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Perylenediimide dyes as a cheap and sustainable cathode for lithium ion batteries

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ABSTRACT

Perylenediimide dyes are a large family of conjugated small molecules with redox-active carbonyl/hydroxyl groups, which can uptake and release Li ions reversibly as low cost organic materials for next generation lithium ion batteries. In this paper, we report a series of industrially available, low price and non-toxic perylenediimide dyes, which can reversibly bind 2 Li^+ ions per molecular unit, delivering a redox capacity of 100–130 mAh g^{-1} with excellent rate capability and cycling stability, offering an attractive alternative to conventional transition-metal-based inorganic cathodes for sustainable Li ion batteries.

1. Introduction

Currently developed Li ion batteries are all based on the intercalation chemistry of graphite anode and transition-metal cathodes, which hindered their widespread application for electric power storage due to the cost and resource limitations of the transition-metal compounds [1–3]. To extend their electric storage application of Li ion batteries from portable electronics to electric vehicles or renewable power stations, it is a key issue to find an alternative cathode that can be produced from cheap, abundant and easily accessible organic materials [4,5].

Redox-active polymers have attracted considerable attention as organic cathodes for Li ion batteries because of their low cost, structural versatility and materials abundance. In recent years, a variety of polymeric cathodes such as anion-doped polypyrrols [6,7], polyimides [8,9] and radical polymers [10,11] have been revealed to deliver a reversible redox capacity comparable to the inorganic cathode materials, demonstrating a potential applicability as organic cathodes for Li ion batteries. In fact, many small organic molecules with carbonyl groups, such as quinones, anhydrides, imides and ketones, can also take place in multi-electron redox reactions, possibly serving as a high capacity cathode for Li ion batteries [12]. Recently, P. Poizot' group reported a number of polyketones with N-cyclic structure as Li insertion cathodes with a 2-electron redox capacity of ~200 mAh g^{-1} [13,14]. D. J. Kim et al. also investigated a series of N-substituted naphthalenediimides with a reversible capacity of 130 mAh g^{-1} [15]. Meanwhile, A. L.M. Reddy et al. described a purpurin-based organic cathode with a capacity of 90 mAh g^{-1} [16]. Recently, K. Krishnamoorthy et. al found hemically reduced perylene diimide (Benzoic-PDI) with hydrazine can increase the rate of redox reaction as well as the conductivity of the Benzoic-PDI [17]. Though these small organic molecules demonstrated quite a reversible capacity or high rate capability at acceptable working potential, their cycling stability needs to improve to meet battery applications, probably due to the dissolution of the organic compounds and their discharge products in the electrolyte. Polymerization of the small molecules has been proposed to circumvent the solubility issue. Recently, a series of polydiimides were synthesized by reacting dianhydried with diamine, although this method can circumvent the solubility issue, their cycling and rate performance still needs to enhance due to the complicated electron transfer in polydiimides [18]. So developing organic small molecules with high stability is of great necessity.

Organic dyes and pigments are a large family of conjugated small molecules with redox-active carbonyl/hydroxyl groups, some of which can uptake and release Li ions reversibly during the charge-discharge process. In this communication, we report a new class of organic cathode materials based on perylenediimide dyes and describe their stable and high-rate Li storage performance as a low cost and sustainable cathode for Li ion batteries.

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2. Experimental

The perylenediimide dyes used in this work were all of industrial grade, and were used without further purification. The electrodes were prepared by mixing 60% perylenediimide powders, 30% conductive carbon (Ketjen Black) and 10% polytetrafluroethylene binder by weight, rolling into ca.100 μm thick film and pressed onto an aluminum grid.

Electrochemical performances were tested in core shape cells using a Li metal disc as the negative electrode and a Celgard 2400 microporous membrane as separator. 1 M lithium hexafluorophosphate dissolved in a mixture of Ethylene carbonate: Diethyl carbonate: Propylene carbonate (4:5:1 by vol.) was used as electrolyte.

The cells were assembled in an argon-filled glove box with water/oxygen content lower than 1 ppm. The galvanostatic charge and discharge were carried out at a voltage interval of 3.5–1.5 V on a CT2001A Land Battery Testing System. CV experiments were performed using coin cells on a CHI 600 C instrument. XRD was performed on a XRD-6000 instrument (Shimadzu). FTIR was tested on a NICOLET 5700 FTIR Spectrometer with KBr pellets. XPS was performed on a XSAM 800 multifunctional electron spectrometer.

3. Results and discussion

To reveal the structural effect of perylenediimides on Li storage reaction, perylene-3,4,9,10-tetracarboxydiimide (PTCDI), a pristine perylenediimide, was chosen as a model molecule for electrochemical characterizations. Fig. 1a shows the CV curves of PTCDI electrode. It is found that the PTCDI cathode shows two pairs of closely overlapped and symmetric redox peaks around 2.5 V, suggesting a reversible two-electron redox reaction. Since PTCDI were initially present in an uncoordinated state, an obvious negative shift of the cathodic peaks was observed at the first scan, possibly due to an initial activation process required for establishing electrochemical reaction interfaces in the PTCDI cathode. In the subsequent scans, the shapes and areas of the CV peaks remained almost unchanged, implying an excellent electrochemical reversibility and cycling stability of PTCDI structure. According to previous analysis of the redox mechanism of aromatic imide groups [13,16], the CV peaks of the PTCDI can be assigned to a two-electron reaction, which involves 2 Li^+ ions associating with and disassociating from the oxygen atoms of the imide groups, as shown in the inset of Fig. 1a.

