

## Design, Synthesis, and Electrochemical Properties of Cyclic 1,2-Diketones as Organic Cathode Materials for Lithium-ion Batteries

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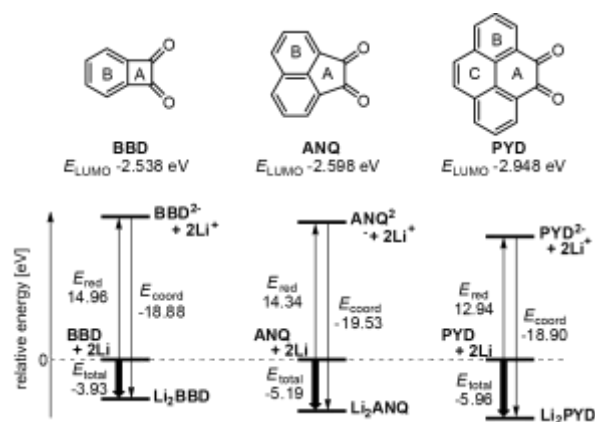
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Organic materials for batteries<sup>1</sup> have received much attention because of their beneficial properties such as light weight, flexibility, and availability from easily accessible natural sources. Although extensive studies have been made in this field, there is still a great demand for organic materials that allow for fast charging and discharging with high cyclability for the storage of electrical energy in practical use.

We initiated our project by designing a core structure of organic cathode materials. The simplicity of the core structure is essential from the viewpoints of capacity, availability, and sustainability of the materials. We focused on 1,2-diketones as a core structure. Two-electron reduction of a 1,2-diketone (one-electron/carbonyl group) leads to the formation of two negatively charged oxygen atoms apart from each other and the formation of one carbon-carbon double bond. Another important point to be considered is that two oxygen atoms in a 1,2-dicarbonyl compound are suitably located for coordination to Li ions, which are incorporated into the cathode during the course of reduction.

Cyclic 1,2-diketones seem to be superior to acyclic 1,2-diketones, because two carbonyl groups in an acyclic compound tend to direct the opposite way to minimize the repulsion of two dipoles, causing a large structural change (bond rotation) for coordination to Li ions. Another important point is that repulsion of two dipoles in a cyclic 1,2-dicarbonyl compound, which direct in similar directions, destabilizes the oxidized form, which eventually leads to a higher potential for the battery.

Next, we examined the effect of the ring size of cyclic 1,2-diketones. We chose benzocyclobutenedione (BBD), acenaphthenequinone (ANQ), and pyrene-4,5-dione (PYD) for representatives of four-, five-, and six-membered ring

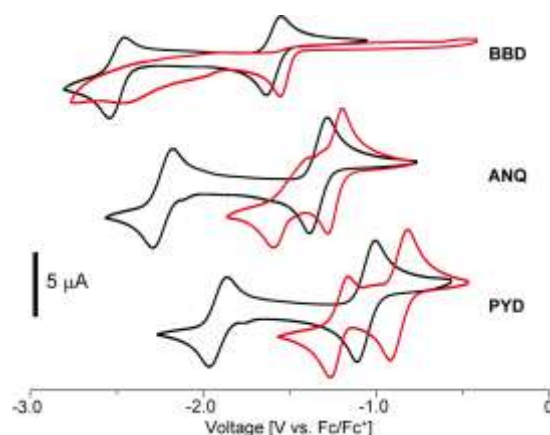


**Figure 1.** Redox properties of cyclic 1,2-diketones obtained by DFT calculations (B3LYP/6-31G(d)). Relative energies (eV) of the reduced forms without and with Li coordination based on the neutral form.

1,2-diketones, respectively (Figure 1). The extra  $\pi$ -bonds are introduced in the ring using fused benzene structures to ensure the planarity of the cyclic system. Such structures

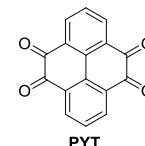
may also enhance chemical stability under redox conditions and increase recyclability of batteries. The redox properties of BBD, ANQ, and PYD were estimated using density functional theory (DFT) calculations, which indicated that the redox energy depends on the ring size. The effect of Li coordination is also sensitive to the ring size. In short, the DFT calculations suggest that six-membered ring 1,2-diketones serve as the best candidates for cathode materials.

Experimental studies on the redox properties of cyclic 1,2-diketones BBD, ANQ, and PYD were carried out using cyclic voltammetry in 0.1 M  $\text{Bu}_4\text{NBF}_4/\text{N,N}$ -dimethylformamide (DMF) (Figure 2). The increase in the ring size causes a positive shift in the reduction peak potentials (first reduction peak, BBD: -1.64 V, ANQ: -1.39 V, PYD: -1.11 V vs.  $\text{Fc}/\text{Fc}^+$ , second reduction peak, BBD: -2.55 V, ANQ: -2.29 V, PYD: -1.97 V vs.  $\text{Fc}/\text{Fc}^+$ ) and this trend is consistent with the DFT calculations. The use of  $\text{LiBF}_4$  as the supporting electrolyte resulted in redox potential shifts to less negative potentials, presumably because of the coordination of the oxygen atoms to Li ions.



**Figure 2.** Cyclic voltammograms of cyclic 1,2-diketones BBD, ANQ, and PYD. Black lines: in 0.1 M  $\text{Bu}_4\text{NBF}_4/\text{DMF}$  (1.0 mM, working electrode (WE): glassy carbon (GC), counter electrode (CE): platinum plate, reference electrode (RE):  $\text{Ag}/\text{AgNO}_3$ ). Red line: in 0.1 M  $\text{LiBF}_4/\text{DMF}$  (1.0 mM, WE: GC, CE: platinum plate, RE:  $\text{Ag}/\text{AgNO}_3$ ). Potentials were corrected using ferrocene ( $\text{Fc}/\text{Fc}^+$ ) as an internal standard.

Based on computational and experimental studies on the redox behavior of cyclic 1,2-diketones, we chose to study pyrene-4,5,9,10-tetraone (PYT), which contains two six-membered-ring 1,2-diketone units as a core structure for the cathode material.



PYT is expected to undergo four-electron reduction, and the theoretical capacity is 408 mAh/g. The redox energy change obtained by DFT calculations is -11.98 eV.

Poly(methacrylate) bearing PYT was synthesized. The battery using this material exhibited two-stage charge-discharge ability based on a reversible Li insertion mechanism (average discharge voltage of circa 2.8 V and 2.2 V vs.  $\text{Li}/\text{Li}^+$ ). High-capacity (231 mAh/g), fast charge-discharge ability (90% of the capacity at 30 C compared with 1 C), and excellent cyclability (83% of the capacity retained after 500 cycles) speak well for the high potential of organic materials for Li-ion batteries, and open a new aspect of energy storage.

## References

- 1) For example, (a) Nishide, H.; Oyaizu, K. *Science* **2008**, *319*, 737–738. (b) Chen, H.; Armand, M.; Demailly, G.; Dolhem, F.; Poizot, P.; Tarascon, J.-M. *ChemSusChem* **2008**, *1*, 348–355. (c) Morita, Y.; Nishida, S.; Murata, T.; Moriguchi, M.; Ueda, A.; Satoh, M.; Arifuku, K.; Sato, K.; Takui, T. *Nat. Mater.* **2011**, *10*, 947–951.