



Preparation and characterization of basic carbonates as novel anode materials for lithium-ion batteries

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Abstract

Three basic carbonates, $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, are prepared and used for the first time as anode materials for lithium-ion batteries. Electrochemical results show that $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$, $\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ can deliver high initial discharge capacities of 1175.8, 1742.6 and 1356.2 mAh g^{-1} , respectively. The lithium storage mechanisms of basic metal carbonates are observed by various electrochemical, *ex-situ* and *in-situ* methods during the initial charge–discharge cycle. It can be found that basic metal carbonates decompose into metal ($\text{M} = \text{Pb}$, Ni or Cu), Li_2CO_3 , LiOH and H_2O upon the preliminary discharge. With further lithiation, the active metal can alloy with Li to form several Li_xM phases. During the reverse charge process, Li extraction from the de-alloying reaction, $\text{M/Li}_2\text{CO}_3$ and M/LiOH mixtures can be observed. However, the cycling efficiency is low. Electrochemically inactive particles generated from pulverization, structural collapse and electronic contact loss result in the large irreversible capacity and low initial cycling efficiency. By using carbon black as conductive additive and buffer layer, the electrochemical properties of composite can be greatly improved. Carbon black– $(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2$ composite shows a reversible charge capacity of 244.7 mAh g^{-1} after 20 cycles, which is much higher than the value (77.2 mAh g^{-1}) of the pristine sample.

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1. Introduction

Lithium-ion batteries, as the potential attractive green energy sources for hybrid/electric vehicles and consumer electronics, have attracted significant interests in the past 3 decades owing to their high capacity, superior stability and environmentally friendly characteristics. As the anode material in lithium-ion batteries, carbon-based materials such as artificial graphite are usually used as the standard electrodes in the present day due to their good electronic conductivity and low volume change during the lithiation and delithiation process [1]. Nevertheless, their poor rate performance (low Li ion diffusion coefficient), serious safety issue (low Li ion insertion potential), and their low capacity (theoretical capacity of graphite is 372 mAh g^{-1}) cannot make the carbon-based anode materials match the

demand of the progressive modern industry [2,3]. Consequently, many substitution materials have been exploited.

Recently, transition metal oxides (M_xO_y , where M is Cu , Ni , Co , Mn , or Fe) have shown great potential as anode materials for lithium-ion batteries owing to their high safety, high theoretical capacity, low cost and environmental friendliness [4–11]. Unfortunately, there are still many challenging issues in using them for lithium-ion batteries. One obstacle is their power performance, resulting from their low intrinsic electronic conductivity. Another hindrance is the poor cycle performance due to the severe volume expansion during cycling process and the formation of unstable solid electrolyte interphase (SEI) film [7,12].

In the most recent years, several metal carbonates, such as manganese carbonate [13], cobalt carbonate [14,15], $\text{Mn}_{1-x}\text{Co}_x\text{CO}_3$ [16], $(\text{BiO})_2\text{CO}_3$ and CdCO_3 [17], have been considered as potential candidates for anode materials in lithium-ion batteries due to high reversible capacity, good

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capacity retention and excellent cycle calendar life. Nevertheless, no literatures about basic carbonates as anode materials for lithium-ion batteries were ever reported. In this paper, we firstly report the electrochemical performance of basic metal carbonates as anode materials by using cyclic voltammetry and galvanostatic charge–discharge techniques. Moreover, further studies are undertaken to clarify the electrochemical reaction mechanisms of basic metal carbonates with Li by various *ex-situ* and *in-situ* techniques.

2. Experimental

In this work, $\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$, $(\text{PbCO}_3)_2 \cdot \text{Pb(OH)}_2$ and $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ were prepared by a co-precipitation method using $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{Pb(NO}_3)_2$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as raw materials and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ as precipitant. All the chemical reagents were analytical grade and obtained from Sinopharm Chemical Reagent Co. Ltd. in China. The obtained deposits were dried at 80°C under vacuum before use.

2.1. Samples characterization

The crystallographic structure of the samples was determined by the X-ray diffraction (XRD, Bruker AXS D8 Focus diffractometer) using $\text{Cu K}\alpha$ ($\lambda=0.15406\text{ nm}$) radiation. The surface morphology and microstructure of the samples were characterized by scanning electron microscopy (SEM, JEOL S3400). Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) measurements were performed on JEOL JEM-2100. Thermogravimetric (TG) and differential

thermal analysis (DTA) curves were obtained in a Seiko TG/DTA 7300 instrument under argon atmosphere.

