



Structure-Property of Metal Organic Frameworks Calcium Terephthalates Anodes for Lithium-ion Batteries



Liping Wang^a, Chengxu Mou^a, Yang Sun^b, Wei Liu^a, Qijiu Deng^a, Jingze Li^{a,*}

^a State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China

^b Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 9 January 2015
Received in revised form 24 March 2015
Accepted 12 May 2015
Available online 15 May 2015

Keywords:

Metal organic frameworks
Carboxylate
Hydration water
Calcium terephthalate
Lithium ion battery

ABSTRACT

Metal organic frameworks have attracted considerable interest as electrode materials for lithium ion batteries. In this paper, the metal organic frameworks hydrated calcium terephthalate ($\text{CaC}_8\text{H}_4\text{O}_4 \cdot 3\text{H}_2\text{O}$) and anhydrous calcium terephthalate ($\text{CaC}_8\text{H}_4\text{O}_4$) as anodes for lithium ion batteries are comparatively studied. Crystallography and local chemical bond analysis are combined to interpret the structure-property of calcium terephthalates. Results show that the anhydrous $\text{CaC}_8\text{H}_4\text{O}_4$ has a spacious ordered layer structure and a higher Ca-O chemical bonding interaction, delivering a higher capacity, better cycling performance and rate performance than $\text{CaC}_8\text{H}_4\text{O}_4 \cdot 3\text{H}_2\text{O}$.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

To date, crystalline metal-organic frameworks (MOFs) with more than 20 000 reported structures are explosively studied as potential applications in gas storage, catalysts and chemical separations [1–3]. MOFs are made of inorganic metal cations and organic anion units (e.g. ditopic or polytopic carboxylates) by strong ionic bonds, leading flexibility in geometry, surface area and functionality. Meanwhile, it is found that the negatively charged carboxylate organic molecules have the ability of storage Li and Na ions, which propel the MOFs into the realms of lithium ion batteries and sodium ion batteries [4–6]. Actually, the most common carboxylate organic material lithium terephthalate $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ proposed by Armand and coworkers is one type of the MOFs [7–9]. It has a theoretical lithium storage capacity of 301 mAh g^{-1} and an operation voltage versus Li/Li^+ at $\sim 0.8 \text{ V}$, providing possibility to build a high energy density and safe full cell. The advantages of these MOFs electrode materials are high theoretical capacity, high thermal stability and low cost, catering the energy storage sources demand for electric vehicles and state grids.

Small molecular weight MOFs suffer from high solubility in the conventional carbonate-based electrolytes resulting in capacity fading [7,10]. To tackle this issue, sulfone and hydrogen-bond

donating character electrolytes instead of carbonate-based electrolytes are supposed to effective solutions [11]. Introduction of functional groups and longer organic units (e.g. benzenedicarboxylic ligand to benzenetribenzoate ligand) to increase the intermolecular interaction and molecular weight are alternative ways. Shimizu et al. have successfully improved the cycling behavior of quinines via incorporating two $-\text{CO}_2\text{Li}$ groups [12]. Another choice is cation exchange to increase the metal-organic bond interaction. Recently, we propose an idea of calcium displacement of lithium in the $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$ taking advantages of the high ionization energy of Ca cation [13]. The as-obtained $\text{CaC}_8\text{H}_4\text{O}_4$ (denoted as CaTPA) has low solubility and good structural stability during charge-discharge process. Its electrochemical performance can be enhanced via addition of high electronic conductivity material graphite [14].

