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Effect of Fe incorporation on cation distributions and hopping conductions in Ni-Mn-Co-O spinel oxides

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ABSTRACT

Effect of Fe incorporation on electrical properties of $(Ni_xCo_yMn_{3-x-y})O_4$ (NMC) spinel compound is investigated for the application to a negative temperature coefficient (NTC) thermistor. Cation distribution of the Fe doped NMC (FNMC) is calculated based on the size of ions located at tetragonal A sites and octahedral B sites in spinel structure, which can be closely related with temperature dependent electrical properties of the FNMC. With change of Fe contents, the ratio of Mn^{3+}/Mn^{4+} in octahedral B site of FNMC is changed which can determine the temperature sensitivity factor (B-value). Hopping conduction mode relating with activation energy and hopping distance was also discussed depending on Fe contents, based on the small polaron hopping theory.

1. Introduction

Environmental concerns about air pollution and expensive oil price lead to develop the eco-friendly electric vehicle (EV), which is driven by lithium-ion battery packs equipped with the battery management system (BMS) [1]. The BMS plays important roles in monitoring the residual capacity state (state of charge; SoC) of lithium-ion battery packs which can be indirectly calculated only with the collected voltage, current and temperature data from the BMS. When it comes to the SoC calculation in the BMS, inaccurate temperature monitoring for the battery packs can result in inefficient operation and shorten life time. Also, in the aspect of safety, less accurate temperature sensing brings about the safety concerns relating with overheating induced by excess loading of battery cells [2].

A negative temperature coefficient (NTC) thermistor has been widely investigated for possible application to temperature sensor in the BMS. As a NTC thermistor for the BMS, high and reliable B value (temperature sensitivity coefficient) at designed temperature range is mainly required for accurate temperature monitoring [3,4]. Ternary spinel compounds such as $(Ni_xCo_yMn_{3-x-y})O_4$ (NMC) is commonly used as NTC thermistor due to suitable electrical properties [4]. It is reported that B value of the NMC can be originated from the unique spinel structure with tetragonal A sites and octahedral B sites where transition elements with possible different oxidation states can be incorporated [3]. The electric conduction of the NMC can be explained by the phonon assisted hopping of charge carriers between transition elements with different valence states at B sites [5]. Therefore, controlling the cation distribution at B sites can lead to different polaron hopping conduction mode depending on temperature, which determines the electrical properties of the NMC including resistivity at 25 °C and B value [6–8].

Electrical properties of the NMC can be further modulated by introduction of transition metals into octahedral B sites. When it comes to the addition of fourth transition elements into B sites, formation of secondary phases should be prohibited. Thus, fourth transition elements should have similar ionic radius and electronic configuration with Ni, Mn, and Co atoms to be incorporated into B sites without altering compositional as well as structural properties of the NMC. In the aspect, Fe, which is placed in-between Co and Mn atoms in the periodic table, can be suitable fourth dopant in NMC compounds, since it can favorably modify cation distribution

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