Journal of Power Sources 250 (2014) 372–378

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Graphene oxide wrapped croconic acid disodium salt for sodium ion battery electrodes

Chao Luo[a], Yujie Zhu[a], Yunhua Xu[a], Yihang Liu[a], Tao Gao[a], Jing Wang[b], Chunsheng Wang[a,*]

[a] Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA
[b] School of Materials Science & Engineering, Jiamusi University, 154007, PR China

HIGHLIGHTS

- Croconic acid disodium salt (CADS) is firstly used as an anode in Na-ion battery.
- The capacity decay of CADS electrode is due to particle pulverization.
- Reducing particle size is an effective approach to enhance battery performance.
- Graphene oxide wrapped CADS exhibits the best electrochemical performance.

ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form
26 October 2013
Accepted 28 October 2013
Available online 14 November 2013

Keywords:
Sodium ion batteries
Croconic acid disodium salt
Graphene oxide
Ultrasonic spray pyrolysis
Particle pulverization

ABSTRACT

Croconic acid disodium salt (CADS), a renewable or recyclable organic compound, is investigated as an anode material in sodium ion battery for the first time. The pristine micro-sized CADS delivers a high capacity of 246.7 mAh g^{-1}, but it suffers from fast capacity decay during charge/discharge cycles. The detailed investigation reveals that the severe capacity loss is mainly attributed to the pulverization of CADS particles induced by the large volume change during sodiation/desodiation rather than the generally believed dissolution of CADS in the organic electrolyte. Minimizing the particle size can effectively suppress the pulverization, thus improving the cycling stability. Wrapping CADS with graphene oxide by ultrasonic spray pyrolysis can enhance the integration and conductivity of CADS electrodes, thus providing a high capacity of 293 mAh g^{-1}.

1. Introduction

Sodium ion batteries are the most promising alternatives to lithium ion batteries due to the low cost and abundance of sodium element in the earth [1]. The chemical similarity of sodium ion toward lithium ion enables some electrode materials used in Li ion batteries to be applied for Na ion batteries [2]. Inorganic materials synthesized through energy-demanding ceramic processes [3] are the most common Li ion electrode materials. However, to satisfy the emerging large-scale applications of energy storage, next generation battery electrodes should be made from renewable or recyclable resources via low energy consumption processes. One possible approach is to use electrode materials fabricated from biomass or recyclable organic materials via solution phase routes [4].

Several organic materials have been investigated as electrodes for Li ion batteries [5], but very few organic materials were explored for Na-ion batteries. The organic electrodes face two major challenges in organic electrolyte batteries: (1) low power density due to poor electronic conductivity of organic compounds, (2) fast capacity decay during charge/discharge cycles which is generally attributed to dissolution of organic compounds into organic electrolytes [3]. One way to mitigate the dissolution of organic materials in organic electrolytes is use of organic salts [3]. Among the salts, carbonyl group based organic compounds such as lithium salt of tetrahydroxy–benzoquinone [6], lithium ethoxycarbonyl-based compound [7], dilithium trans–trans-muconate and dilithium terephthalate [8] have been investigated as electrodes for Li ion batteries. These organic salts normally contain more than two carbonyl groups which are connected by conjugated carbon matrix. These carbonyl groups are redox centers which enable the electrochemical reaction to take place in the electrodes. During the discharge process, each carbonyl group can obtain an

---

* Corresponding author.
E-mail address: cswang@umd.edu (C. Wang).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.10.131

electron and a lithium ion that induces electron transfer in the conjugated carbon matrix. The reaction between carbonyl group and lithium ion enables the ion transfer and electron transfer in Li ion batteries. Although the solubility of organic salts in the electrolyte has been reduced, these organic salts still suffer from fast and continuous capacity decline during charge/discharge cycles [6–8]. The mechanism behind the fast capacity decline is still not fully understood.

Most reported organic salts experience phase transformation during lithiation/delithiation as evidenced by a flat voltage plateau in charge/discharge profile and structure change in X-ray diffraction (XRD) patterns [8]. The phase transformation is normally accompanied with volume change. The large volume expansion in the first lithiation can even change the crystal structure of organic salts into amorphous structure and retain amorphous structure in the following charge/discharge cycles [8], which is also observed in Si anodes [9]. The structure change of Si from crystal to amorphous structure is attributed to the large volume change (300%) of Si during lithiation [9]. The severe volume change of Si pulverizes the Si particle, resulting in rapid capacity decline during charge/discharge cycles [10]. Therefore, the volume change of organic salts during lithiation/delithiation may be also responsible for the capacity decay.

In principle, the carbonyl group based organic electrode compounds used in lithium ion batteries can potentially be applied to sodium ion batteries [11]. However, due to larger ion size of Na$^+$ than Li$^+$, only few organic salts are suitable for Na ion batteries. In addition, the larger ion size of Na$^+$ causes much more severe volume change of organic salts, resulting in fast capacity decay of organic compounds in Na ion batteries [11c]. Therefore, only few organic compounds were explored for Na-ion batteries. Due to the large volume change, these organic compounds showed quick capacity decline during Na insertion/extraction [11c]. However, how the volume change of organic salts affects the cycling stability has not been investigated yet.

