Heteroaromatic organic compound with conjugated multi-carbonyl as cathode material for rechargeable lithium batteries

Meixiang Lv, Fen Zhang, Yiwen Wu, Mujuan Chen, Chunfeng Yao, Junmin Nan, Dong Shu, Ronghua Zeng, Heping Zeng & Shu-Lei Chou

The heteroaromatic organic compound, N,N'-diphenyl-1,4,5,8-naphthalenetetra-carboxylic diimide (DP-NTCDI-250) as the cathode material of lithium batteries is prepared through a simple one-pot N-acylation reaction of 1,4,5,8-naphthalenetetra-carboxylic dianhydride (NTCDA) with phenylamine (PA) in DMF solution followed by heat treatment in 250 °C. The as prepared sample is characterized by the combination of elemental analysis, NMR, FT-IR, TGA, XRD, SEM and TEM. The electrochemical measurements show that DP-NTCDI-250 can deliver an initial discharge capacity of 170 mAh g⁻¹ at the current density of 25 mA g⁻¹. The capacity of 119 mAh g⁻¹ can be retained after 100 cycles. Even at the high current density of 500 mA g⁻¹, its capacity still reaches 105 mAh g⁻¹, indicating its high rate capability. Therefore, the as-prepared DP-NTCDI-250 could be a promising candidate as low cost cathode materials for lithium batteries.

Rechargeable lithium batteries dominate the portable electronics market because lithium cells offer the largest energy density in all the rechargeable battery technologies available. Additionally, they are well-positioned to take over the emerging large-scale application markets of electric vehicles and off-grid storage devices. The performance of rechargeable lithium batteries is mainly restricted by the cathode based on inorganic intercalation compounds with low specific capacity. Recently, organic carbonyl compounds as high-energy cathode materials for rechargeable lithium batteries have been extensively explored owing to redox stability, structural diversity, high theoretical capacities, and infinite availability from biomass. Nevertheless, organic carbonyl compounds suffer from some mortal shortages, such as the intrinsic drawback of poor cyclic performance and rate capability owing to low electronic conductivity, high solubility in organic electrolyte, no well-defined Li⁺-conducting channel, and no interstitial sites due to the lack of lattice in organic electrode materials. To address these issues, first, the combination of multi-carbonyl groups and low molecular weight should be used to achieve high specific capacity, where multi-carbonyl groups can capture more lithium to offer multi-electron reactions. Second, the carbonyl-based electrode generally demands certain functional structures to stabilize the negatively charged carbonyl groups under the electrochemical reduction state. Carbonyl groups are directly connected to an aromatic core to disperse charge through delocalization. Third, from the design of electronic conductivity for organic semiconductors, one method is the judicious incorporation of heteroaromatic structures. The morphological and electronic properties of the target compounds can be predictably tuned in a wide range by this method. For example, pyridine is an important electron-withdrawing moiety in electron-transporting materials. According to the above function-oriented design strategies of organic compounds, many carbonyl-based positive electrode materials with high capacity and good electrochemical performance have been reported. For example, Sun et al. reported 3,4,9,10-perylene-tetracarboxylicacid-dianhydride (PTCDA) sulfide polymers, which showed average reversible capacity of ~130 mAh g⁻¹ in current density of...
100 mA g\(^{-1}\), Yao et al. prepared 2,5-dimethoxy-1,4-benzoquinone (DMBQ) as cathode material, the electrode material demonstrated an initial discharge capacity of 312 mAh g\(^{-1}\) at current density of 10 mA g\(^{-1}\), and the capacity decayed sharply with the increase of cycles\(^{28}\). Chen et al. synthesized two new carbonyl electrodes, pyrene-4,5,9,10-tetraone (PTO) and 1,10-phenanthroline-5,6-dione (PhenQ), delivering a reversible capacity of 360 mAh g\(^{-1}\) in current density of 0.05 C\(^{8}\). Tarascon et al. reported an organic salt, lithium 2,6-bis(ethoxycarbonyl)-3,7-dioxo-3,7-dihydro-s-indacene-1,5-bis (olate), delivering an overall capacity of 125 mAh g\(^{-1}\). Poizot et al. obtained tetralithium salt of tetrahydroxybenzoquinone (Li\(_4\)C\(_6\)O\(_6\)), the Li\(_4\)C\(_6\)O\(_6\) compound showed good electrochemical performance with a sustained reversibility of ~200 mAh g\(^{-1}\). Our group previously reported a series of polycarbonyl organic compounds with different number of hydroxyl groups and a lithium-organic coordination compound, [Li\(_2\)(C\(_{14}\)H\(_{6}\)O\(_4\))]\(^{29,30}\). However, one of the great challenge for these organic compounds is that most of the synthesis procedure were involved by many pot reactions or in high-temperature, with long time consuming. Furthermore, there is extremely large space to design the low molecular weight compounds with more carbonyl groups, conjugated system and fused heteroaromatic structures, which can improve the capacity, cyclic stability and rate performance of small molecules.

