



# Intrinsic factors attenuate the performance of anhydride organic cathode materials of lithium battery



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## ABSTRACT

Anhydride organic materials are promising candidates for lithium batteries on account of reversible insertion and de-insertion of  $\text{Li}^+$  on the conjugated carbonyl structure. However, anhydride compounds suffer from drawbacks that rapidly attenuate the capacity of lithium batteries. This study aims to reveal the essential reason for the rapid capacity attenuation of four anhydride organic compounds by characterizing the morphological features of the lithium foil surface and the loss of active materials before and after charge-discharge cycles, to speculate the reasons for the electrochemical property attenuation along with molecular weight decreases. This study proposes that the phenomenon is because the anhydride monomer react  $\text{Li}^+$  during the charge and discharge processes, then cross the separator and deposits on the surface of lithium foil (Li-foil), leading to loss of active materials and low utilization of the Li-foil. Based on the mechanism study, anhydride compounds will face the new development in the field of energy storage.

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## 1. Introduction

Energy resources play a more crucial role in the development of the economy and society [1–3]. The extensive use of coal and fossil oil cannot meet the sustainable demand for a low-carbon environment [4,5]. Lithium battery has become the ideal energy storage for future because of its high specific energy [6] and good cycle performance [7]. Currently, researches on lithium battery cathode materials mainly focus on inorganic transition metal compounds. However, from the perspective of sustainable energy development, lithium battery cathode materials derived from natural organic matter which have abundant raw material reserves are environment-friendly [8,9].

The first organic material used in an energy storage device was dichlorid isocyanuric acid (DCA) as the disposable lithium battery cathode materials [10] applied. Afterwards, scientists have exerted significant efforts in obtaining new electrode materials, such as organic conducting polymers [11] and organic polysulfide compounds [12], to provide sufficient energy for the future. Nitrogen oxygen free radical polymer [9] and carbonyl compound [13,14] have also shown significant potential in the application of energy storage devices. K. Nakahara [15] synthesized poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate)

PTMA, a nitrogen oxygen free radical polymer, which delivers a discharge capacity of 70% compared with the theoretical capacity after 500 cycles.

Molecules containing carbonyl [16,17] have been the focus of considerable attention from researchers because of their reversible insertion and de-insertion of  $\text{Li}^+$  on the CO bond. Quinone [18,19], anhydrides [20], and polyimide [21–23] have been successfully certified in lithium batteries. For example, (Perylene-3,4,9,10-tetracarboxylic dianhydride) PTCDA, a large molecular weight anhydride compound, [24] could deliver an initial capacity of 135 mAh/g but have poor cycling stability for lithium batteries because of partial dissolution in the electrolytes during the charge–discharge process. Scientists thus exerted significant efforts in stabilizing the anhydride compound active material to ensure superior properties of organic materials. Song et al [25], prepared polyimides based on the polymerization of (naphthalene-1,4,5,8-tetracarboxylic acid dianhydride) NTCDA, and PTCDA, which served as active materials of lithium batteries and achieved good electrochemical property. Wu et al obtained anhydride-based sulfide polymers by reaction between PTCDA and sulfur by replacing the hydrogen atom with the sulfur atom on the aromatic ring to improve electroconductivity and cycling stability [21]. Researchers also designed a quasi-solid cell to improve the electrochemical property and solve the dissolution problem of the anhydride compound [18,26,27]. The results indicate that the polymerization process may produce uncontrollable derivatives [11], which can lead to an unstable potential [28]. However, systematic studies on the charge–discharge intrinsic mechanism of

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anhydride monomer compound electrodes are limited, however it is important for the widely application in the field of lithium batteries.

According to existing reports, many factors can account for this poor cyclability of organic molecules, such as low mass density [11], low electronic conductivity, the unwanted dissolution of active materials in the electrolyte [29,30], serious safety issue in practical use of Li metal anode [31]. The application of organic anhydride is mainly limited by poor conductivity and high solubility in electrolytes (especially carbonate-based). In fact, the largest number of anhydride organic compound just as one of basal synthetic material such as polyimide. So we will discuss the phenomenon that how the solubleness influence the electrochemistry property of the anhydride cells in detail. In this study, SAD, NAD, NTCDA, and PTCDA represent organic anhydride materials that are structurally similar with the increase in molecular weight. The reason for capacity attenuation of organic acid anhydride is also explored. The electrochemical test system evaluates cell performance under the same test voltage range (1–3 V) and charge–discharge rate (0.1 C). The material morphologies and structures of positive and negative electrodes are characterized by SEM, FT-IR, and other characterization methods.

## 2. Experimental methods

### 2.1. Materials

The anhydride organic materials SAD, NAD, NTCDA, and PTCDA were purchased from Sigma-Aldrich. The electrode consists of 60 wt% active material, 30 wt% carbon black (Super-P), and 10 wt% PVDF. PVDF (20 mg) was dissolved in NMP (1 mL) and stirred for half an hour before it was used. This step ensures that the powder is fully dissolved in solvent and is in slurry form. The mixture was stirred three times using the stir pulp machine before being casted onto a C–Al foil current collector by an automatic coater machine. The electrodes were dried at 60 °C under a vacuum for 24 h.

