



Zinc Oxalate as a Green Anode Material for Commercial Li-Ion Batteries: a Preliminary Study

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ABSTRACT: Li ion batteries is a crucial energy storage for new and renewable energy (NRE)-based power plant due to its high energy density. However, the anode materials of commercial Li-ion batteries such as graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are considered less eco-friendly due to its requirement of high temperature processing which is also uneconomical. In this research, for the first time ever, zinc oxalate was prepared via mild temperature precipitation process and applied as anode material in commercial Li-ion batteries. XRD, FTIR and SEM analysis were conducted to examine the physical and chemical properties of the as obtained zinc oxalate. The effect of precursor concentration was investigated. Charge-discharge analysis shows that zinc oxalate dihydrate as anode material delivered a discharge capacity of 25 mAh/g.

Keyword: Anode, Zinc, Zinc oxalate, precipitation, batteries, Li-ion batteries

1. Introduction

A sustainable energy storage technology has become the dream technology of the current era. It is a crucial aspect in clean energy development that involve new and renewable energy (NRE). NREs are highly abundant but sometime produce intermittent energy, such as: solar energy and wind energy. These energy sources have an enormous prospect to be harvested but their dependability is limited by the presence of energy storage. Li-ion batteries (LIBs) are considered as reliable energy storage due to their features such as

long shelf life and high energy storage capability. Inside an LIB, there are four main parts namely cathode, anode, separator and electrolyte. The commercial cathode materials in the market are LiFePO_4 , LiNixMnyCozO_2 , and LiCoO_2 . Commercial separator used in LIBs is celgard while commercial anode material is artificial graphite [1]

Graphite can be used as anode material due to its ability to store Li-ion during the charging process. Since it contains carbon, it is considered highly abundant and reliable for LIBs

commercialization. Carbon based anode is also consistently developed due to its economic benefit [2][3] However, to obtain carbon-based anode, it requires efforts such as high energy consumption and potential organic waste management as a result of carbonization process. A graphitic anode material requires ultra-high temperature process which makes the overall production of graphite less eco-friendly and less economical. Metal oxides have been developed as the next generation of anode materials. Lithiated metal oxides such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and Li_2ZrO_3 (LZO) have been successfully adapted for commercial LIBs, however the presence of Li, and not to mention the synthesis process are both considered uneconomical [4][5]. Therefore, an anode material synthesized at mild temperature for commercial LIBs application development is highly necessary to obtain a cheap and more sustainable energy storage.

Recently hydroxide of Ni and Co have been employed as an active material in lithium metal batteries [6][7]. However, Ni and Co also considered expensive and not eco-friendly. Zinc-based anode material is promising to be applied as anode material [8][9]. It is eco-friendly, cheap and highly abundant. Herein, for the first time ever, we propose a preliminary study of zinc oxalate utilization in commercial Li-ion batteries. Zinc-oxalate or ZnC_2O_4 is obtained via aqueous precipitation at various concentration with no further high temperature processing.

2. Experimental Method

$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ obtained from Xiangtan New Sunshine, China was used as the precursor. Oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) obtained from Yuanping, China was used as an oxalate source. Both materials were used directly without any purification step.

In equimolar composition, ZnSO_4 and oxalic acid were dissolved in separate beakers at various concentration of 0.5 M, 1 M and 2 M. After the material thoroughly dissolved, the oxalic acid was transferred to a beaker containing ZnSO_4 solution with same concentration. Precipitation reaction occurred and the beaker was continuously stirred for 1 hour at 50 °C The precipitate was allowed to settle and separated from the liquor using filter paper. The precipitate was washed for three times and dried in an oven. The ZnC_2O_4 samples prepared at concentration of 0.5 M, 1 M and 2 M were labelled as ZnOx-A, ZnOx-B, and ZnOx-C, respectively.

The as prepared samples were characterized using XRD (MD-10 diffractometer, MTI), FTIR (IR-Spirit, Shimadzu), and SEM (Jeol, Japan). The electrochemical performance test was employed by assembling ZnOx samples electrode sheet prepared via doctor blade method, separator, and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode material into a cell with LiPF_6 carbonic solution. The overall process is described elsewhere. The cell was charged and discharged using Neware battery testing system (Neware, China) at working voltage of 2.2-4.3 V and current density of 20 mA/g.

