

Characterization of $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ ($x = 0, 0.2,$ and 0.4) pyrochlore oxide cathode materials for intermediate temperature solid oxide fuel cells

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The $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ ($x = 0, 0.2,$ and 0.4) pyrochlore oxides have been studied as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs). All the samples synthesized by co-precipitation method were single phase pyrochlore oxides. $\text{Pb}_2\text{Ru}_2\text{O}_7$ shows high electrical conductivity of over $2 \times 10^3 \text{ S}\cdot\text{cm}^{-1}$. Both electrical conductivity and thermal expansion coefficient decrease with an increase in the Bi content. $\text{Pb}_2\text{Ru}_{1.8}\text{Bi}_{0.2}\text{O}_7$ showed the lowest polarization resistance of $0.12 \Omega\cdot\text{cm}^2$ at 800°C in an air atmosphere.

Key words: Solid oxide fuel cell, Cathode, Pyrochlore, Lead ruthenate, Oxygen reduction reaction, Thermal expansion.

Introduction

Solid oxide fuel cells (SOFCs) are attractive energy conversion devices due to their many advantages such as high energy conversion efficiency, low pollution emissions and various environmental compatibilities [1, 2]. However, the conventional operating temperature of $\sim 1000^\circ\text{C}$ leads to performance degradation and durability problems resulted from chemical reactivity and thermal expansion mismatch. Therefore, one of the main issues in SOFCs is a reduction in the operating temperature to an intermediate temperature range ($500\text{-}800^\circ\text{C}$). However, the conventional cathode material, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is not adequate, since the lower temperature leads to poor oxygen reduction reaction kinetics at the cathode side. To address this issue, various cathode materials have been investigated [3-5].

Recently interest has been shown in the physical properties of pyrochlore oxides [6-10], and it has been reported that the pyrochlore oxides, $\text{A}_{2-x}\text{Ln}_x\text{Ru}_2\text{O}_7$ ($\text{A} = \text{Pb}$ and Bi , $\text{Ln} = \text{Y}$, Nd , Sm , and Gd), revealed excellent electrical conductivity [6-9]. In addition, pyrochlore oxide cathode materials have demonstrated a sufficient catalytic activity for the oxygen reduction reaction [11, 12]. In accordance with these benefits, pyrochlore oxides such as bismuth ruthenates, lead ruthenates, and yttrium ruthenates have been recently investigated as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) [11-14].

Since lead ruthenates ($\text{Pb}_2\text{Ru}_2\text{O}_7$) can exhibit high electronic conductivity and catalytic activity for oxygen reduction [12], which is critical to improve the performance of IT-SOFCs, the solid solutions of lead ruthenates could give

these advantages. In this regards, the modified lead ruthenates by substituting bismuth for ruthenium in B site have been investigated as cathode materials for IT-SOFCs.

Experimental

The $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ ($0 \leq x \leq 0.6$) pyrochlore oxides were synthesized by a co-precipitation method. The required amounts of metal nitrates were dissolved in distilled water, and the metal ions were precipitated as hydroxides by adding NH_4OH as a precipitant. The precipitate was washed and dried, then fired at 900°C for 24 h for the $x = 0$ and 0.2 samples, and at 850°C for 48 h for the $x = 0.4$ and 0.6 samples, respectively. The $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) electrolyte was prepared by the combustion method using the so called glycine nitrate process (GNP) [15].

The phase identification of the prepared powders was carried out by analyzing the X-ray diffraction data. The thermal expansion coefficients (TECs) of the sintered samples were measured by thermomechanical analysis (TMA) from room temperature to 700°C with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. Thermogravimetric analysis (TGA) was carried out from room temperature to 1000°C with a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$ in air. The electrical conductivity was measured by a four-probe DC method in the temperature range of $100\text{-}800^\circ\text{C}$. For the electrical conductivity and TEC measurements, the samples with $x = 0$ and 0.2 were sintered at 900°C for 24 h, and the $x = 0.4$ sample were sintered at 850°C for 24 h. Microstructural characterization of the cathodes was carried out with a Hitachi (SN-3000) scanning electron microscope.

The electrochemical performance was evaluated by AC impedance spectroscopy with symmetrical half cells in various atmospheres. The applied frequency was in the range of 1 mHz to 100 kHz with a voltage amplitude of 20 mV . Symmetric half cells were manufactured by a screen printing

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method, followed by firing at 900 °C for 4 h for the $x = 0$ and $x = 0.2$ compositions, and at 850 °C for the $x = 0.4$ composition.