### 2.2. Battery assembly and testing

The coin cells (CR2016) were assembled in an argon-filled glove box using lithium metal as the counter electrode, Celgard 2400 membrane as the separator, and LiPF<sub>6</sub> (1 M) in ethylene carbonate/diethyl carbonate/methyl-ethyl carbonate (EC/DEC/EMC, 1:1:1 w/w/w) as the electrolyte. The cells were tested by galvanostatic charge–discharge on a Land battery measurement system (Land, People's Republic of China) at a voltage range of 1–3 V and a rate of 0.1 C (1 C is 536,

270.5, 200, and 136.5 mAh/g for SAD, NAD, NTCDA, and PTCDA, respectively). CV and EIS were conducted using a VMP-3 electrochemical workstation.

### 2.3. Electrodes prepared

We disassembled the cells after completion of 1, 10, 30, 50, and 100 cycles in the argon-filled glove box. The Li-foil and electrodes were soaked in the solvent (EC/PC, 1:1 w/w) three times to remove LiPF<sub>6</sub>, after which they are dried in vacuum for 12 h at room temperature to eliminate any trace of the solvent before characterizing the Li-foil using SEM. Meanwhile, we used the same method to deal with the electrodes, except for the step where the electrodes were dried at a temperature of 60 °C rather than room temperature in vacuum. Afterward, the electrode materials were exfoliated from the C–Al foil under an infrared lamp to differentiate the material using an infrared spectrometer.

## 3. Results and discussion

Fig. 1 shows the cyclic voltammogram (CV) of (a)SAD, (b)NAD, (c)NTCDA, and (d)PTCDA in 1 M LiPF<sub>6</sub>/EC:DEC:DMC = 1:1:1 electrolyte at a scan rate of 0.01 mV/s. For SAD, the CV curve shows a weak reduction peak centered at 1.65 V for the first cycle and the oxidation peak is close to the zero line with a wide range at 1.00 V for the second cycle. The situation of NAD is similar to that of SAD, in which the CV curve displays a reduction peak at 1.90 V for the first cycle and no oxidation peak either on the first or second cycle. This finding indicates that, during the charge and discharge processes, the reaction of the active materials with Li<sup>+</sup> formed a lithium enolization compound where lithium enolization is an important reaction of carbonyl double bonds, which can be useful in stabilizing the conjugated structure and making it easy to insert and desert Li<sup>+</sup>. However, for SAD and NAD, Li<sup>+</sup> ions were inserted in CO and formed C–O–Li on the monomer molecule during the initial discharge of the oxidation process. This structure forms a dissolved lithium compound in electrolyte, which is consistent with previous reports. The situation of NTCDA is homologous to that of SAD and NAD. The reduction and oxidation peaks of NTCDA occur at 2.20, 2.60, and 2.35 V [32] on the initial cycle. For the second cycle, the reduction and oxidation peaks slightly weakened. For PTCDA, one pair of symmetric redox peaks can be observed; the oxidation peak are 2.3, 2.5 V and reduction peaks is 2.6 V [33]. This result indicates that PTCDA, whose molecular weight is the largest among the four materials, has the best reversible electrochemical property.

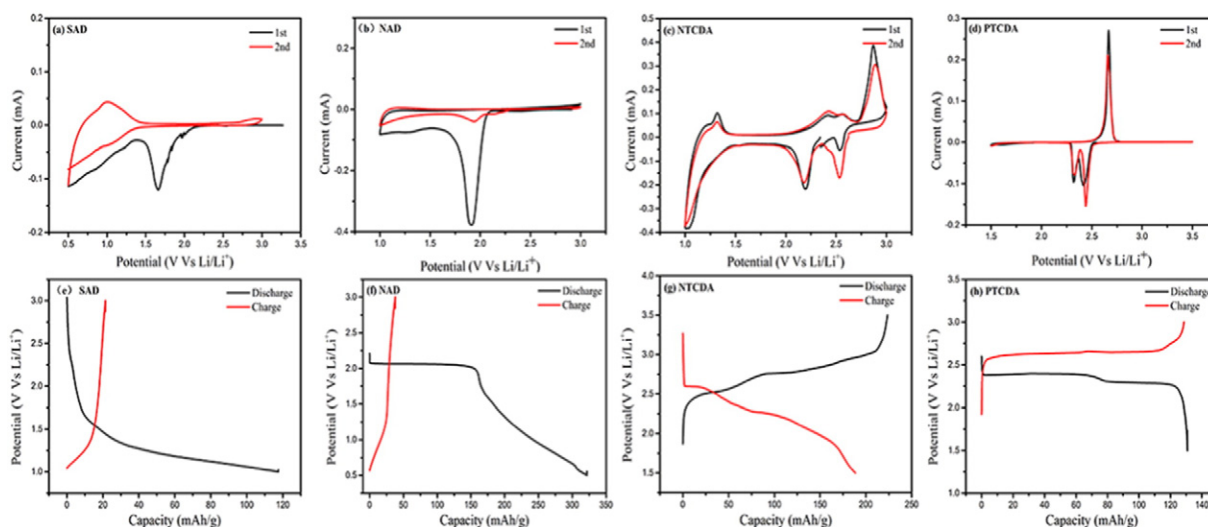


Fig. 1. CV curves (a–d) and charge–discharge curves (e–h) of SAD, NAD, NTCDA, and PTCDA.

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