3. Result and Discussion

Figure 1 displays the FTIR spectra of ZnC_2O_4 samples obtained at various concentration. Absorbance peaks observed at wavenumber 400-1600 shows a typical metal oxalate compound while absorbance peak detected at 3400-3300/cm can be attributed to H_2O molecule; thus, it can be concluded that hydrate crystal is presence in the sample[9], [10]

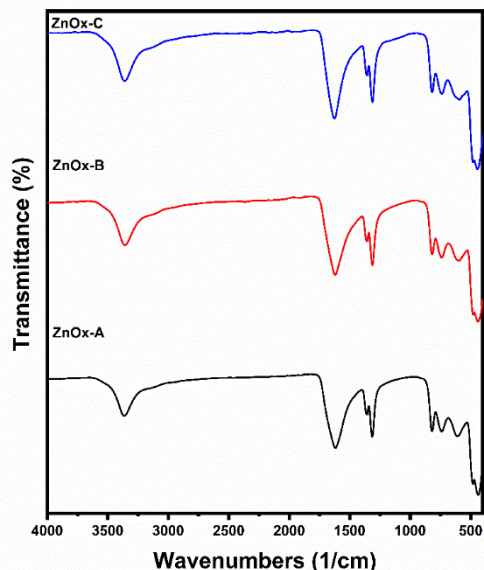


Figure 1. Fourier-transformed infra-red spectra of ZnC_2O_4 (ZnOx) powder

Based on previous researches, hydrated crystal often found in the oxalate precipitation. The total amount of hydrate crystal can be estimated by thermal gravimetric analysis[11]. However, it is not conducted in this research. The total hydrate crystal of each sample is x-ray diffraction characterization. It can be assumed that the $ZnC_2O_4 \cdot xH_2O$ samples are obtained with precursor concentration of 0.5 M, 1.0 M, and 2.0 M. The effect of concentration is insignificant since the peak intensity are similar between each sample.

Figure 2 presents the x-ray diffraction pattern of zinc oxalate (ZnOx) obtained from precipitation process of $ZnSO_4$ solution with oxalic acid solution at equimolar proportion. All of the peaks are similar one to another and can be indexed to JCPDS card no.25-1029. Based on this finding, all of the sample is categorized to a monoclinic structure of $\alpha-ZnC_2O_4 \cdot 2H_2O$ with space group C2/c no. 15A. The solution route of ZnOx precipitation is proved to be an effective method to produce such product. In the XRD pattern, there are no impurities phase can be

observed, hence a pure $ZnC_2O_4 \cdot 2H_2O$ samples are successfully synthesized[12], [13].

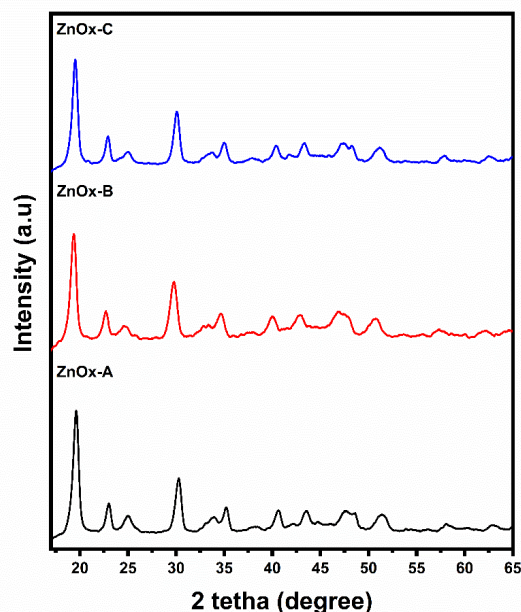
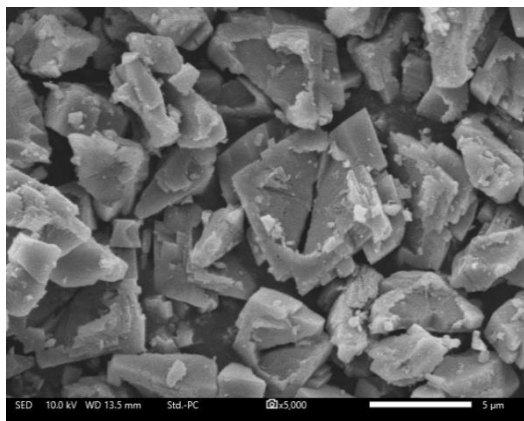
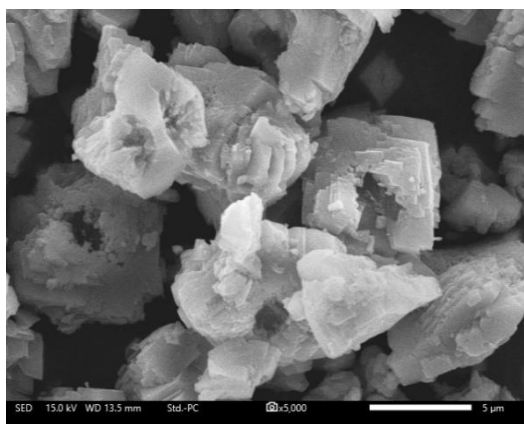


Figure 2. X-ray diffraction of zinc oxalate obtained at various precipitation concentration of (a) 0.5 M, (b) 1.0 M, and (c) 2.M

