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Effect of Ni and Ti substitutions on $Li_{1.05}Mn_2O_{4-\delta}$ electrical conductivities at high temperature

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ABSTRACT

Samples of $Li_{1.05}Mn_2O_{4-\delta}$, $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$, and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ were prepared by a solid-state reaction technique and ultimately refined to a space group $Fd-3m$ of spinel structure by the Rietveld method using synchrotron powder X-ray diffraction data. Comparison of lattice constants suggested that Ni-substitution increased the covalency in the bonding of MO_6 (M: metal ion at 16d site) octahedrals, but Ni/Ti co-substitution decreased the covalency of M–O bonds and introduced structural distortion. Electrical conductivity measurements by a four-probe method resulted in the determination that electrical conduction (within all samples) exhibits a nonadiabatic hopping process at high temperatures. The activation energies of $Li_{1.05}Mn_2O_{4-\delta}$ and $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$ were found to be of similar values. The Ni/Ti co-substituted sample of $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$, on the other hand, showed the highest activation energy among all the measured samples. Substitution reduced the electrical conductivity relative to $Li_{1.05}Mn_2O_{4-\delta}$; furthermore, both the substituted samples ($Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$ and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$) were found to exhibit functional independence from oxygen partial pressure (P_{O2}).

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1. Introduction

$LiMn_2O_4$ and related materials in spinel structures are widely investigated as prospective cathode materials for rechargeable lithium ion batteries because of their high energy densities and large recharge capabilities [1–5]. $LiMn_2O_4$ has certain advantages such as low cost, non-toxicity, and high thermal stability; however, capacity fading during its charge-discharge cycles can be a serious problem for commercial applications [6]. Jahn-Teller distortions [7], oxygen defects [8,9], and two-phase coexistences [10] are often responsible for the poor cyclability of $LiMn_2O_4$.

The crystal structure of $LiMn_2O_4$ around room-temperature (RT) belongs to the $Fd-3m$ space group of a cubic system [11]. The oxygen ions at 32e sites form a cubic-close-packed array in which the Li and Mn ions reside at tetrahedral 8a and octahedral 16d sites, respectively. In the stoichiometric spinel structure, the same amount of Jahn-Teller active Mn^{3+} and Mn^{4+} ions occupy octahedral sites [12]. Jahn-Teller distortion is essentially caused by the cooperative interaction of local distortions around Mn^{3+} in octahedral sites.

Thermopower and electrical conductivity measurements show that $LiMn_2O_4$ is an n-type semiconductor [13–17]. Goodenough et al. [13] and Shutte et al. [14] suggested that electrical transport in $LiMn_2O_4$ is a hopping process of small polaron e_g electrons in Mn^{3+} ions. Some studies have reported that conduction may simply be due to a hopping process of adiabatic small polarons [15,16]. Sugiyama et al. [17], on the other hand, plotted the Arrhenius relationship of $\sigma T^{3/2}$ vs. $1/T$, which held linearity; this analysis was based, however, on nonadiabatic small polarons [18,19]. Moreover, Iguchi et al. [20,21] analyzed the dielectric relaxation process of $LiMn_2O_4$ based on the Debye model [22,23] and ultimately demonstrated that the majority carriers in $LiMn_2O_4$ near RT were likely nonadiabatic small polarons.

A partial substitution for Mn by other metals, such as Ti, Cr, Fe, Co, Ni, Cu, Zn, and Al, are reported to improve structural stability and electrochemical performance [24–30]. As such, a partial substitution of Mn can be a useful strategy in the application of $LiMn_2O_4$ as a cathode material. Hence, in this study, Ni and Ti were focused upon as partial substitution metals with associated effects on electrical conductivity at high temperatures (in tandem with oxygen partial pressures) evaluated.

2. Experimental

Samples of nominal compositions of $Li_{1.05}Mn_2O_{4-\delta}$, $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$, and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ were synthesized

by a solid-state reaction technique using Li_2CO_3, Mn_2O_3, NiO, and TiO_2 powders. A lithium-rich content should be prepared for the undertaking of effectively evaporating lithium oxide. The mixed powders were calcined in air at 843 K for 5 h, and then heated at 1143 K for 10 h. After grinding, the heated powders were pressed into pellets and finally sintered in air at 1143 K for 12 h. The cooling rate following the heating process was 100 K per hour.

Powder X-ray diffraction data were then collected at beam line BL5S2 of the Aichi Synchrotron Radiation Center. The applicable wavelength was calibrated using a CeO_2 standard sample (SRM674b, fabricated by NIST). The diffraction patterns of $Li_{1.05}Mn_2O_{4-\delta}$, $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$, and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ were then measured at RT.

DC conductivity was then subsequently measured as a function of temperature and P_{O2} by a conventional four-probe method. The associated applied temperatures ranged from 473 K to 723 K, with P_{O2} ranging from 3.0×10^{-2} Pa to 1.0×10^5 Pa.

