Ceramics International 43 (2017) 16070–16075

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Hopping conduction in $(Ni,Co,Mn)O_4$ prepared by different synthetic routes: Conventional and spark plasma sintering

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ARTICLE INFO

Keywords:
Nickel cobalt manganese oxides
Spinel
Hopping conduction
Nanopowder
Spark plasma sintering
Conventional sintering

ABSTRACT

$(Ni,Co,Mn)O_4$ (NMC) oxides were prepared by conventional sintering (CS) and spark plasma sintering (SPS) using micro and nanopowders. Small hoping polaron theory was used in order to investigate effect of processing routes on electrical properties of NMC oxides as negative temperature coefficient (NTC) thermistors. Also, X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) techniques were utilized to analyze compositional and structural effects on the electrical properties of NMC compounds. Hopping conduction in NMC prepared by SPS and CS using nanopowder occurs via variable range hopping (VRH) mechanism, however conduction in NMC prepared by CS using micropowder follows nearest neighboring hopping (NNH) mode. Hopping distance and activation energy for the VRH mode were calculated using corresponding physical model.

1. Introduction

$(Ni,Co,Mn)O_4$ (NMC) oxides as a negative temperature coefficient (NTC) thermistor has been extensively studied for various applications such as temperature sensor devices, surge protection devices, and infrared detecting bolometers [1–3]. As a temperature sensor, important property of the NMC is exponentially decreasing resistance with increasing temperature, which is described by following equation;

$$R = R_0 \cdot \exp\left(\frac{E_a}{k \cdot T}\right) = R_0 \cdot \exp\left(\frac{B}{T}\right) \quad (1)$$

$$B = \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln\left(\frac{R_1}{R_2}\right) \quad (2)$$

where B is the thermal sensitivity factor which is closely related to the activation energy for hopping conduction (E_a). Also, R, k and T are resistance, the Boltzmann constant and absolute temperature, respectively.

Generally, NMC oxide is prepared via conventional solid-state-reaction route which requires extremely high firing temperature up to 1400 °C and long sintering time up to 10 h. In the conventional sintering (CS) process, phase transition from cubic to tetragonal structure during cooling is inevitable for NMC compounds [4,5]. The phase transition in NMC causes several issues for the application of NTC thermistor; microcracks, phase separation, and secondary phase formation. Among these, microcracks in the sintered body, which is induced by volume difference between cubic and tetragonal phases, is directly related to the reliability of the fabricated NTC thermistors. Thus, search for alternative sintering processing route which can suppress phase transition in NMC compounds is necessary.

Spark plasma sintering (SPS) is a fast-firing sintering process where high amplitude of current (> 1000 Amp) at a low voltage (5 V) is applied to powder compact [6,7]. The resistive heating thanks to high amplitude of direct current leads to a rapid temperature rise within the powder compact. Thus, the powder can be sintered at significantly lower temperature in a shorter period of time compared to CS process. Therefore, the phase transition of NMC compounds during cooling from the elevated temperature can be avoidable, when SPS technique is adapted for sintering process. Additionally, SPS is conducted under vacuum which can facilitate the formation of oxygen vacancies

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http://dx.doi.org/10.1016/j.ceramint.2017.08.105
Received 13 August 2017; Accepted 16 August 2017
Available online 26 August 2017

combined with the reduction of cations in the NMC oxide.

Small polaron hopping model is commonly proposed for the electrical conduction of the NMC [8,9]. Hopping conduction in spinel compounds is significantly influenced by the oxygen content and the cation distributions on the different crystallographic sites which are very sensitive to sample preparation methods [8,10]. The reduction of cations can be boosted when nanopowder is used as starting materials due to the high surface area to volume ratio [10,11]. As more charge balance of cations are uncompensated, cation distribution in the NMC can be significantly disturbed leading to unique charge transfer mechanism in the compound.

In this work, we prepared NMC ceramics using NMC nanopowder combined with SPS sintering process (SPS NP) to obtain single cubic phase with disturbed cation distributions. Compositional and structure analysis were performed on SPS NP ceramics using appropriate techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Furthermore, in-depth analysis on charge transfer mechanism in the SPS NP compound is conducted using small polaron hopping theory and the corresponding hopping conduction model is proposed.

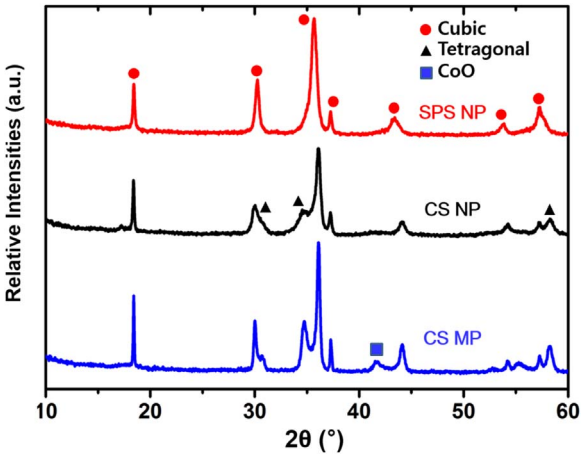

Fig. 1. XRD patterns of the NMC oxides, CS MP (blue), CS NP (black), and SPS MP (red) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