To investigate the reaction mechanisms in the basic carbonates, *ex-situ* XRD and *ex-situ* Fourier transform infrared spectroscopy (FTIR, Nicolet FTIR-6700) patterns of basic carbonates were collected at selected capacities during the initial discharge and charge process. The lithiated and delithiated samples for *ex-situ* XRD were prepared in an argon-filled glove box, dried under vacuum condition, and put in the sample holder covering with a polymer film, then immediately analyzed by XRD in the angle range from 10° to 80° . The lithiated and delithiated samples for *ex-situ* FTIR were washed by dimethyl carbonate and vacuumed for 5 h before mixing with KBr. The semi-transparent slices were pressed and prepared using the mixed powder in the argon-filled glove box and transferred to the sample chamber within 10 s. The semi-transparent slices were studied by Nicolet FTIR-6700 instrument under argon environment.

2.2. Electrochemical characterization

The working electrodes were prepared by blending the basic carbonates, carbon black (CB) and polyvinylidene fluoride at the weight ratio of 4:1:1 in N-methylpyrrolidone and pasted on a Cu foil. The working electrodes were dried at 120°C under vacuum condition for 12 h and then cut into discs with a diameter of 15 mm. In the simulated batteries, a pure lithium metal foil (Jiangxi Ganfeng Lithium Co. Ltd.) was used as counter electrode. The organic electrolyte (Zhangjiagang Guotai Huarong New Chemical Materials Co. Ltd.) was

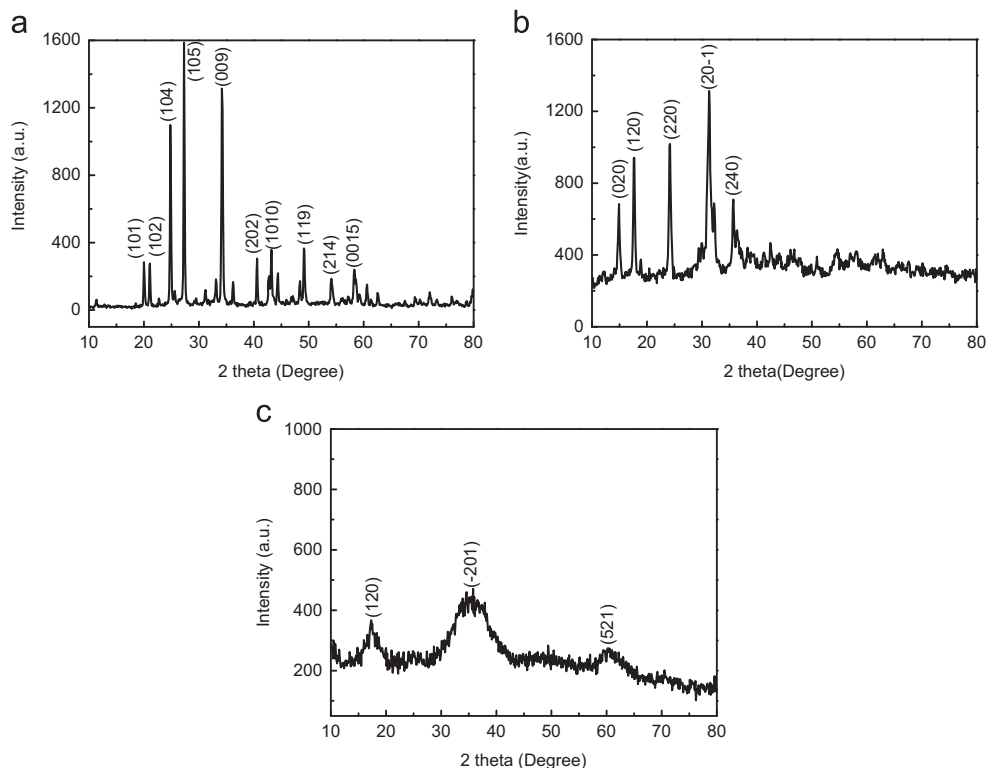


Fig. 1. XRD patterns of (a) $(\text{PbCO}_3)_2 \cdot \text{Pb(OH)}_2$, (b) $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$ and (c) $\text{NiCO}_3 \cdot 2\text{Ni(OH)}_2 \cdot 4\text{H}_2\text{O}$.

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