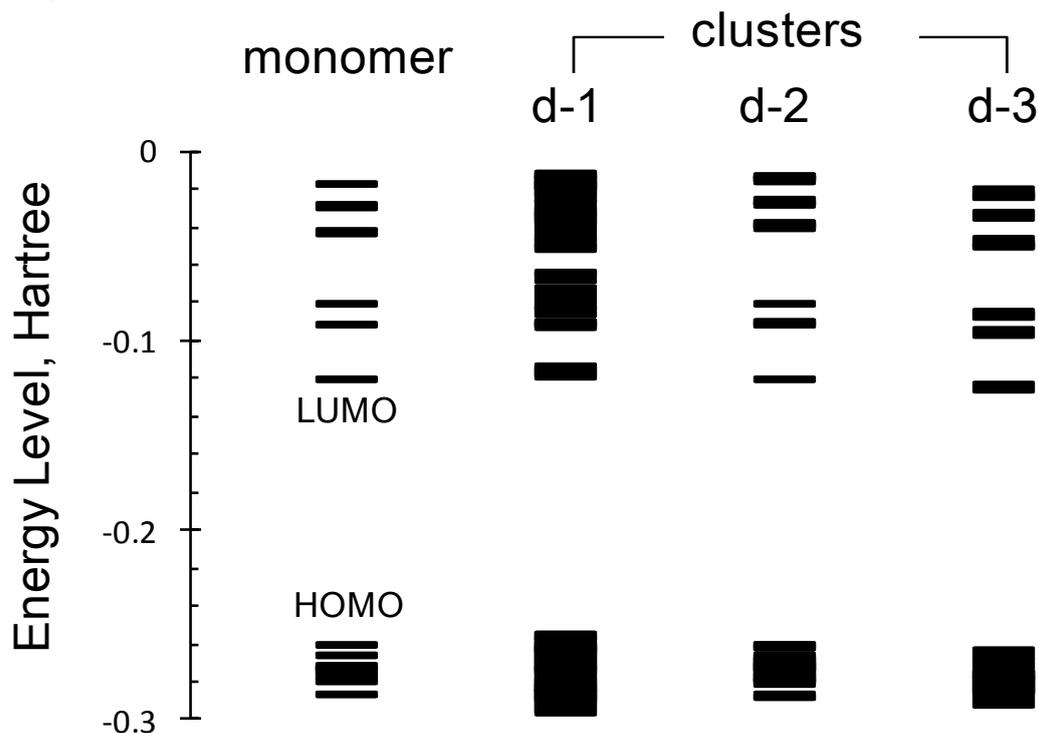


Figure 6. Calculated energy diagrams of the monomer and clusters of PT. The computation was performed at the B3LYP/6-31G(d) level.

The calculated energy levels of the clusters are shown in Figure 6 along with that of the monomer. For the cluster along the d-1 direction, the energy levels of the molecular orbitals develop a band-like structure due to overlapping of the π -orbitals. On the other hand, the widths of the energy levels for the clusters along the d-2 and d-3 directions are narrower, which indicates less overlapping of the orbitals along these directions. Therefore, the electronic band structure along the π -stacked direction appears to be a possible electron-transfer pathway in the crystal during the charge/discharge process.

4. CONCLUSIONS

The applicability of the redox reactions of 5,7,12,14-pentacenetetrone (PT) as a positive-electrode material for rechargeable lithium batteries was examined. This material showed a high initial discharge capacity of 304 mAh/g_(PT), which corresponds to a four-electron redox behavior of the PT molecule. Although the capacity gradually decayed upon cycling, the electrode exhibited a much better cycle stability than an electrode containing the smaller quinone (anthraquinone, AQ). The DFT

calculation suggested the formation of electronic band structures along the π -stacked column in the crystalline state, which can act as electron-transfer pathways during the redox process.

The electrochemical properties of such organic compounds can be adjusted by chemical modifications of the molecule. Further improvements in the discharge capacity and cycle stability can be expected by expanding the aromatic system of the molecular structures.

References

1. H. Nishide and K. Oyaizu, *Science*, 319 (2008) 737.
2. M. Armand and J.-M. Tarascon, *Nature*, 451 (2008) 652.
3. P. Novák, K. Müller, S.V. Santhanam and O. Hass, *Chem. Rev.*, 97 (1997) 207.
4. M. Liu, S.J. Visco and L.C. De Jonghe, *J. Electrochem. Soc.*, 138 (1991) 1891.
5. N. Oyama, T. Tatsuma, T. Sato and T. Sotomura, *Nature*, 373 (1995) 598.
6. K. Nakahara, S. Iwasa, M. Satoh, Y. Morioka, M. Suguro and E. Hasegawa, *Chem. Phys. Lett.*, 359 (2002) 351.
7. M. Yao, H. Senoh, S. Yamazaki, Z. Siroma, T. Sakai and K. Yasuda, *J. Power Sources*, 195 (2010) 8336.
8. M. Yao, H. Senoh, M. Araki, T. Sakai and K. Yasuda, *ECS Trans.*, 28(8) (2010) 3.
9. J.S. Foos, S.M. Erker and L.M. Rembetsy, *J. Electrochem. Soc.*, 133 (1986) 836.
10. T.L. Gall, H.R. Reiman, M. Grossel and J.R. Owen, *J. Power Sources*, 119–121 (2003) 316.
11. H. Chen, M. Armand, G. Demailly, F. Dolhem, P. Poizot and J.-M. Tarascon, *ChemSusChem*, 1 (2008) 348.
12. Z. Song, H. Zhan and Y. Zhou, *Chem. Commun.*, 4 (2009) 448.
13. X. Han, C. Chang, L. Yuan, T. Sun and J. Sun, *Adv. Mater.*, 19 (2007) 1616.
14. M. Yao, M. Araki, H. Senoh, S. Yamazaki, T. Sakai and K. Yasuda, *Chem. Lett.*, 39 (2010) 950.
15. D. Käfer, M.E. Helou, C. Gemel and G. Witte, *Cryst. Growth Des.*, 8 (2008) 305.
16. Gaussian 03, Revision E.01, M.J. Frisch, et al. Gaussian, Inc. Wallingford CT (2004).
17. A.D. Becke, *Phys. Rev.*, A38 (1988) 3098.
18. C. Lee, W. Yang and R.G. Parr, *Phys. Rev.*, B37 (1988) 785.