In this work, we report a compound with multi-carbonyl groups, conjugated system and fused heteroaromatic structures, N,N\(^{\prime}\)-diphenyl-1,4,5,8-naphthalenetetracarboxylic diimide (DP-NTCDI-250) through a simple one-pot N-acylation reaction of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) with phenylamine (PA) in DMF and Et\(_3\)N solution. The key features of this method are time-saving and low energy consumption.

Results and Discussion

Synthesis mechanism. The synthesis of DP-NTCDI was adapted by one-pot N-acylation reaction (Fig. 1). NTCDA dissolved in DMF was reacted with PA, in which the -N- replaced the oxygen of -C-O-C- in NTCDA to form heteroaromatic compound, resulting in the generation of DP-NTCDI. The reaction was carried out in nitrogen atmosphere to avoid oxidation or decomposition of the PA. A brown precipitate, which can easily be separated by centrifugation and filtration, occurred as the reaction proceeds. It should be noted that the Et\(_3\)N can act as catalyst and can be used to stimulate the reaction of NTCDA and PA. After washing with EtOH and recrystallizing in DMF and drying, the as-synthesized orange acicular product (DP-NTCDI), with a yield of 91.2%, was further heated at 250 °C to get DP-NTCDI-250 compound. The sample was prepared within 1 h through a simple one-pot N-acylation reaction. The key features of the synthesized method are time-saving and low energy consumption.

Physical properties. The as-prepared DP-NTCDI and DP-NTCDI-250 were comparatively characterized against each other by various techniques. From the scanning electron microscopy (SEM) image in Fig. 2a, DP-NTCDI consists of uniform rod structure, and the mean diameter of DP-NTCDI is estimated to be ~2 μm. After heat treatment of DP-NTCDI, the morphology of DP-NTCDI-250 is almost same with DP-NTCDI (Fig. 2b). The transmission electron microscopy (TEM) image in Fig. 2c manifests that DP-NTCDI is well faceted and have very smooth surface with diameter of ~2 μm.

X-ray diffraction (XRD) patterns in Fig. 3 are performed to investigate the crystal phase composition of DP-NTCDI and DP-NTCDI-250. It can be seen from Fig. 3 that most of the peaks from the experimental XRD patterns of DP-NTCDI and DP-NTCDI-250 can match with the simulated patterns based on single-crystal X-ray
solution\textsuperscript{35}, indicating that the ordered material is similar in the structure. All the diffraction peaks of DP-NTCDI could be indexed to monoclinic lattice of space group P2\textsubscript{1}/c with the lattice constants: a = 5.136 Å\textsuperscript{2}, b = 7.522 Å\textsuperscript{2}, c = 25.623 Å\textsuperscript{2}. After heat treatment of sample, the characteristic peaks of DP-NTCDI-250 become sharply and strong. However, the characteristic peaks of DP-NTCDI and DP-NTCDI-250 are overall broad and weak in comparison with the simulated peaks, indicative of the poor crystallinity of as prepared materials.

Thermogravimetric (TG) analysis was conducted to follow the heat treatment process of DP-NTCDI and DP-NTCDI-250 in air (Fig. S1, ESI\textsuperscript{1}). The obtained results show no weights lost were observed before 380 °C for DP-NTCDI and DP-NTCDI-250, exhibiting good thermal stability for the two samples. Upon further heating, the samples start to decompose and the framework collapses.

Figure 2. (a) SEM image of DP-NTCDI; (b) SEM image of DP-NTCDI-250; (c) TEM image of DP-NTCDI.

Figure 3. XRD patterns of DP-NTCDI-250, DP-NTCDI and simulative DP-NTCDI of ref. 35.
DP-NTCDI is further supported by FTIR, $^1$H NMR and $^{13}$C NMR. As shown in Fig. 4, the typical absorption band at around 1711, 1661 and 770 cm$^{-1}$ are attributed to the stretching vibration of C=O, 3068 and 982 cm$^{-1}$ is the vibration C-H of aromatic ring, 1670 and 1350 cm$^{-1}$ are the C-N stretching vibration of imide, 1582 cm$^{-1}$ is the stretching vibration of naphthalene ring skeleton. As can be from the $^1$H NMR spectrum (Fig. S2a, ESI†), there is a multiplet peak at 7.46–7.59 ppm, which is the peak of proton on the benzene ring. A singlet at 8.73 ppm can be assigned to the proton of naphthalene ring. The two different environmental proton give an integration ratio of 5:2. For $^{13}$C NMR (Fig. S2b, ESI†), 163.42 ppm is the characteristic peak of C=O, the other seven characteristic peaks are attribute to carbon on the aromatic ring.

**Electrochemical Performance.** The initial three cyclic voltammograms (CVs) of DP-NTCDI electrode between 1.5 and 4.0 V at a scan rate of 0.1 mV s$^{-1}$ is shown in Fig. 5. It can be seen from Fig. 5a that two separated steps for lithium insertion and removal in DP-NTCDI are not obvious. The first reduction peaks at about 2.3 V corresponds to one-electron transfer reaction in one of the four carbonyl groups, forming the radical-anion.
The synthesization of DP-NTCDI was carried out through a simple one-pot 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA), phenylamine (PA), triethylamine (Et3N), N,N'-dimethylformamide (DMF), ethanol (EtOH) were obtained from commercial sources and used without purification.

