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Synthesis, characterization and electrochemical behavior of $LiNi_{1-x}Ba_xO_2$ ($x = 0.0$, 0.1, 0.2, 0.3 and 0.5) cathode materials

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Abstract

$LiNiO_2$ and Ba-doped $LiNiO_2$ were synthesized by a simple solid state reaction, and used as cathode active materials for lithium rechargeable batteries. Physical properties of the synthesized products are discussed in the light of structural (TG/DTA, XRD, TEM, SEM with EDAX) and spectroscopic (FTIR) measurements. XRD results show that the compounds are similar to $LiNiO_2$ in structure. TEM and SEM analyses were used to examine the particle size, nature and morphological aspects of the synthesized oxides. The composition of the materials was explored by EDAX analysis. Performances of lithiated oxides as cathode materials in lithium-ion batteries and substitutive effect on electrochemical properties have been investigated by cyclic voltammetry and galvanostatic charge–discharge cycling. By substitution of Ni with Ba, in $LiNi_{0.8}Ba_{0.2}O_2$ has yielded better cycling results compared to all other materials revealed through charge–discharge studies.

Keywords: Cathode material; FTIR; Lithium-ion battery; Nanoparticles; Cyclic voltammograms; Charge–discharge cycling

1. Introduction

In the last few years, lithium nickelate ($LiNiO_2$) has been considered as a promising positive electrode material for high energy rechargeable lithium-ion batteries [1–5]. However, because of its propensity for non-stoichiometry [6–8], which strongly influences its electrochemical properties [6,8,9], of its thermal instability in the oxidized state [10–12] and of the deterioration of its reversible behavior upon cycling [3], an increasing research activity is now being devoted to new substituted $LiNi_{1-y}M_yO_2$ materials, since partial substitution for nickel can monitor the structural and electrochemical properties of $LiNiO_2$.

In an effort to stabilize the two-dimensional (2D) layered structure of $LiNiO_2$, $LiNi_{1-y}M_yO_2$ phases (where M is a transition or a non-transition metal) have been investigated [16]. The purpose of replacing/doping divalent nickel in the rhombohedral R3-m crystal structure of $LiNiO_2$ with some of the same sized divalent cations of alkaline earth metals is to improve cyclability, high voltage capacity and high temperature performance. In this aspect Ba has been tried as an effective dopant. Further with Ba doping published literature is absent and only few patents are available [13–15]. It has become clear from the limited information available that capacity fading per cycle is 0.4% with Barium against 0.3% per cycle with calcium and strontium in lithium nickel cobalt oxide matrix. The presence of Ba^{2+} cations in the inter-slab is expected to provide structural stability when cycled to 4.5 V. Again to compare the performance of Ba doping with others, partial substitution of Ba in the $LiNiO_2$ matrix in varying compositions of 0%, 10%, 20%, 30% and 50% (stoichiometric ratio) were prepared by solid-state reaction method and their structural and electrochemical properties were studied.

2. Experimental

All the chemicals used were of E-Merck grade except graphite powder which is of Sisco brand. $LiNi_{1-x}Ba_xO_2$

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($x = 0.0$, 0.1, 0.2, 0.3 and 0.5) has been prepared using $LiNO_3$, $Ni(NO_3)_2$, and $Ba(NO_3)_2$ as precursor materials through low temperature solid-state reaction routine. The stoichiometric amounts of the precursors were weighed accurately and thoroughly mixed with three times of urea as fuel. Ten percentage excess of $LiNO_3$ is added to avoid the loss of Li as Li_2O. During precursor material preparation, glycerol was used as the binding material (for every gram of the cathode material preparation 3 or 4 drops of glycerol was used) which helps the mass of the ingredients to be brought into intimate mixing. A dark green color paste material obtained and was heated under air atmosphere in the furnace at 150 °C for 2 h. Foam like mass of fly ash colored material was obtained and crushed. The precursor sample was ignited at 600 °C for 8 h (identified from the thermal studies) for all the compositions of the cathode materials.