Results and Discussion

The X-ray diffraction patterns of the $Pb_2Ru_{2-x}Bi_xO_7$ ($x = 0, 0.2, 0.4, \text{ and } 0.6$) pyrochlore oxides synthesized by the co-precipitation method are shown in Fig. 1. The cubic lead ruthenate phases are confirmed for the $x = 0, 0.2, \text{ and } 0.4$ compositions, while the $x = 0.6$ composition is not formed as a single phase solid solution, and contained $PbBiO_2Cl$ as an impurity phase. Therefore, the $x = 0.6$ composition was excluded for the further investigation.

The thermal expansion behaviors of the $Pb_2Ru_{2-x}Bi_xO_7$ ($x = 0, 0.2, \text{ and } 0.4$) pyrochlore oxides in the temperature range of 50-700 °C are shown in Fig. 2, and the calculated overall linear thermal expansion coefficient (TEC) values are presented in Table 1. The linear TEC of the $Pb_2Ru_{2-x}Bi_xO_7$ ($x = 0, 0.2, \text{ and } 0.4$) pyrochlore oxides decreases with an increase in the Bi content. The TEC values of $9.9\text{--}11.0 \times 10^{-6}/K$ for the $Pb_2Ru_{2-x}Bi_xO_7$ samples well match with those of 8YSZ ($10.5\text{--}11 \times 10^{-6}/K$) [1].

The electrical conductivities of the $Pb_2Ru_{2-x}Bi_xO_7$ ($x = 0, 0.2, \text{ and } 0.4$) pyrochlore oxides measured as a function of temperature from 100 to 800 °C in an air atmosphere are shown in Fig. 3. All the compositions show superior electrical conductivity values, and similar results have been also reported [12]. The electrical conductivity of all compositions was found to decrease with an increase in the Bi content, and decrease with an increase in the temperature showing metallic conducting behavior. Beyerlein *et al.* [16]

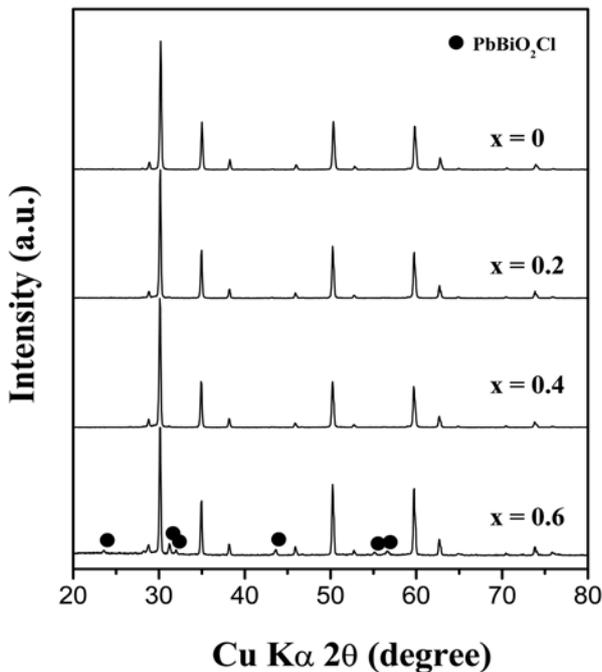


Fig. 1. X-ray diffraction patterns of the $Pb_2Ru_{2-x}Bi_xO_7$ pyrochlore oxides.

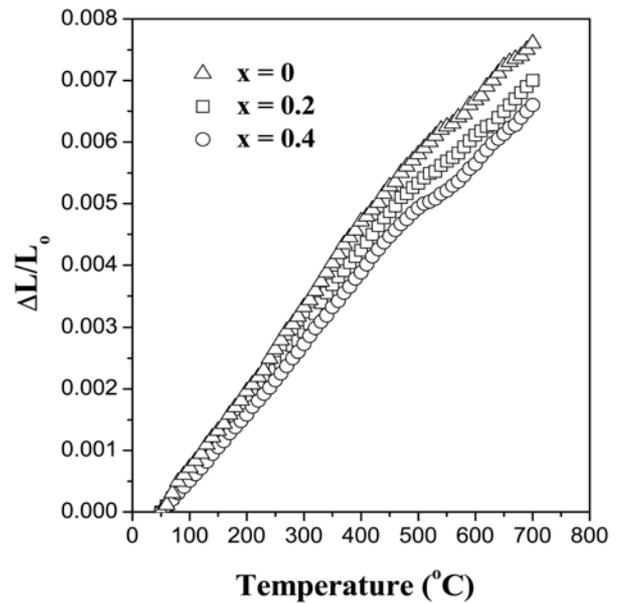


Fig. 2. Thermal expansion behavior of the $Pb_2Ru_{2-x}Bi_xO_7$ pyrochlore oxides in the temperature range of 50-700 °C.