Preparation of N,N'-diphenyl-1,4,5,8-naphthalenetetracarboxylylic diimide (DP-NTCDI). N,N'-diphenyl-1,4,5,8-naphthalenetetracarboxylylic diimide (DP-NTCDI) was prepared by 1,4,5,8-naphthalenetetracarboxylylic dianhydride (NTCDA) with phenylamine (PA) in DMF solution. Typically, 2.0 g NTCDA (7.6 mmol) was dissolved in 40.0 mL DMF at 130 °C under stirring. Then 2.1 mL PA (23.0 mmol) and 4.3 mL of Et3N (30.0 mmol) were added dropwise into the solution, respectively, and continued to reflux under stirring for 1 hour to form a brown precipitate, and the mother liquid was removed by centrifugation and filtration. The as-obtained brown precipitate was redissolved in EtOH, washed thoroughly with EtOH. Then the as-obtained product with recrystallization in DMF afforded orange acicular DP-NTCDI. The as-obtained pure DP-NTCDI was washed with EtOH and collected by filtration again. Finally, the pure DP-NTCDI was dried in vacuum at 80 °C for 12 h (2.9 g, 92.1%): 1H NMR (DMSO) δ 8.73 (s, 4H), 7.46–7.59 ppm (m, 10H); 13C NMR (DMSO) δ 127.14, 127.45, 128.94, 129.43, 129.47, 130.88, 136.06, 163.42 ppm. IR (KBr pellets): ν = 3068, 981.77 (benzene C-H), 1710.86 (C-H), 1630.35 (imide), 1660.71 (C=C, vs), 1581.63 (naphthalene C=C, v), 1350.17 (C=N, v), 769.60 cm⁻¹ (C=O, b). The elemental analysis by a Thermo Flash EA 1112 (CHNS-O) element analyzer indicated that the synthesized DP-NTCDI consists of 74.60% C, 3.37% H, 6.70% N and 15.30% O.
The as-prepared DP-NTCDI was further annealed at 250 °C for 3 h under air atmosphere to obtain DP-NTCDI-250 sample.

**Characterization.** The morphology and structure of as-prepared DP-NTCDI and DP-NTCDI-250 were characterized by a field-emission scanning electron microscopy (FESEM, ZEISS Ultra 55, 5 kV, Pt-spraying treatment), transmission electron microscopy (TEM, JEM-2100HR, 200 kV), powder X-ray diffraction (XRD, BRUKER D8 ADVANCE, Cu K radiation (1.5406)). Elemental analyses were performed on a Thermo Flash EA-1112 (CHNS-O) element analyzer. The FT-IR spectra were recorded from KBr pellets in the 4000 ~ 400 cm⁻¹ range.

**Figure 6.** (a) The initial three cycles discharge-charge curves of DP-NTCDI-250 (current density: 25 mA g⁻¹); (b) The cyclic performance of DP-NTCDI-250 (current density: 25 mA g⁻¹); (c) The rate capabilities of DP-NTCDI-250.
Electrodes and Cells Fabrication. Coin-type cells (size: 2016) consisting of a working electrode and a lithium foil counter electrode separated by a Celgard 2300 microporous membrane were assembled in an argon-filled glove-box. The working electrodes were prepared by mixing a powder of DP-NTCDI-250, acetylene black as a conductive additive, and polyvinylidene fluoride (PVDF) as a binder in a weight ratio of 5:4:1 using a mortar. The sheet was then attached to an aluminum foil current collector, and the resultant working-electrode was dried. The amount of active material deposited was approximately 3 mg cm$^{-2}$. The electrolyte was 1M LiPF$_6$-EC + EMC + DMC (V$_{EC}$:V$_{EMC}$:V$_{DMC}$ = 1:1:1). The charge/discharge experiments were performed by using a LAND cell test system (Land CT 2001A) in the potential range of 1.5−4.0 V versus Li/Li$^+$ at different constant current densities (25, 50, 125, 250, 500 mA g$^{-1}$). Cyclic voltammogram was obtained on PGSTAT-30 (Autolab) in the potential range of 1.5−4.0 V at a scanning rate of 0.1 mV s$^{-1}$. The electrochemical impedance spectroscopy (EIS) analysis were carried in the frequency range from 100 kHz to 10 mHz with an AC signal amplitude of 10 mV.

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Author Contributions
F.Z. designed the material structure. M.X.L. performed the experiment. Y.W.W. and M.J.C. collected the experimental data. C.F.Y. performed the XRD. J.N.M. and D.S. analysed datas. M.X.L., H.P.Z., R.H.Z. and S.L.C. wrote the manuscript. All authors contributed to preparing the manuscript.

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