

Chemical state of Fe in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ and its effect on electrical conduction property

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Abstract Mössbauer absorption spectra of single phase $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($0.2 \leq x \leq 1.0$) have been measured. Increase of quadrupole splitting with increasing x from 0.2 to 0.6 suggested successful substitution of Fe ion for Ni. Variation of isomer shift with x suggested valence of Fe approached $4+$, i.e., concentration of itinerant hole on Fe increased with decrease of Fe content, showing agreement with increase of electrical conductivity with decreasing x from 1.0 to 0.4. It can be prospected that higher electrical conductivity might be obtained if sintering property of the specimens with x less than 0.4 is improved.

Keywords $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ · Solid oxide fuel cells · Electrical conductivity · Mössbauer spectroscopy · Chemical State of Fe

1 Introduction

$\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ attracts much interest as a new cathode material for solid oxide fuel cells (SOFC). It has been reported that the specimen with $x=0.4$ is the most promising since it shows the highest electrical conductivity and stability among $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ [1, 2]. In order to clarify the origin of this high property of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$, the variation of chemical state of Fe on its content and its effect on the electrical conduction property of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ should be analyzed. So far, the chemical state of Fe in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ has been investigated by Mössbauer spectroscopy [3–7]. However, analyzed specimens by Goeta et al. [3] and Asai

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and Sekikawa [4] were limited to ones with x smaller than 0.25. Marzec [5] and Świerczek et al. [6] reported Mössbauer spectra of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$. They succeeded in the observation of a magnetic phase transition at room temperature between antiferromagnetic and paramagnetic around $x = 0.7$. However, their measured specimen was limited within $0.6 \leq x \leq 1.0$ owing to the difficulty in single phase preparation of specimens with x less than 0.5 by their employed solid state reaction method, resulting in the failure to analyze the variation of the chemical state of Fe around $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$. We succeeded in the preparation of single phase of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with $0.3 \leq x \leq 1.0$ by the optimization of preparation conditions of the solid state reaction method [7]. Mössbauer spectroscopy was performed on the specimens and not only a magnetic phase transition around $x = 0.7$ but also the paramagnetic properties in the specimens with $0.3 \leq x \leq 0.6$ at room temperature were observed. However, the chemical state of Fe was not discussed in the paper since single phase material with x less than 0.2 could not be prepared. Recently, we have succeeded in the preparation of single phase $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ regardless of Fe content employing a solution mixing process, the so-called Pechini method [2]. In this paper, Mössbauer spectroscopy has been carried out for specimens with $0.2 \leq x \leq 1.0$. Compositional variation of the chemical state of Fe has been investigated and its effect on electrical conduction property has been discussed.

2 Experimental

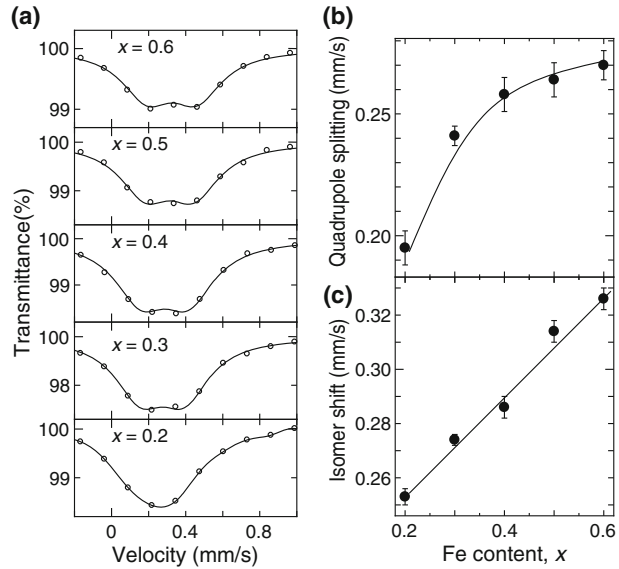
$\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ceramic specimens were prepared by solid state reaction of La_2O_3 , NiO and Fe_2O_3 powders or by the Pechini method from aqueous solution of La_2O_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Detailed preparation conditions of solid state reaction and Pechini method are referred in [7] and [2], respectively. The perovskite phase without second phase was obtained for the specimens with $0.3 \leq x \leq 1.0$ and $0.0 \leq x \leq 1.0$ by solid state reaction and the Pechini method, respectively. For the specimens with $0.0 \leq x \leq 0.4$ and $0.6 \leq x \leq 1.0$, rhombohedral and orthorhombic distorted perovskite single phase were observed, respectively. For $\text{LaNi}_{0.5}\text{Fe}_{0.5}\text{O}_3$, mixture of the both phases were obtained at room temperature.

