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# Improved electrochemical performance of lithium/sodium perylene-3,4,9,10-tetracarboxylate as an anode material for secondary rechargeable batteries

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## ABSTRACT

Lithium perylene-3,4,9,10-tetracarboxylate (Li-PTCA) is synthesized starting from perylene-3,4,9,10-tetracarboxylic acid-dianhydride (PTCDA). In Li-PTCA, the carbonyl group of the carboxylate redox centers exhibits excellent electrochemical reversibility at an average voltage of 1.2 V with respect to  $\text{Li}^+/\text{Li}$ . We have improved the rate capability and capacity of Li-PTCA based electrode by in-situ coating of Li-PTCA with conducting acetylene black carbon. We have demonstrated enhanced rate capability, improved capacity and reduced charge transfer resistance in the in-situ carbon coated electrode vis a vis electrode fabricated by conventional method. A capacity of  $120 \text{ mAh g}^{-1}$  is observed at the end of the 50 cycles, at  $240 \text{ mA g}^{-1}$ . Ex-situ XRD studies have revealed that the crystal structure is robust and is stable for reversible insertion of Li. In-situ carbon coated Na-PTCA shows better reversibility and high capacity retention even after 100 cycles when cycled using current densities as high as  $500 \text{ mA g}^{-1}$ .

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## Introduction

Li-ion batteries (LIBs) contribute prominently to the energy storage field due to their acceptable cyclability and higher energy density in comparison to Lead-acid, Ni–Cd and Metal-hydride rechargeable batteries [1]. The traditional inorganic intercalation based electrodes materials are suffering due to the constraint imposed by their structural aspects and low specific capacity, holding back the further improvement in energy density of LIBs. Moreover the most challenging problems with the transition metal based electrode materials

( $\text{LiCoO}_2$ ,  $\text{LiFePO}_4$ , etc.) are scarcity, polluting and energy intensive process of production and lack of recycling methodology [1–6]. Hence, focus is on the environmentally benign and sustainable organic redox materials [7,8].

Till date many organic compounds have been reported as both cathode and anode materials for Li-ion batteries [9]. Among these, carbonyl compounds are the preferred candidates due to their highly active redox carbonyl centers yielding fast kinetics, higher capacity and a wide structural diversity [1,3]. Organic materials, especially, carbonyl compounds exhibit reasonably high capacity. Simple benzoquinone gives

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about 500 mAh g<sup>-1</sup> [10]. However, they have associated problems such as low electronic conductivity and dissolution in the electrolyte causing loss of capacity with cycling [1,11–13]. By increasing the conductive carbon content and/or in-situ carbon coating on the organic electrode materials conductivity problem can be overcome. Using a solid polymer electrolyte, the dissolution problem can be overcome. An elegant way to mitigate dissolution is rational design of the organic molecule constituting the electrode material. Tarascon et al. reported conjugated lithium carboxylates and polymer dianhydride derivatives in place of simple carbonyl compounds to mitigate the dissolution of active material in the electrolyte solution [7,14–16]. As the redox potentials of conjugated carboxylates are very low (1.5–0.6 V w.r.t. Li<sup>+</sup>/Li), these organic materials could be promising anode materials for LIBs [1,16–20]. However, the issue of poor electronic conductivity needs to be addressed.

In this paper we have explored Lithium perylene-3,4,9,10-tetracarboxylate (Li-PTCA) as an anode material for LIBs. In the literature, perylene-polyimide (PI) based compounds have been reported as cathode materials [21,22]. To improve the electronic conductivity of Li-PTCA based electrode thereby enhanced capacity and rate capability, acetylene black was added in solution during the synthesis of Li-PTCA and in another variation after synthesizing Li-PTCA by a conventional pestle and mortar method. Secondary rechargeable sodium battery attracted attention in recent times [23–27]. The issues with regard to choice of anode material are akin to those in the Li-ion batteries. Keeping in view the contextual significance of exploring new anodes in the organic materials regime, we have studied Na-PTCA with respect to Na<sup>+</sup>/Na.

## Experimental

### Materials

Absolute ethanol 99% (Jiangsu Huaxi International Trade Co. Ltd. China), Li<sub>2</sub>CO<sub>3</sub> (Sd-fine-Chem. Ltd.) and perylene-3,4,9,10-tetracarboxylic acid-dianhydride (PTCDA, Acros Organics) were used without further purification.