There are limited reports on the structure-properties of these MOFs as electrode materials for batteries [15–18]. Poizat and coworkers find that isomeric effect in dilithium (2,3-dilithium-oxy)-terephthalate compound ($\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$) offers a voltage gain [19]. Yasuda et al. discovered that 2,6-naphthalene dicarboxylate dilithium with higher ordering structure has better electrochemical performance for providing more efficient electron and ion pathways [4]. It is known that water molecules are easily attached into the MOFs in the synthesis procedure [16]. In this study, we continue our effort on the calcium terephthalates. Both of anhydrous CaTPA and hydration form $\text{CaTPA} \cdot 3\text{H}_2\text{O}$ are applied as anodes for lithium ion batteries. The effects of hydration water on their structure and electrochemical properties are systematically studied. Their electrochemical properties in terms of cycling

* Corresponding author. Tel.: +86 28 83207620; fax: +86 28 83202569
E-mail address: lijingze@uestc.edu.cn (J. Li).

performance, rate performance are elucidated via structure and chemical bond point of views.

2. Experimental

2.1. Materials Synthesis

Calcium terephthalate (CaTPA) and calcium terephthalate trihydrate (CaTPA·3H₂O) were prepared by a displacement reaction between di-lithium terephthalate and calcium chloride. Typically, 0.02 mol LiOH·H₂O and 0.01 mol p-phthalic acid were dissolved in 100 ml de-ionized water under continuous stirring for 6 hours. Afterward, 0.01 mol calcium chloride solution was added dropwise into the transparent solution with formation of white precipitates (CaTPA·3H₂O). The mixture was kept in a thermostatic box at 80 °C for 12 hours to ensure a complete reaction. After that, the white precipitates (CaTPA·3H₂O) were filtered, subsequently to wash with de-ionized water and alcohol for several times. The CaTPA powders were obtained via drying the as-prepared CaTPA·3H₂O under vacuum oven at 110 °C for 12 hours.

2.2. Materials characterization

X-ray diffraction patterns were collected on a Philips X'Pert MPD (40 KV/100 mA) diffractometer ($\lambda = 0.154056$ nm). Each pattern was recorded in the range of 5–70° (2 θ) with a step size of 0.03°. The patterns were analyzed by Rietveld refinement method using Fullprof_suite program. The morphologies were investigated by a field-emission scanning electron microscope (FE-SEM, Hitachi, S3400N). Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from RT to 800 °C using a TA instrument Q500. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on SHIMADZU FT-IR 8400.

2.3. Cell assembling and electrochemical test

For the electrochemical measurements, the electrodes were prepared by casting a slurry of 60 wt% active material, 30 wt% carbon black and 10 wt% PVDF binder on Cu foil. CaTPA electrodes were dried in vacuum at 110 °C for 12 hours. While, CaTPA·3H₂O electrode was dried at room temperature under vacuum condition for preserving its crystal water. The electrolyte consisted of 1 M LiPF₆ was dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). The polypropylene (PP) membrane (celgard 2400) was employed as the separator.

The galvanostatic charge-discharge measurements were performed under various current densities from 14–300 mA g⁻¹ in a potential range of 0.5–2.9 V on a CT2001A cell test instrument (LAND Electronic Co.) at room temperature. The cyclic voltammetry (CV) curves were performed at a scan rate of 0.08 mV s⁻¹ using Solartron SI1287 electrochemical workstation. All the measurements were carried out at room temperature. The weight of the active materials was 1–2 g cm⁻².

3. Results and Discussion

Infrared spectra of CaTPA·3H₂O and CaTPA in the wavenumber region between 400 and 4000 cm⁻¹ are shown in Fig. 1. Absence of characteristic absorption peaks of terephthalic acid (C₈H₆O₄) (e.g. 1671 cm⁻¹ and 1420 cm⁻¹) and di-lithium terephthalate (Li₂C₈H₄O₄) (e.g. 1569 cm⁻¹ and 1390 cm⁻¹) [20] demonstrates a complete reaction in our synthesis procedure. The band in the CaTPA·3H₂O spectrum at 3300 cm⁻¹ attributes to the coordinated

