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Electrochemical decomposition of Li_2CO_3 in NiO–Li_2CO_3 nanocomposite thin film and powder electrodes

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HIGHLIGHTS

► NiO–Li_2CO_3 composite thin film and powder electrodes are prepared.
► Li_2CO_3 phase is decomposable after being charging to 4.1 V.
► NiO acts as a catalyst to decompose Li_2CO_3.

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ABSTRACT

Two types of NiO–Li_2CO_3 nanocomposite electrodes have been prepared for the electrochemical decomposition studies. The thin film electrode with a thickness of 225 nm and grain size around 5–8 nm is prepared by a pulsed laser deposition method. The powder sample is prepared by a solution evaporation and calcination method with primary particle size in the range of 20–50 nm. Using *ex situ* TEM, Raman and FTIR spectroscopy and synchrotron based *in situ* XRD, the electrochemical decomposition of Li_2CO_3 phase in both types of the NiO–Li_2CO_3 nanocomposite electrodes after charging up to about 4.1 V vs Li^+/Li at room temperature is clearly confirmed, but not in the electrode containing only Li_2CO_3. The NiO phase does not change significantly after charging process and may act as catalyst for the Li_2CO_3 decomposition. The potential of using NiO–Li_2CO_3 nanocomposite material as additional lithium source in cathode additive in lithium ion batteries has been demonstrated, which could compensate the initial irreversible capacity loss at the anode side.

1. Introduction

Since the first report on reversible heterogeneous lithium storage in transition metal oxides by Poizot et al. in 2000 [1], the mechanism of conversion reaction has attracted a lot of attention. It is fundamentally interesting that the inert Li_2O is electrochemically decomposable at room temperature when forming nanocomposite with transition metals (TM). Later, analogous reversible lithium storage was also observed in transition metal fluorides, sulfides, nitrides, phosphides and selenides [2–7]. The enhanced electrochemical reactivity of LiX (X = F, O, S, N, P) is mainly related to the nanocomposite microstructure where the LiX and TM phases have extremely small grain size (<5 nm) and disperse uniformly. It is also noticed that the solid electrolyte interphase (SEI) on these materials is decomposable upon charging [1,8–10]. This is quite different than the case of the SEI film on the graphite anode [11,12]. Our previous investigations confirmed that the oligomer, lithium alkyl carbonate and polymer like SEI components on Cr_2O_3 anode are not stable after charging to 3.0 V [9]. It is well known that inorganic phases, such as Li_2O, LiF and Li_2CO_3 are important components in the SEI films. Since Li_2O or LiF can be electrochemically decomposed in the conversion reaction on transitional metal compound anodes, it is very important to see if Li_2CO_3 is also electrochemically decomposable in its nanocomposite with transitional metal or metal compounds. Recently, reversible lithium storage in $MnCO_3$ in a voltage range of 0–3.0 V vs Li^+/Li was reported by Tirado et al [13,14]. A conversion reaction mechanism was proposed but no experimental evidences were provided. This implies the possible decomposition of Li_2CO_3 when forming nanocomposite with Mn.

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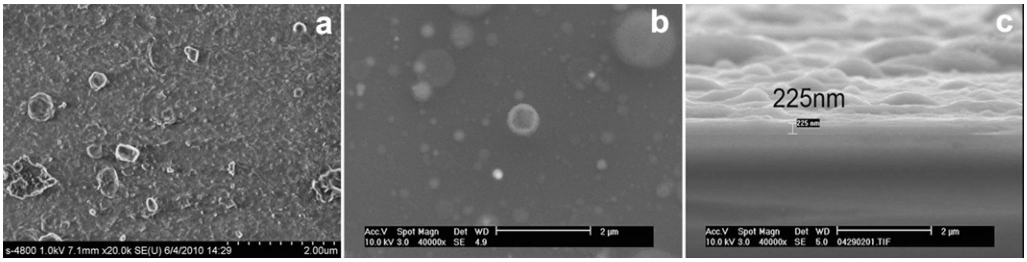

Fig. 1. (a and b) Top view of SEM images of the NiO–Li_2CO_3 composite thin films on Ti and Si substrates, respectively. (c) Cross-section view of the film on Si substrate.

It is also known that Li_2CO_3 phase can be found on the surface of Ni-based $LiMO_2$ type layered cathode materials after exposing in air for long time [15–17]. The existence of Li_2CO_3 on the surface of cathode materials produces severe deleterious effects on the capacity and power performance of the cathodes [16,17]. It has been noticed that aged Ni-based $LiMO_2$ shows an irreversible capacity loss. The origin is suggested to be related to the electrolyte decomposition. However, it is not clear whether the capacity loss is also related to the irreversible decomposition of Li_2CO_3.

In addition, it was regarded that the poor cycle life of the Li-air batteries using carbonate-based electrolytes is probably due to the undesirable discharge products of carbonates (lithium alkyl carbonates and/or Li_2CO_3) rather than the desired Li_2O_2 and Li_2O [18–20]. Therefore, the electrochemical decomposition of Li_2CO_3 could be applied in a positive way for the Li-air batteries.