In accord with the potential positions of the CV peaks, the PTCDI electrode shows flat charge/discharge plateaus at 2.75/2.4 V at 20 mA g^{-1}, as displayed in Fig. 1b. The discharge/charge capacities in the first cycle are 138/134 mAh g^{-1} respectively, indicating a surprisingly high initial coulombic efficiency of the PTCDI electrode. The rate capability of PTCDI electrode was also evaluated at various current rates from 20 to 500 mA g^{-1}. As given in Fig. 1c, the reversible capacity decreases slightly from 130 to 110 mAh g^{-1} as the current rate increases from 20 to 300 mA g^{-1}. Even at a very high rate of 500 mA g^{-1}, the PTCDI electrode can still deliver a quite high capacity of 103 mAh g^{-1}, which corresponds to a ~80% capacity retention at such a high rate.

In addition to its high rate capability, the PTCDI electrode also demonstrates an excellent long-term cyclability. As shown in Fig. 1d, When cycled at a constant current of 100 mA g^{-1}, the reversible capacity of PTCDI electrode decreased from its initial value of 123–118.9 mAh g^{-1} after 200 cycles,corresponding to a capacity retention of 96.7%. Such a stable cyclability is really surprising because most of the organic imides used as redox-active materials usually suffer from their poor cycling performance [13–17]. If

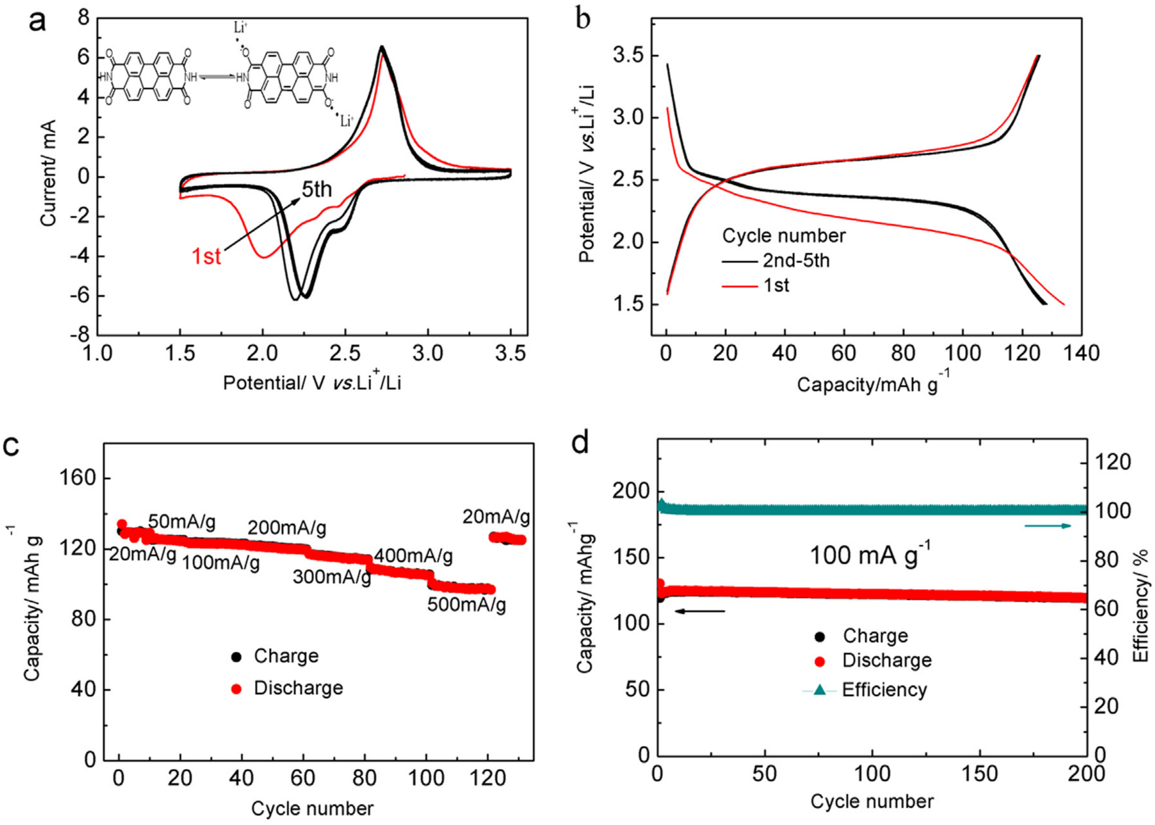

Fig. 1. Electrochemical redox properties of PTCDI: a. CV curves at a scan rate of 5 mV s^{-1}; b. Charge and discharge profiles at 20 mA g^{-1}; c. Rate capabilities of PTCDI at different current density; d. Cycling performance of PTCDI at 100 mA g^{-1}.