SYNTHESIS AND CHARACTERISTICS OF La$_{1-x}$Sr$_x$MnO$_3$
CERAMICS FOR CATHODE MATERIALS OF SOFC

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ABSTRACT

The fine powders of cathode materials with composition La$_{1-x}$Sr$_x$MnO$_3$
($x=0$-$0.6$) for solid oxide fuel cells (SOFC) were prepared by the buffer
solution method. TG-DTA was applied to study the formation of perovskite
oxide and the sintering behaviour of strontium-doped lanthanum manganite
powders. The crystal structure and morphology of La$_{1-x}$Sr$_x$MnO$_3$ were
observed by XRD, SEM and TEM. The high-temperature electrical
conductivity was measured by the four-probe method.

It was indicated that the formation temperature of perovskite-type
La$_{1-x}$Sr$_x$MnO$_3$ decreased with the increase of Sr content. The La$_{1-x}$Sr$_x$MnO$_3$
display three lattice types at room temperature: orthorhombic ($0 < x < 0.15$),
hexagonal ($0.15 < x < 0.45$) and cubic ($x < 0.45$). As $x$ increased, the primary
volume of La$_{1-x}$Sr$_x$MnO$_3$ decreased, and an abrupt decline was found
around the phase-transformation point. Results showed that the electrical
conductivity of La$_{1-x}$Sr$_x$MnO$_3$ was influenced remarkably by the content of
Sr, the peak value of 200s/cm was located at $x=0.5$ (at 1273K in air).

INTRODUCTION

Perovskite-type LaMnO$_3$ Ceramics as cathodes (air electrodes) of solid oxide
fuel cells (SOFC) have been extensively investigated and have many applications
because of their high electrical conductivity and catalytic activity, being chemically
compatible with and matching the thermal expansion of solid electrolyte ZrO$_2$, being
stable towards oxidation (7-6). At present, there are many methods for preparing the
powders, such as solid-state reaction method, sol-gel method, hydrothermal method,
and liquid-phase method. The cathode represents about 65% of the resistance of the
cell, so we should decrease its resistance to improve the output power.
In this study, the synthesis of the fine powders by the buffer solution method, the formation of perovskite oxides, the crystal structure and morphology, the sintering behaviour and the electrical conduction characteristics of La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} ceramics are investigated. The relation of composition, structure and function, the principle of defect chemistry and the mechanism of conductivity are discussed.

**EXPERIMENTAL PROCEDURE**

Samples of composition La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} with x ranging from 0.0 to 0.6 were used. The starting materials were Mn(NO\textsubscript{3})\textsubscript{2} (A.R.), Sr(NO\textsubscript{3})\textsubscript{2} (A.R.), La(NO\textsubscript{3})\textsubscript{3} \cdot H\textsubscript{2}O (A.R.) and the buffer solution composed of ROH and RHCO\textsubscript{3} (A.R.) (R stands for K, Na, NH\textsubscript{4}). The method of chemical coprecipitation in the buffer solution was utilized in order to prepare the fine powders. Samples were respectively calcined at 500, 700, 800, 900°C for 2 hours, and then sintered at 1300, 1350, 1400, 1550°C.

In the various stages, the analyses and observations by the methods of TG-DTA, XRD, SEM, and TEM were practised.

After the sintered samples cut into rectangle shape and coated by Pt electrodes, the resistivity-temperature characteristics of them were determined by the four-probe method in air from room temperature to 1300°C.

**RESULTS AND DISCUSSION**

**Synthesis of the Fine Powders and the Formation of Perovskite Oxide**

Synthesis by the buffer solution method can maintain approximate pH value of the solution during the reaction, as a result, the homogenous and uniform precipitate is obtained. The average particle size of the powders calcined at 800°C is less than 25 nm (See Fig. 1).

The TG-DTA curves of the composition LaMnO\textsubscript{3} (solid line) and La\textsubscript{0.9}Sr\textsubscript{0.1}MnO\textsubscript{3} (dashed line) after drying at about 90°C are illustrated in Fig. 2. As shown in Fig. 2, for LaMnO\textsubscript{3}, the endothermic peak and the violent weight loss appear at about 110°C. This is due to the loss of the absorption water, the crystallization water and the organic reagent. Between 170°C and 260°C, the two exothermic peaks represent the decomposition of the precipitate. The small exothermic peak at 335°C may be considered as the decomposition of MnCO\textsubscript{3} and the generation of MnO\textsubscript{2} and CO. The endothermic peak at 475°C associates with the decomposition of salt and the
production of CO₂ and La₂O₃. Around 810°C, an endothermic peak and weight loss corresponds the procedure of Mn⁴⁺ changing into Mn³⁺ and the formation of oxygen vacancy. After 852°C, TG curve levels off and there is no weight loss, which proves that the perovskite oxide has been formed. For La₀.₉Sr₀.₁MnO₃, the formation temperature of the perovskite oxide is shifted left to 815°C, that is to say, the formation temperature of the perovskite oxide declines because La is replaced partly by Sr; more, the patterns of XRD in Fig.3 shows that with the increase of Sr content, on one hand, the formation temperature of perovskite-type La₀.xSrₓMnO₃ decreases; on the other hand, the decomposition of the precipitate does not lead to the monoxides and, rather, directly leads to the perovskite-type oxides.