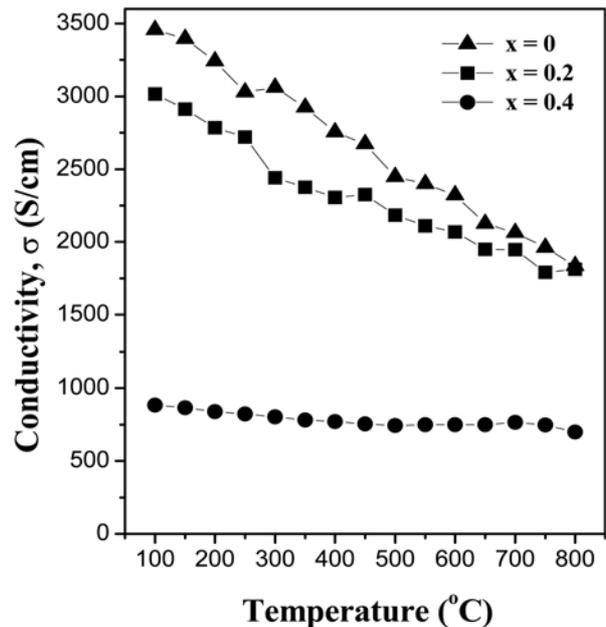


Fig. 3. Variations of the electrical conductivity of the $Pb_2Ru_{2-x}Bi_xO_7$ pyrochlore oxides measured in an air atmosphere.

Table 1. Linear TECs of the $Pb_2Ru_{2-x}Bi_xO_7$ samples calculated from the thermal expansion curves as a function of temperature

Composition	TEC ($\times 10^{-6}/K$)
$Pb_2Ru_2O_7$	11.0
$Pb_2Ru_{1.8}Bi_{0.2}O_7$	10.2
$Pb_2Ru_{1.6}Bi_{0.4}O_7$	9.9

have suggested that the electrical conduction in $Pb_2Ru_2O_{6.5}$ takes place via Ru-O band states in the connected network of RuO_6 octahedra. In this regard, the presence of the localized Bi^{3+} , which has no electrons to give up to the

conduction band, could be expected to cause the disconnection of the Ru-O-Ru conduction pathway. Therefore, the electrical conductivity of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ ($x = 0, 0.2, \text{ and } 0.4$) pyrochlore oxides decreases with an increase in the Bi content. Meanwhile, in contrast with the perovskites, the conductivity values of pyrochlore oxides are much higher [17], and the highest conductivity of $3.5 \times 10^3 \text{ S}\cdot\text{cm}^{-1}$ was observed for $\text{Pb}_2\text{Ru}_2\text{O}_7$.

TGA plots of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxides for various x values are shown in Fig. 4. The observed weight loss during heating is due to the loss of oxygen from the lattice. In $\text{Pb}_2\text{Ru}_2\text{O}_7$, the Ru ions in B sites exist in the Ru^{4+} state [18]. The substitution of lower valence Bi^{3+} for Ru^{4+} leads to the formation of additional oxygen ion vacancies in order to maintain the charge neutrality in the lattice. Meanwhile, the X-ray diffraction patterns of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxides after TGA measurements shown in Fig. 5 also indicate no phase changes, compared with the XRD patterns of the as-prepared samples shown in Fig. 1. These results support the idea that neither phase transition nor decomposition occurs during the heating.

Surface and cross-sectional micrographs of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxide cathodes on GDC electrolyte are shown in Fig. 6. The electrodes are porous enough, and the thickness of the electrodes is approximately $15 \mu\text{m}$. Both the $x = 0$ and 0.2 samples show area contact and good adhesion, and the grain size of the $x = 0.2$ sample is rather larger than that of the $x = 0$ sample. However, the $x = 0.4$ sample shows only point contact among particles and poor adhesion between the cathode and the electrolyte compared with the $x = 0$ and 0.2 samples.