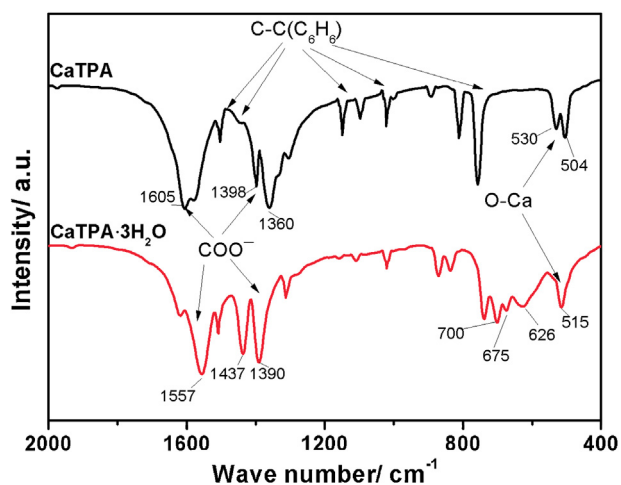


Fig. 1. Infrared spectra of CaTPA·3H₂O and CaTPA.

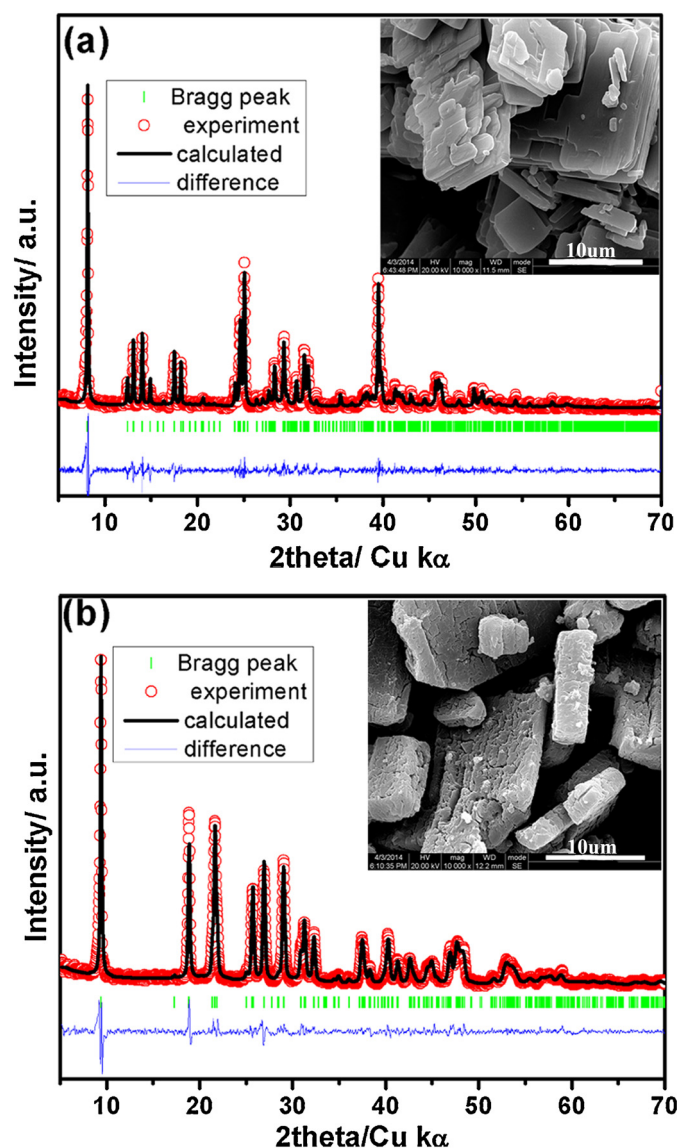


Fig. 2. XRD patterns and their refinement with observed data points (red points), calculated data (black line), Bragg positions (green bars), difference (blue line) for as-obtained CaTPA·3H₂O powder (a) and CaTPA powder (b). The corresponding scanning electron micrographs for each sample are reported (insets). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/183780>

Download Persian Version:

<https://daneshyari.com/article/183780>

[Daneshyari.com](https://daneshyari.com)