Accordingly, the studies on electrochemical decomposition of Li_2CO_3 will have very important implication for both Li-ion batteries and Li-air batteries. In this work, the NiO–Li_2CO_3 thin films and powder nanocomposite electrode have been prepared and characterized by SEM, XRD, TEM, Raman, and FTIR. The electrochemical decomposition phenomenon of Li_2CO_3 in the nanocomposite electrodes is investigated.

2. Experimental

The NiO–Li_2CO_3 nanocomposite thin film electrodes were prepared by a pulsed laser deposition (PLD) system. A mixture of NiO (99%, Sinopharm Chemical Reagent Co., Ltd) and Li_2CO_3 (98%, Sinopharm Chemical Reagent Co., Ltd) at a molar ratio of 1:1.1 was ball-milled for 6 h, and then pressed into a one-inch diameter pellet. The pellet was then sintered at 450 °C under argon atmosphere for 24 h to form a PLD target. In the PLD system, a KrF excimer laser (Tuilaser, 248 nm beam, Germany) was used as a light source. The laser beam was focused on the rotating NiO–Li_2CO_3 target with an angle of 45°, and the target–substrate distance was 35 mm. The energy density was fixed at 5 J cm^{-2} with a repetition rate of 9 Hz. Before deposition, the PLD chamber was evacuated to 1.0×10^{-4} Pa and then kept at 20 Pa under high-purity argon (99.999%) during deposition. The thin film was deposited for 1.5 h on two different types of substrates: on Ti foil (99.99%, Alfa, polished by 1000 # sand paper) at RT for Raman, Fourier transformed infrared (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical studies; and on Si (100) wafer for thickness measurements.

The NiO–Li_2CO_3 composite powder was synthesized as follows. Firstly, 6.242 g of $C_4H_6NiO_4 \cdot 4H_2O$ (99%, Sinopharm Chemical Reagent Co., Ltd) and 5.075 g of $C_2H_3LiO_2 \cdot 2H_2O$ (98%, Shanghai Huajing Biological High-Tech Co., Ltd) were dissolved in 100 ml of distilled water, then 100 ml aqueous solution contained 0.075 M NH_4HCO_3 (AR, Beijing Chemical Reagents Company) was dripped in the pre-blended solution. The suspension was kept stirring for 1 h after the addition, and then was dried at 80 °C for about 72 h. The as-prepared powders were ground and heated in air at 400 °C for 1 h. The final product, the NiO–Li_2CO_3 composite material, was ground and used for further tests. The NiO–Li_2CO_3 powder electrodes were composed of the NiO–Li_2CO_3 powder, carbon black and PVDF at a weight ratio of 80:10:10. An Al foil was used as current collector and the electrode area was 0.64 cm^2 (8 × 8 mm). The electrochemical experiments for both the powder and the thin film electrodes were performed using Swagelok type two-electrode cells. The electrolyte was 1 M $LiPF_6$ dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1 (Shanghai Topsol Ltd., $H_2O < 5$ ppm). The cells were assembled in an argon-filled glove box and cycled using a Land automatic battery tester. The thin films and powders were analyzed by an X'Pert Pro MPD X-ray diffracter (Philips, Holland) using Cu Kα1 radiation ($\lambda = 1.5405$ Å), a micro-Raman spectrometer (Horiba/Jobin Yvon HR800, France) with a 532 nm laser line, a scanning electron (SEM) microscope (XL 30 S-FEG, FEI Co., USA or Hitachi S4800, Hitachi, Japan), and a transmission electron (TEM) microscope (FEI Tecnai F-20). The sample for TEM investigation was prepared by scratching the surface of the thin film using stainless steel doctor blade and dispersing the scrapings into dimethyl carbonate then transferring onto holey carbon Cu grids in the glove box. Each Fourier transformed infrared (FTIR) spectrum was taken as the average of 400 scans on a BIO-RAD FTS-60 spectrometer. The investigation of *in situ* XRD pattern was accomplished on the beam line X14A with the energy of 16 keV (0.776 Å) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, USA. The optics was designed to focus the beam into

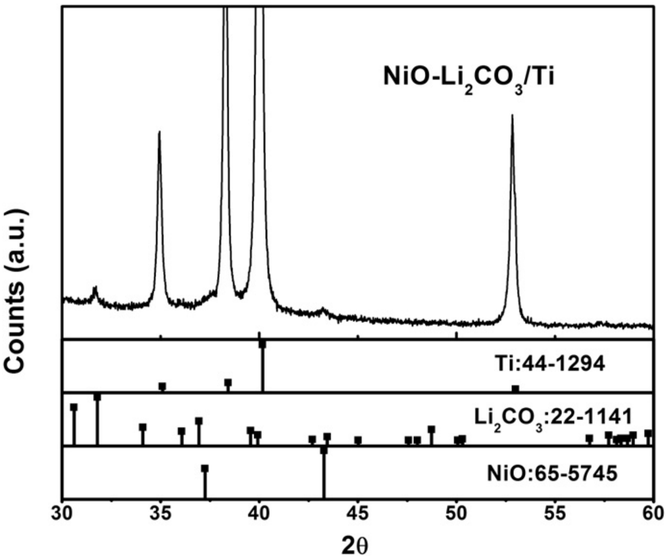

Fig. 2. XRD pattern of NiO–Li_2CO_3 nanocomposite thin film.