3. Results and discussion

Structural refinements of $Li_{1.05}Mn_2O_{4-\delta}$, $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$, and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ at RT were carried out by the Rietveld method using RIETAN-FP [31], with associated results summarized below in Table 1. Fig. 1, moreover, shows both the experimental and calculated patterns of $Li_{1.05}Mn_2O_{4-\delta}$, with all peaks demonstrating the capacity for indexing using the cubic cell space group $Fd-3m$. In addition, it was likewise found that the other two substituted samples also belonged to the same space group ($Fd-3m$). Both the lattice constant and M–O distance of the Ni-substituted sample ($Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$) trended smaller than those of $Li_{1.05}Mn_2O_{4-\delta}$ even though the ionic radius of Ni is larger than that of Mn. This phenomenon therefore suggests that Ni-substitution enhances the bonding covalency of MO_6 octahedra. Ni/Ti co-substitution, on the other hand, made the lattice constant and M–O distance larger compared to those of $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$. The substitution by Ti, which has a larger ionic radius than Mn, essentially weakens the covalency of M–O bonds; this condition results in an increased level of structural distortion.

The DC conductivities of $Li_{1.05}Mn_2O_{4-\delta}$, $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$, and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ from 473 K to 723 K were measured with a dependence on P_{O2}. Fig. 2 illustrates the Arrhenius relationship of $\sigma T^{3/2} = A\exp(-E_\sigma/k_BT)$ for three samples with $P_{O2} = 2.0 \times 10^4$ Pa, where k_B is the Boltzmann constant. All samples behaved as semiconductors because their conductivities regularly increased

with temperature. A form of $\sigma = A\exp(-E_\sigma/k_BT)/T^{3/2}$ represents conductivity due to the hopping conduction of nonadiabatic small polarons [18,19]. The three separate lines in Fig. 2 show the results of fitting the linear approximation to the conductivity plots of each sample. These plots respectively hold linear relationships and follow Arrhenius' law within the evaluated temperature range of 473–723 K. The primary mechanism behind electrical conduction of samples with and without substitution, therefore, seems to be a hopping-process of nonadiabatic small polarons at high temperatures.

Activation energies (E_σ) were derived from the slopes in the ln ($\sigma T^{3/2}$) vs. $1000/T$ Arrhenius plots and are summarized in Table 1. It was found that $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$ had a similar E_σ value to that of $Li_{1.05}Mn_2O_{4-\delta}$ and that the E_σ value for $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ was about 1.2 times larger than both of the former. It was determined that the activation energy required for polaronic conduction maintains a functionality of $E_\sigma \cong W_H = W_P/2 - t$, where W_H is the hopping energy of nonadiabatic small polarons, W_P is the polaron binding energy, and $2t$ is the $3d$-narrow bandwidth [19]. The large activation energy of $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$, therefore, implies that Ti-doping causes strengthening of local deformations in the lattice and reduces the $3d$ bandwidth.

The electrical conductivity of the Ni-substituted sample ($Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$) decreased compared with that of $Li_{1.05}Mn_2O_{4-\delta}$. The Ni/Ti co-substituted sample ($Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$) demonstrated the lowest conductivity of the three investigated samples. The pre-exponential factor (A) in the three samples also consistently decreases as the amount of substitution for Mn increases. In the nonadiabatic small polaron theory, A is directly proportional to the carrier density (n) and inversely proportional to $W_H^{1/2}$ [19,22]; n primarily seems to contribute to a reduction in electrical conductivity by substitution for Mn.

The conductivities of the three samples from 623 K to 723 K with different P_{O2} values are plotted in Fig. 3. $Li_{1.05}Mn_2O_{4+\delta}$ may possibly display an oxygen-nonstoichiometric effect; moreover, it is likely that the subject sample is an n-type semiconductor within a P_{O2} range of 3.0×10^{-2}–2.0×10^4 Pa due to deficient oxygen levels, and a p-type semiconductor within a P_{O2} range of 2.0×10^4–1.0×10^5 Pa due to enhanced oxygen levels. The conductivities of $Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$ and $Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$ were ultimately found not to vary as a function of P_{O2}. As indicated in Table 1, the activation energies of both substituted samples were independent of P_{O2}, although the opposite was the case for $Li_{1.05}Mn_2O_{4-\delta}$. The imperfections, including structural distortions and the absence of

Table 1
Space group, Rietveld factors (R_{wp} and R_B), lattice constants (a), M–O distances, oxygen partial pressures (P_{O2}), and activation energies (E_σ)⬚.

Sample composition	Powder X-ray diffraction at RT					Electrical conductivity (473–723 K)	
	Space group	R_{wp} (%)	R_B (%)	Lattice constant a (Å)	M–O distance (Å)	P_{O2} (Pa)	Activation energy E_σ (eV)
$Li_{1.05}Mn_2O_{4-\delta}$	$Fd-3m$	4.49	2.96	8.23889(3)	1.9600(8)	3.0×10^{-2}	0.41
						1.0×10^3	0.40
						2.0×10^4	0.37
						1.0×10^5	0.45
$Li_{1.05}Mn_{1.5}Ni_{0.5}O_{4-\delta}$	$Fd-3m$	4.42	4.38	8.17984(2)	1.9386(7)	3.0×10^{-2}	0.43
						1.0×10^3	0.43
						2.0×10^4	0.43
						1.0×10^5	0.43
$Li_{1.05}Mn_{1.0}Ni_{0.5}Ti_{0.5}O_{4-\delta}$	$Fd-3m$	5.16	3.58	8.23282(4)	1.9662(8)	3.0×10^{-2}	0.50
						1.0×10^3	0.51
						2.0×10^4	0.51
						1.0×10^5	–