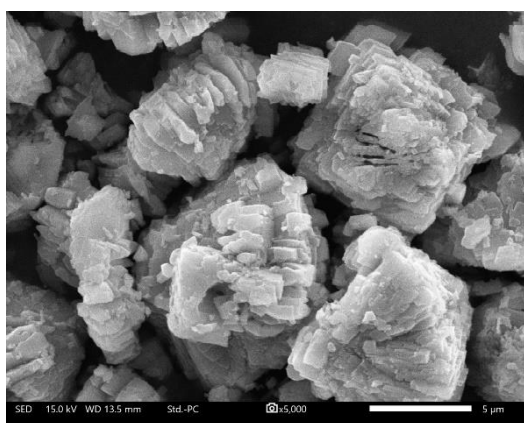
SEM image of as obtained zinc oxalate samples is depicted in figure 3. Triangular shaped particle with clear crystal facet can be seen in figure 3a. Agglomerated secondary particle consist of sheets-like primary particle can be seen in figure 3b. Meanwhile, in figure 3c, a denser particle with similar morphology to figure 3b can be observed. Based on the figures, it can be concluded that while the concentration difference of the precursors is not significantly affecting the structural and surface chemistry properties of the sample, it is significantly affecting the morphology of the particle. At lower concentration, the particle has a clear facet crystal while in the higher concentration, the particle has sheet-like particle with increase in density.



(a)



(b)

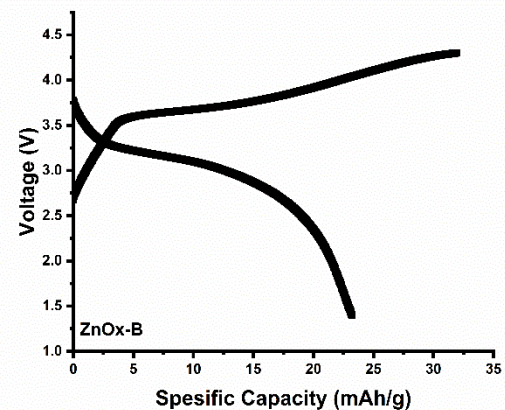


(c)

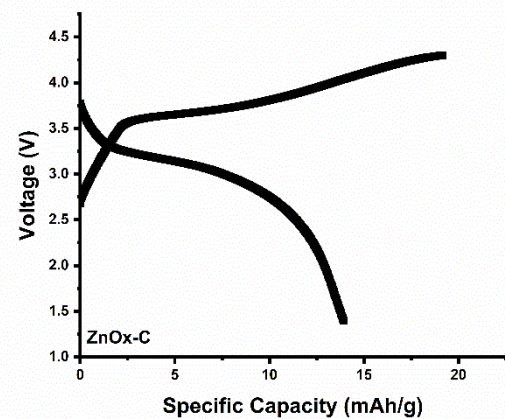
Figure 3. SEM Image of ZnC₂O₄ powder at various precursor concentration of (a) 0.5 M, (b) 1.0 M, and (c) 2.0 M

It can be predicted that during the precipitation, higher concentration results in increase of reaction and crystal nuclei growth. Based on Ostwald ripening mechanism, rapid crystal growth may

reach a better distribution of particle sizes and formation of pseudo-spherical morphology. Particle with rough surface and sheet-like particle has higher surface area which affect the Li storage capability. Considerably, ZnOx-B and ZnOx-C were selected to be tested in the electrochemical performance test[14]–[16].



(a)



(b)

Figure 4. Charge-discharge analysis of (a) ZnOx-B and (b) ZnOx-C as anode material in Li-ion batteries

Electrochemical performance testing was performed in a cylindrical battery cell by using the NMC811 (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂) as the counter cathode and ZnOx as an anode and weight basis. The specific capacity of the ZnOx sample in the cylindrical battery can be seen in Figure 4. Based on the figure, the specific capacity of ZnOx-B is 24 mAh/g and the specific

capacity of ZnOx-C is 14 mAh/g. The initial charging capacity is near 200 mAh/g_{cathode} (figure is not shown), however the discharge capacity is only 10%. 90% of irreversible Li storage is occurred due to the conversion of active Li to inactive Li through chemical reaction of Li ion with Zn-oxalate to LiC₂O₄. However, the ZnOx sample is considered functional since it can deliver discharge capacity of 24 mAh/g_{anode} and can be improved by tuning the size and morphology of the particle. This opens for possible future projects on developing green anode material for Li-ion batteries.

4. Conclusions

A pure zinc oxalate dihydrate powder with good structural characteristic is successfully synthesized. The effect of precursor concentration does not significantly alter the structural characteristic of the products, but highly affected the morphology features. Based on charge-discharge analysis, the as obtained zinc oxalate dihydrate as an anode material can deliver a discharge capacity of 24 mAh/g of anode in commercial batteries using NMC811 as the cathode material.

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