2. Experimental procedure

NMC nanopowder (NMC NP) was synthesized by auto-combustion method using manganese (II) nitrate ($Mn(NO_3)_2$; 50% aqueous solution), Cobalt (II) nitrate hexahydrate ($Co(NO_3)_6{\cdot}H_2O$), Nickel (II) nitrate hexahydrate ($Ni(NO_3)_6{\cdot}H_2O$), and citric acid as starting materials. Stoichiometric amounts of $Mn(NO_3)_2$, $Co(NO_3)_{26}H_2O$, $Ni(NO_3)_{26}H_2O$, and citric acid were dissolved in distilled water. The molar ratio of nitrate to citric acid was 1:1. Ammonia was dropped into the solutions to change pH value from 1 to 6. The solution was heated at 80 °C to transform to sol followed by heating at 130 °C under constant stirring for the formation of brownish gel. Processing temperature for the formation of sol and gel was measured by infrared thermometer (AR 500, Smart sensor®, China). Subsequently, gel was heated at 300 °C until all the gel was completely burnt out for the formation of fine powder. The prepared powder was calcined at 700 °C with a heating rate of 5 °C/min for 2 h under air. More information relating with preparation of NMC NP is available in our previous paper [4,5].

Prepared NMC NP was sintered via two different sintering technique; CS and SPS. For CS, NMC NP prepared by auto combustion method was pressed to prepare pellets of 1 mm-thick and 2 cm in diameter and then, sintered at 1200 °C for 8 h with heating rate of 5 °C/min and subsequently, cooled down naturally to room temperature. For SPS, NMC NP prepared by auto combustion method was introduced to graphite die with the internal diameter of 25 mm. The powder was then sintered under 50 MPa for 5 min between 700 °C and 750 °C with heating rate of 50 °C/min using Dr. Sinter (SPS-625, SPS Syntex Inc., Japan). After sintering, both side of the prepared pellets were polished to remove the $(Mn, Co)O_x$ reduced phase.

Diffraction patterns of NMC oxides prepared by different processing method were recorded using Panalytical X′pert–pro MPD with CuKα radiation. Microstructure and elemental mapping of Ni, Co and Mn at the NMC oxides were investigated using scanning electron microscopy (SEM; Nova NanoSEM, FEI, USA) equipped with energy-dispersive X-ray (EDX) spectroscopy. Also, oxidation states of Ni, Mn and Co were analyzed using X-ray Photoelectron Spectroscopy (XPS; ESCALAB 250xi, thermoscientific, USA). Resistivity as a function of temperature in the range of 25 °C and 80 °C was measured using LCR meter (IM3570, Hioki, Japan).

3. Results and discussion

XRD patterns of the NMC oxides prepared by different processing routes are shown in Fig. 1. XRD patterns for the prepared pellets via CS using NMC nanopowder (CS NP) and micropowder (CS MP) are also shown for the comparison purpose. XRD pattern of CS MP shows the mixed phase with cubic and tetragonal spinel structure. As we previously reported, cubic spinel structure is thermodynamically stable at NMC oxides over 1000 °C at heating and then, gradually transforms to tetragonal spinel during cooling a as confirmed by in situ XRD study [4]. As far as high temperature (~1200 °C) and comparatively long sintering time are required to sinter NMC, the phase transformation from cubic to tetragonal spinel is unavoidable. Also, the formation of CoO as a secondary phase can occur due to the phase decomposition of NMC during sintering at high temperature above 1200 °C. It can be attributed to the reduction of NMC oxides at high temperature. For CS NP, although the secondary phase of CoO was disappeared, the mixture of cubic and tetragonal phases is still existed. However, when SPS was applied with NMC NP (i.e., SPS NP), XRD pattern clearly shows the cubic spinel structure ($Fd\bar{3}m$; JCPDS card No. 23–1237) without any secondary phases. It indicates that the cubic spinel structure of the NMC retained without formation of secondary phases owing to fast quenching from lower sintering temperature (~700 °C). Thus, sintering of NMC NP at lower temperature combined with fast quenching can prohibit the phase transformation of cubic spinel to tetragonal spinel during cooling resulting in phase pure cubic spinel structure.

Microstructure of the NMC pellets prepared via different routes is shown in Fig. 2. Grain sizes between 1 μm and 10 μm were observed at both CS MP and NP, while grain size below 100 nm was observed SPS NP implying that SPS can prohibit grain growth due to shorter sintering time at lower temperature. Also, mechanical loading for the pellet during SPS leads to the formation of more dense pellets. Element mapping results confirm homogeneous distribution of Ni, Co and Mn indicating no phases segregation during sintering process.

XPS spectra of Ni, Co and Mn for NMC samples are shown in Fig. 3. For all samples, Mn 2p spectra features strong spin-orbit peaks of the $2p_{3/2}$ and $2p_{1/2}$ centered at 642 eV and 654 eV, respectively. Each peak of Mn2p can be deconvoluted into two characteristic peaks which assigned to Mn^{3+} and Mn^{4+}, respectively, implying that Mn^{3+} and Mn^{4+} coexist [12]. Similarly, mixed valence of Co^{2+} and Co^{3+} was observed at Co 2p spectra of all samples [13–15]. Co 2p spectra shows two major peaks at 780 eV and 795 eV, which can be assigned to Co $2p_{3/2}$ and Co $2p_{1/2}$ energy levels. Given that the spin orbit splitting for the Co 2p is approximately 15 eV [15]. Also, shake-up satellite peaks centered at 788 eV and 802 eV confirmed the presence of Co^{3+} in Co $2p_{3/2}$ and Co $2p_{1/2}$ states, respectively. All major and satellite peak may be able to be deconvoluted into two characteristic curves, indicating the presence of Co^{2+} cations in NMC compounds. In the Ni 2p spectra, $Ni2p_{3/2}$ and $Ni2p_{1/2}$ centered at 855 eV and 873 eV were observed with