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Tetrakis coumarin as efficient electrode material for rechargeable lithium ion battery

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Highlights

- Tetrakis coumarin (TKC) is investigated as an electrode material for lithium ion battery.
- Incorporation of coumarin units helps in addressing solubility related issues.
- TKC demonstrates capacities of 300 and 203 mAh g^{-1} at 50 and 1000 mAg^{-1}.
- Good rate capability up to 1 A g^{-1} with good cyclability is achieved.

Abstract

Coumarin based tetramer type molecule – Tetrakiscoumarin (TKC) has been synthesized and investigated as an electrode material for lithium ion battery. TKC comprises four hydroxyl and four carbonyl sites for lithium uptake and it can undergo multiple redox reactions. It is observed that TKC exhibits discharge capacities of 300 and 203 mAh g^{-1} at 50 and 1000 mAg^{-1} with good rate capability in the potential range of 0.01–3.0 V vs Li^+. The present work involves the investigation of lactone group – containing coumarin based molecule as an electrode material and helps explore the potential of coumarin based organic materials.

Introduction

Lithium-ion batteries (LIBs) owing to their high energy density and long service life have become important in various applications related to energy-storage technology, electronics and electromobiles [1], [2], [3], [4], [5]. The development of efficient anode is one of the important factors to fabricate cost effective LIBs [6]. The advent of 2D layered graphene has resulted in a new class of promising anode materials as compared to graphite, though the electrochemical characteristics still require improvement [7], [8]. On the other hand, high capacity anodes such as silicon (Si), tin (Sn) and derived materials suffer from issues such as large volume expansion resulting in poor cyclability [9], [11]. Several inorganic-based metal alloys [10], transition metal sulfides [12]/oxides [13]/carbides [14]/carbodiimides [15], organometallic polymers [17] have been proposed and discussed in the literature. Recently, ionic crystals [16], organo-palladium complexes [18] have also been explored as anode materials. Metal organic frameworks (MOFs) with tunable structure and high surface area form another class of materials that make them promising in this direction [19].

Use of electrodes based on organic compounds is advantageous to build sustainable energy storage systems [20], [21]. Flexible nature of organic molecules helps in tuning physicochemical as well as electrochemical characteristics. Organic electrode materials for batteries date back to 1969 [22] and have received considerable attention in recent years. Large number of nature-derived and synthetic organic materials have been proposed both as anodes and cathodes for metal-ion battery systems [23], [24]. However, most of the organic compounds suffer from issues such as, low conductivity and solubility in commonly used non-aqueous battery solvents leading to poor stability. Various approaches [25], [26], [27], [28], [29] like polymerization [25], [26], salt formation [27], grafting [28] etc. have been

proposed to overcome the instability of organic materials. These methods are not totally successful since the capacity values are compromised with reduced reversibility. Few organic anode materials exhibit stable performance without any modification [34], [35]. Recent reports exploit the flexible nature of organics to design thin, free-standing electrodes [30], [31]. Covalent organic porous polymers are evolving as promising anode materials [32], [33]. Use of oligomers, tetramer-type molecules open another possible way to achieve stability in organic electrode materials and recently a few cathode materials have been reported in this category [36], [37], [38], [39].

In the present studies, tetramer type tetrakiscoumarin (TKC) is explored as a possible electrode material for LIBs. TKC is known for its antiviral, antiprotease, and anti-integrase activity [40]. TKC possesses lactone groups and hydroxyl groups which are known to be active sites for lithium uptake [41]. It is observed that TKC shows electrochemical characteristics better than recently reported polymers and organic salt-based, non-polymerized anode materials [27], [28], [29]. Furthermore, its ease of synthesis using inexpensive materials, possibility to obtain derivatives, ease of tuning properties by introducing additional active sites/removing inactive site help contribute towards low cost materials for energy storage.

Section snippets

Chemicals

Terephthaldehyde, 4-hydroxycoumarin, battery grade copper foil, lithium metal purchased from Sigma, USA. Acetylene black (Alfa-Aesar), PVDF (Fluka, Sigma), Electrolyte containing 1 M $LiPF_6$ in EC:DMC (1:1 w/w) (Merck, Germany) were used as-obtained. The solvents used for the synthesis were obtained from S D fine chemicals, India.…

Synthesis and characterization

Tetrakiscoumarin (TKC) was synthesized by following a reported procedure [42]. Briefly, a mixture of terephthaldehyde and 4-hydroxycoumarin in the ratio 1:4 respectively …

Results and discussion

Tetrakiscoumarin (TKC) was synthesized by Knoevenagel condensation as shown in Fig. 1a. The compound has been characterized by Fourier-transform infrared spectroscopy (FTIR), ^{1}H NMR Spectroscopy and X-ray diffraction (XRD) techniques. In the FTIR spectrum, vibrations of aromatic –C—H bonds show signals at 700–900 cm^{-1}. A strong peak located at 1660 cm^{-1} is due to the carbonyl stretching(-C═O). Small signals around 2600 cm^{-1} are due to the stretching of C—H groups. Stretching vibration peaks at…

Conclusions

Lactone based organic coumarin molecule has been proposed and utilized as an electrode material for lithium storage. Initial studies using the tetramer coumarin – TKC as anode reveal fairly stable electrochemical characteristics with a capacity of 287 mAh g^{-1} at 50 mAg^{-1}, with good rate capability and moderate cycling stability. Use of inexpensive organic molecule, low energy synthesis help in designing organic-based batteries. This reveals additional possibilities in tuning the structure of…

CRediT authorship contribution statement

Y.K. Guruprasadagowda: Methodology, Validation, Investigation, Writing – original draft. **M.N.K. Harish:** Conceptualization, Validation, Writing – review & editing. **Debashis Tripathy:** Validation, Investigation, Writing – review & editing. **S. Sampath:** Supervision, Conceptualization, Methodology, Writing – review & editing.…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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