The typical AC impedance spectra of the symmetrical half cells measured at 800°C in oxygen, air, and nitrogen atmospheres are shown in Fig. 7. In all the samples, the total resistance R_{tot} (right intercept on the Z_{re} axis) increases with a decrease in the oxygen partial pressure due to the lack of reactants. The ohmic resistance R_o (left intercept on the Z_{re} axis) and polarization resistance R_p ($R_{\text{tot}} - R_o$) of all cathode samples at 800°C in an air atmosphere are listed in Table 2. The cathode polarization resistance is strongly

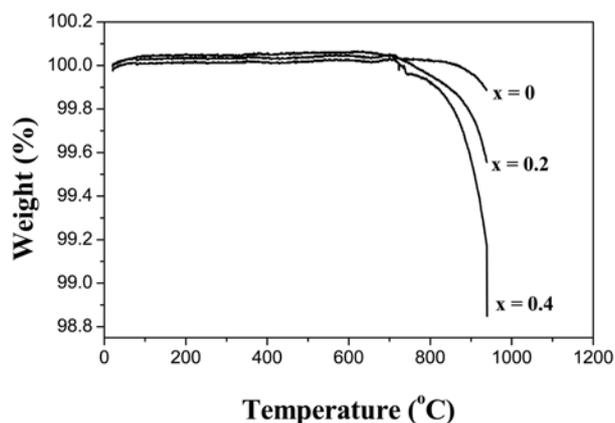


Fig. 4. TGA plots of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxides recorded in air with a heating rate of $2 \text{ K}\cdot\text{min}^{-1}$.

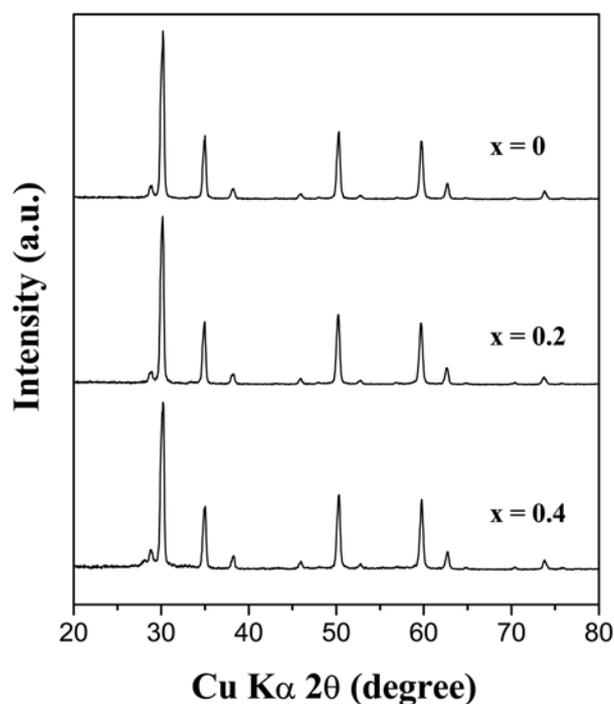


Fig. 5. X-ray diffraction patterns of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxides after TGA measurements.

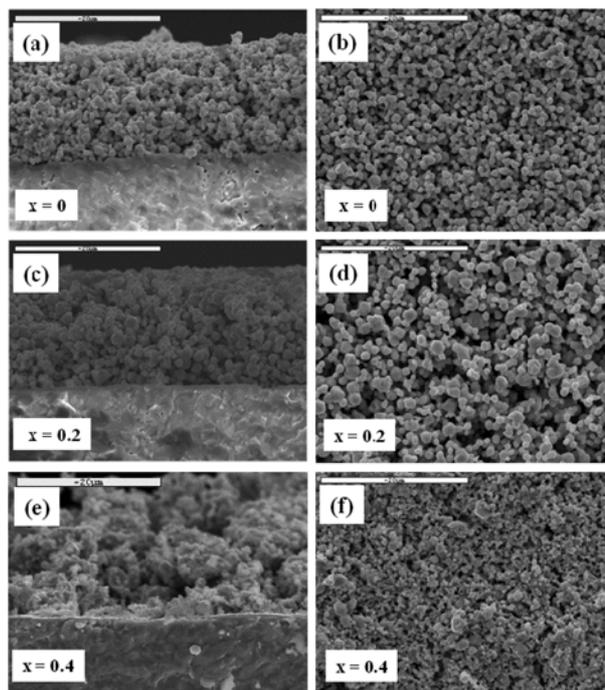


Fig. 6. SEM micrographs of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxide cathodes on GDC electrolyte; (a), (c), and (e): cross sectional, and (b), (d), and (f): surface images.

related to the oxygen reduction reaction. The variation of R_o values corresponds to the microstructural differences as shown in Fig. 6. Area contact and better adhesion leads to a reduction in contact resistance, which can reduce the ohmic resistance. Meanwhile, the initial doping of 0.2 mol

