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Effect of Cu/Fe addition on the microstructures and electrical performances of Ni–Co–Mn oxides

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A B S T R A C T

The reliability of negative temperature coefficient (NTC) thermistors is one of the important factors for the excellent performance of the battery management system in electric vehicles. The electrical properties of the thermistor can be explained by the indirect electron jump between Mn^{3+} and Mn^{4+} at the B-sites in a spinel-type thermistor. Additionally, different types of dopants, such as Fe, Cu, Zn, Cr, and Mn, are considered as electrical modifiers that can further improve the electrical properties of the thermistor. For example, Cu is often added to NTC thermistors, occupying the octahedral sites in a spinel-type thermistor, which can play an important role in conduction with the Mn cations. Addition of Fe is also widely used in NTC thermistors owing to its high sensitivity, *B* constant, and stability. In this study, composition-dependent structural and electrical properties of $Cu_{0.2}/Fe_y$-co-doped $Ni_{0.3}Mn_{a\text{-}x\text{-}y}Co_{0.9}O_4$ (NMC) are investigated. Cu/Fe-co-doped NMC shows the R_{25} and $B_{25/85}$ constant values of 4490–12730 Ω and 3185–3490 K, respectively, exhibiting a typical ρ–T curve of NTC thermistors. Higher *B* constant and reliable electrical stability are observed for Cu/Fe-co-doped NMC. Based on the relationship between the cationic oxidation states and electrical properties of Cu/Fe-co-doped NMC, the hopping conduction mechanism is discussed.

1. Introduction

Spinel-type materials, with the general formula AB_2O_4, have been widely used for diverse practical applications in industry because of their unique thermal, electronic, magnetic, and optical properties [1–5]. Among the spinel oxides, Ni–Mn–Co oxides (NMC) have been extensively investigated to explore their interesting electrical properties [6,7]. High-temperature sensitivity and fast response of NMC are suitable for applications in automotives, cellular phones, telecommunication, and aerospace for temperature measurements and control, as well as compensation for other circuit elements [8–12]. The NMC is characterized using parameters such as thermal *B* constant and room temperature resistivity, ρ_{25}. The *B* constant is related to activation energy E_α and Boltzmann constant k_b, which is indicative of the sensitivity to temperature change [13,14]. The conduction mechanism of NMC is generally explained by the thermally activated phonon-assisted hopping of charge carriers among the cations with different oxidation states in the octahedral sites of the spinel structure, induced by lattice vibrations [15–18]. The migration of the cation vacancies and chemical composition of NMC are also considered as important factors that affect the cation distribution, resulting in the electrical properties of the NMC [15,16,19,20].

To control the electrical properties, Cu is often added to the NMC, occupying the octahedral sites and thereby increasing the electrical conductivity [21,22]. However, the addition of Cu often induces a resistivity drift and low sensitivity to temperature excursions, which is harmful for the reliable performance of NMC in

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