### Synthesis and electrode fabrication methods

Li-PTCA was prepared in two steps; in the first step perylene-3,4,9,10-tetracarboxylic acid-dianhydride (PTCDA) was converted into its carboxylic acid by addition of aq. KOH, followed by dil. HCl. The typical procedure is as follows; 0.3 g of PTCDA was dissolved in 30 ml of 0.5 M KOH and 1.0 M HCl was added gradually to the solution until a complete precipitation is achieved. This orange red precipitate of perylene-3,4,9,10-tetracarboxylic acid (PTCA) was centrifuged and washed several times with distilled water to remove excess reagents.

In the second step, 50 ml of 1:1 (v/v) ethanol and water solution, 0.429 g of PTCA, 0.15 g of Li<sub>2</sub>CO<sub>3</sub> were added and stirred at 60 °C for 3 days (Scheme-1) to produce Li-PTCA. The obtained Li-PTCA in suspension was centrifuged and washed thoroughly with absolute ethanol and dried at 150 °C overnight in a vacuum oven. Yellow crystalline powder of Li-PTCA

was obtained in 95% yield. Using this powder, electrode of Li-PTCA was fabricated by two different methods as detailed below.

Method-A: Li-PTCA, acetylene black and polyvinyl difluoride (PVDF) binder were taken in 55:35:10 mass ratio and ground in a mortar with N-methylpyrrolidinone (NMP) to obtain slurry. The slurry was applied on a stainless steel foil and was used as cathode (electrode-A) versus Li-metal anode.

Method-B: In order to improve the electronic conductivity of the Li-PTCA electrode, 35% acetylene black carbon w.r.t. Li-PTCA was added directly to PTCA in ethanol and water solution, followed by treatment with Li<sub>2</sub>CO<sub>3</sub> as mentioned before. To this in-situ carbon Li-PTCA dispersed material, 10 wt.% of PVDF was added along with NMP to make a slurry, which was applied on a stainless steel foil (electrode-B).

### Material characterization and electrochemical measurements

Brunauer–Emmet–Teller (BET) surface area of the electrode materials prepared by method A and method B were obtained using Micromeritics ASAP 2020. The IR spectrum of PTCA and Li-PTCA were recorded using KBr pellets on JASCO 4100 FT-IR spectrometer. In order to check if any occluded Li<sub>2</sub>CO<sub>3</sub> on acetylene black, we have prepared Li<sub>2</sub>CO<sub>3</sub>-acetylene black mixture following the same procedure adopted in method B but without PTCA. IR spectrum of this is recorded for comparison. <sup>1</sup>H NMR and <sup>13</sup>C NMR of Li-PTCA and Na-PTCA were recorded in D<sub>2</sub>O solvent on a Bruker AVANCE 500 MHz spectrometer. Powder XRD patterns of Li-PTCA were recorded using a Bruker AXS D8 Advance diffractometer. The electrochemical properties of Li-PTCA were studied using a two electrode Swagelok cell, fabricated in an argon filled glove box with lithium metal foil serving as both reference and counter electrode, and a borosilicate glass fiber sheet separator soaked with 1 M LiPF<sub>6</sub> in 1:1(v/v) of Ethylene carbonate and Dimethyl carbonate (EC&DMC) solution as the electrolyte. Both electrode-A and electrode-B were tested as cathodes. All cells were galvanostatically cycled between 0.95 V and 2.0 V vs. Li<sup>+</sup>/Li at room temperature by using a multichannel galvanostat, Arbin BT-2000. Electrochemical impedance spectroscopy (EIS) was carried out at the end of 1st and 50th charging using 5 mV<sub>rms</sub> sinusoidal perturbation in the frequency range of 100 kHz–10 mHz. EIS and cyclic voltammetry (CV) studies were done using Biologic science instruments VSP model. Specific capacities were calculated based on the mass of the active material (Li-PTCA) alone. Na-PTCA is synthesized following the same methodology adopted for synthesis of Li-PTCA by using Na<sub>2</sub>CO<sub>3</sub> instead of Li<sub>2</sub>CO<sub>3</sub>. In-situ carbon dispersion was also done adopting the same method as in the case of Li-PTCA. Since Na-PTCA is highly soluble in water, and the compound was crystallized from the solution by removing the solvent under the reduced pressure and washed with absolute ethanol several times to remove excess reagents. All the electrochemical studies were performed on in-situ carbon dispersed electrodes. Cells were assembled with sodium metal as anode and 1 M NaClO<sub>4</sub> in propylene carbonate as the electrolyte. Discharge-charge cycle was done in the voltage window 2–0.5 V (vs. Na<sup>+</sup>/Na).

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