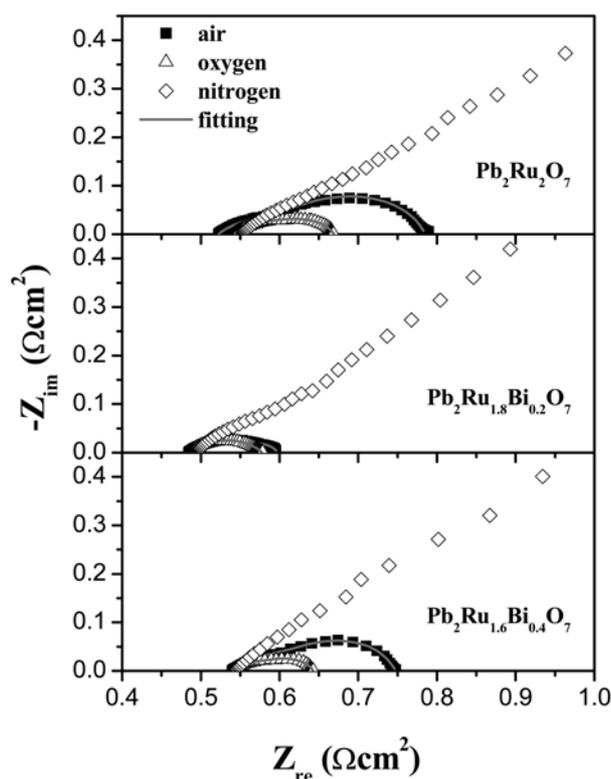


Fig. 7. Typical AC impedance spectra of the symmetrical half cells with GDC electrolyte in air, oxygen, and nitrogen atmospheres at 800 °C.

Table 2. The ohmic resistance (R_o) and polarization resistance (R_p) of cathode samples at 800 °C in an air atmosphere

Composition	R_o ($\Omega\text{-cm}^2$)	R_p ($\Omega\text{-cm}^2$)
$\text{Pb}_2\text{Ru}_2\text{O}_7$	0.52	0.27
$\text{Pb}_2\text{Ru}_{1.8}\text{Bi}_{0.2}\text{O}_7$	0.48	0.12
$\text{Pb}_2\text{Ru}_{1.6}\text{Bi}_{0.4}\text{O}_7$	0.54	0.21

Bi leads to a significant decrease in the R_p and further addition to the Bi content such as $x = 0.4$ increases the R_p , but the R_p value of the $x = 0.4$ sample is lower than that of the $x = 0$ sample.

It has been reported that a high oxygen ion vacancy concentration in cathode materials could improve the surface oxygen exchange kinetics as well as the bulk diffusion of oxide ions [19], which leads to an increase in the electrochemical performance. Therefore, the substitution of Bi results in an enhanced electrochemical performance of the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxide cathodes due to an increase in the amount of oxygen ion vacancies, as shown in Fig. 4. However, the $x = 0.4$ sample shows poorer electrochemical performance than the $x = 0.2$ sample despite a larger amount of oxygen ion vacancies. This is due to poorer contact and adhesion for the $x = 0.4$ sample, which results in the disconnection of the oxygen ion pathway.

Conclusions

The $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxide cathode materials were synthesized by a co-precipitation method. All samples show predominant electrical conductivities, in particular, $\text{Pb}_2\text{Ru}_2\text{O}_7$ gives over $2 \times 10^3 \text{ S}\cdot\text{cm}^{-1}$ in the entire temperature range measured. The substitution of Bi for Ru might generate supplementary oxygen ion vacancies, and the $x = 0.2$ and 0.4 compositions thus displayed better electrochemical performance than the $x = 0$ composition. The $x = 0.2$ composition, $\text{Pb}_2\text{Ru}_{1.8}\text{Bi}_{0.2}\text{O}_7$, presented the lowest polarization resistance of $0.12 \Omega\cdot\text{cm}^2$ at 800 °C in an air atmosphere. This study implies that the $\text{Pb}_2\text{Ru}_{2-x}\text{Bi}_x\text{O}_7$ pyrochlore oxides are potential candidates for cathode materials for IT-SOFCs with an excellent electrical property and adequate catalytic activity for the oxygen reduction reaction. However, the poor electrode microstructure might be an issue to enhance electrochemical performance further.

Acknowledgement

This paper was supported by research funds of Chonbuk National University in 2007.

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