Electrochemical characterizations were performed in a 2016 coin cell-type two-electrode assembly. Cathode mix was prepared using of 85% of the active material mixed with 10% acetylene black and 5% polyvinylidene difluoride (PVDF) in *N*-methyl-2-pyrrolidinone (NMP). The prepared mix was coated onto an aluminium foil that serves as the current collector by applying 2 tons cm^{-2} pressure using a hydraulic press. Graphite was mixed with 5% of PVDF in NMP. This was stored for a period of 24 h under vacuum atmosphere in presence of phosphorous pentoxide (P_2O_5) before use. Circular disks of the cathodes were then punched and were used for fabricating the coin cell. The coin-type cells were assembled in an argon-filled glove box with the prepared circular disks of $LiNi_{1-x}Ba_xO_2$ as cathode, graphite as anode, and with Celgard 2600 as separator in a non-aqueous electrolyte consisting of 1 M $LiBF_4$ in 50:50 by volume ethylene carbonate (EC)/dimethyl carbonate (DMC). The cyclic voltammetry technique was used to assess the topotactical reaction of lithium in the synthesized cathode materials. The cell with $LiNi_{1-x}Ba_xO_2$ ($x = 0.0$, 0.1, 0.2, 0.3 and 0.5) as working and Li metal as reference and counter electrode was cycled between 3.0 and 4.5 V at a scan rate of 0.1 mVs^{-1}. The cyclic voltammetry studies were carried out by using EG&G Instruments, PAR, Model 6310. Charge–discharge studies were performed at 0.1 mA cm^{-2} in the voltage range 3.0–4.5 V using WPG 100 (Pontentiostat/Galvanostat) Won-A-Tech Instrument, South Korea.

TG/DTA data were obtained between room temperature and 800 °C employing Perkin–Elmer Diamond TG/DTA thermal analyzer Module at the heating rate of 10 °C min^{-1} under O_2 atmosphere. The purity and structural properties of the synthesized products were investigated by JEOL (JDX-8030) X-ray diffraction analyzer using Cu Kα radiation. The FT-IR spectra were recorded for all the synthesized active cathode materials to confirm the expected moieties in the oxide material using Perkin Elmer FT-IR spectrophotometer in pressed KBr pellets. To analyze the particle nature, morphology and distribution of homogeneous size particles of the synthesized powder, Scanning Electron Microscope (SEM) photographs were taken by JEOL (JSM – 840A) Scanning electron microscope. The chemical compositions of the synthesized samples were confirmed by Energy Dispersive X-ray

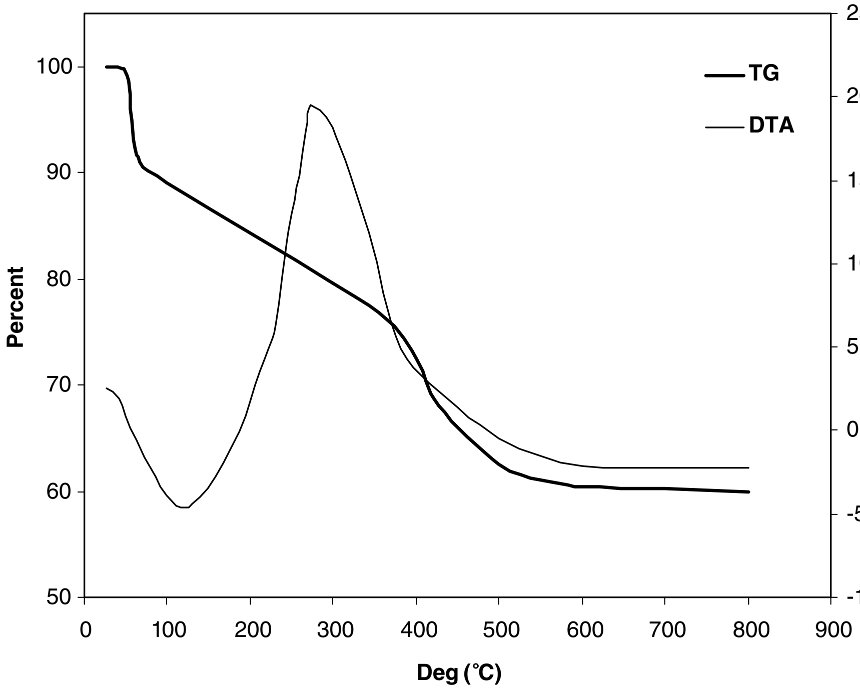

Fig. 1. TG/DTA curves of precursor of $LiNi_{0.9}Ba_{0.1}O_2$.