Mössbauer absorption spectra of the specimens were measured using 14.4 keV γ -ray from $^{57}\text{Co}/\text{Rh}$ foil at room temperature. Curve fitting using Lorentz functions was carried out on the spectra for the evaluation of isomer shift, quadrupole splitting and internal magnetic field by using an originally manufactured program. The isomer shift was expressed with respect to the centroid of the spectrum of α -Fe. The electrical conductivity at 500~800°C in air was measured by the four probe method [2].

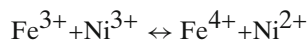
3 Results and discussion

Mössbauer spectra of the specimens with $0.3 \leq x \leq 1.0$ were reproduced with those reported in ref. [7]. A magnetic phase transition between antiferromagnetic and paramagnetic was also observed at $x = 0.7$. Figure 1(a) shows enlarged Mössbauer spectra of the specimens with $0.2 \leq x \leq 0.6$. Only doublet peaks were observed in the spectra, indicating paramagnetism in these specimens. The quadrupole splitting

Fig. 1 Fig. 1 (a) Mössbauer spectra of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($0.2 \leq x \leq 0.6$) at room temperature. (b) Quadrupole splitting and (c) isomer shift of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ ($0.2 \leq x \leq 0.6$)



and isomer shift were evaluated and represented in Fig. 1(b) and (c) as a function of composition. With increasing Fe content from 0.2 to 0.6, not only Ni ions but also Fe ions appear as a second neighbor of the Fe ion, resulting in lower symmetry of the electrical field around the Fe ion. The increase of quadrupole splitting with increasing x can be ascribed to the lowering of the electrical field symmetry around the Fe ion, indicating successful substitution of Fe for Ni. From the isomer shift shown in Fig. 1(c), it can be concluded that the valence of Fe in the specimens is fundamentally $3+$. The isomer shift decreased with decreasing Fe content, suggesting a slight increase of the valence of Fe, *i.e.* generation of itinerant hole on Fe orbital according to slightly shifting the following chemical equilibrium to the right side.



It can be suggested that the chemical equilibrium shifts to the left side and that the concentration of itinerant holes decreases with increase of Fe up to 0.6. For Mössbauer spectra of the specimens with x larger than 0.8, sextet peaks were observed, indicating an interaction between electrons of Fe^{3+} resulting in antiferromagnetic properties and localized holes. From this evaluation of the chemical state of Fe, it was prospected that the electrical conductivity of $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ increased with decreasing Fe content, showing correspondence with the variation of the electrical conductivity on x from 1.0 to 0.4. However, the electrical conductivity of polycrystalline specimens decreased with decreasing Fe content from 0.4 to 0.1 [2]. We regard that the origin of the decrease of electrical conductivity should be the poor sintering property of the specimens with small x and that the electrical conductivity might increase if the sintering property is improved.

4 Conclusion

Mössbauer spectra revealed that the chemical state of Fe in $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ approached 4+ with decreasing Fe content, which indicated increase of concentration of itinerant hole. This showed agreement with the increase of electrical conductivity with decreasing x from 1.0 to 0.4. It can be probable that $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ with higher electrical conductivity can be prepared if the sintering property of specimens with x less than 0.4 is improved.

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