In this paper, croconic acid disodium salt (CADS) is used as a model electrode to investigate the capacity decline mechanism of organic salt electrodes in Na ion batteries. To our best knowledge, CADS has never been studied as a battery electrode material in Li-ion and Na-ion batteries. In addition, this is also the first effort to study the effects of phase change on capacity decay of organic salt electrodes in Na ion batteries. As shown in Fig. 1, three CADS samples, micro-sized pristine CADS, submicrometer-size CADS (sCADS), and graphene oxide wrapped CADS (GO-CADS), are employed to investigate their electrochemical behaviors toward Na. sCADS and GO-CADS are fabricated by ultrasonic spray pyrolysis.

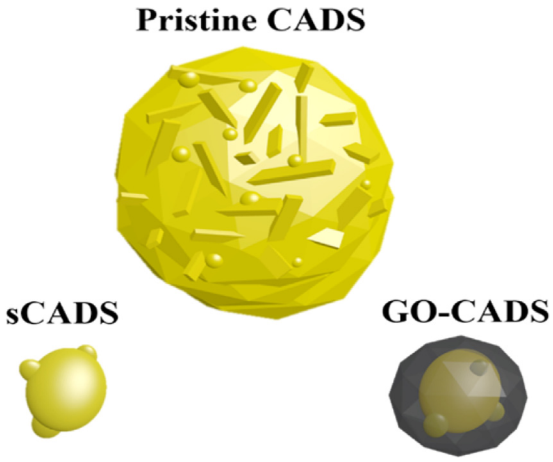
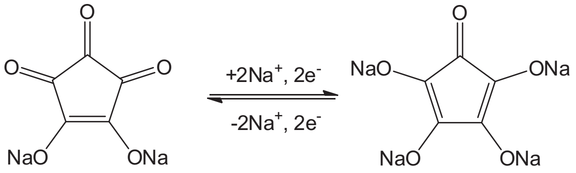


Fig. 1. Schematic illustration for pristine CADS, sCADS and GO-CADS.



Scheme 1. The sodiation/de-sodiation mechanism for croconic acid based molecule.

Our results show that the particle pulverization is a main reason for capacity decline. Minimizing particle size and wrapping CADS with graphene oxide can effectively stabilize the electrodes during Na ion insertion/extraction, thus improving the cycling stability.

2. Experimental

All chemicals were purchased from Sigma Aldrich and used as received. The CADS with small particle size of 0.5–1.0 μm (denote

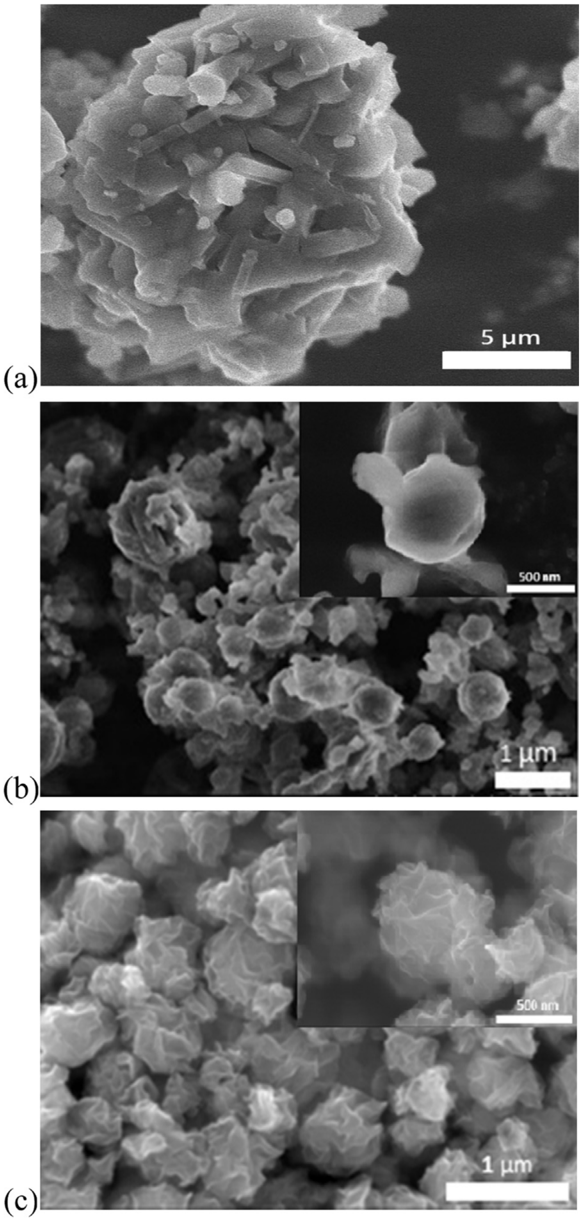


Fig. 2. The SEM images of pristine CADS (a), sCADS (b), and GO-CADS (c).