Crystal Structure and Morphology

The crystal structure of La₀.xSrₓMnO₃ is of distorted perovskite type. According to XRD analysis of the sintered samples, the La₀.xSrₓMnO₃ display three lattice types at room temperature: orthorhombic (0 ≤ x ≤ 0.15), hexagonal (0.15 ≤ x ≤ 0.45) and cubic (x ≥ 0.45). Their lattice constants and primary cell volumes have been measured and calculated. It is found that as x increases, the primary cell volumes of La₀.xSrₓMnO₃ decrease and an abrupt fall occurs around the phase-transformation point (See Fig.4).

The SEM micrographs of the porous ceramics and the dense ceramics are given in Fig.5. The open porosity of the porous sample is about 50%, the density of dense sample is 5.87g/cm³ which is greater than 80% of the theoretical density.

Electrical Conduction Characteristics

The electrical conductivity of La₀.xSrₓMnO₃ is influenced dramatically by the content of Sr. Fig.6 gives the relation between the electrical conductivity and Sr content of the porous La₀.xSrₓMnO₃ samples calcined at 800°C and then sintered at 1350°C. It indicates that with the increasing of the amount of Sr in the solid solution, the electrical conductivity determined at 1000°C in air rises until x=0.5 which corresponds the peak value (>200S/cm).

From the viewpoint of the defect chemistry, the partial La³⁺ ions in LaMnO₃ are replaced non-isovalently, the defect chemistry reaction with vacancy compensation occurs as follows (in oxidation atmosphere):

$$\frac{1}{2}O_2 + 2SrO\xrightarrow{La_{0.5}O_3} 2Sr_{1+x} + 2h^+ + 3O_2^-$$
the electron hole \( h^* \) is bound weakly to the space around Mn\(^{3+} \), thus Mn\(^{4+} \) is formed, that is, La\(_{1-x}\)Sr\(_x\)Mn\(_{1-x}\)Mn\(_x\)\(^{3+}\)Mn\(_x\)\(^{4+}\)O\(_3\) is formed. The electron hole \( h^* \) which is bound weakly to the space around Mn\(^{3+} \), can form the electronic conduction in the form of jump under the driving force of an electric field.

According to the small-polarons mechanism, the conduction of LaMnO\(_3\) is due to the diffusion of p-type small polarons among manganese ions. The polarons are associated with a particular manganese site if the ion is in the +4 valence state, rather than the stoichiometric +3 valence state. When the concentration of small polarons is independent of temperature, conductivity expected to take the form

\[
\sigma = \frac{A}{T^S} \exp(-E_\alpha/kT)
\]

where \( A \) is both a charge carrier concentration and material constant, \( T \) is the absolute temperature, \( S=1 \) in the adiabatic limit and \( S=3/2 \) in the non-adiabatic regime, \( E_\alpha \) is the activation energy, and \( k \) is Boltzmann's constant. Therefore, for materials which obey the small-polaron mechanism, Arrhenius plots are expected to be linear, with a slope proportional to the activation energy associated with small-polaron jump.

Fig. 7 is typical Arrhenius plot of \( \log \sigma T \) versus reciprocal temperature for La\(_{1-x}\)Sr\(_x\)MnO\(_3\). The linearity of the data in it over such an extended temperature range verify that the conduction of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) is due to a temperature-independent concentration of p-type small-polarons. The activity energies for the motion of the charge carriers calculated from Fig.7 are plotted in Fig.8 as the function of Mn content. As can be seen from the figure, as Mn content increases, the activation energy \( E_\alpha \) decreases at first, then reaches the bottom, and then begins to go up.

In terms of the small-polarons mechanism, the small-polaron site energy is lower at the Mn site if the ion is in +4 valence state than at other sites. In case of the strontium content is lower, the concentrations of p-type small-polarons and Mn\(^{4+} \) are low, the lower-energy-state Mn\(^{4+} \) sites act as traps of carriers; in case of the strontium content is higher, the concentrations of p-type polarons and Mn\(^{4+} \) increase, the direct transmigration among Mn\(^{4+} \) sites becomes possible, the conductivity increases and activation energy decreases. But the substitution of strontium for lanthanum in LaMnO\(_3\) will causes the decrease of the density of the sintered samples and results in the drop of conductivity. On the other hand, the association of remainder defects will also decrease the conductivity. Therefore, with the increase of the Sr content, the conductivity increases gradually, reaches the peak and then goes down (See Fig.6).
CONCLUSIONS

The method of chemical coprecipitation in the buffer solution can be utilized to prepare the fine powders with composition \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \). Both porous and dense samples are obtained. \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) display three lattice types at room temperature: orthorhombic \((0 < x < 0.15)\), hexagonal \((0.15 < x < 0.45)\) and cubic \((x > 0.45)\). With the increase of Sr content, the formation temperature of perovskite oxide and the primary cell volume of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) decrease with an abrupt decrease around the phase-transformation point. At the same time, the relative density of samples and the sinterability of the powders becomes worse.

The electrical conductivity of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) is influenced apparently by the content of Sr. The conductivities measured at 1273K in air of the porous samples are greater than 100s/cm. The peak value which is more than 200s/cm is found at \( x=0.5 \). The conductivities of the dense samples are greater than that of the porous ones.

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Fig. 1 TEM photograph of \( \text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3 \)

Fig. 2 TG-DTA curves of \( \text{LaMnO}_3 \) (solid line) and \( \text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3 \) (dashed line)
Fig. 3 Patterns of XRD of LaMnO$_3$ (A) and La$_{0.4}$Sr$_{0.6}$MnO$_3$ (B) calcined at different temperatures

(Δ: La$_{1-x}$Sr$_x$MnO$_3$, •: MnO$_2$, ○: La$_2$O$_3$)
Fig. 4 Primary cell volume versus strontium content in La$_{1-x}$Sr$_x$MnO$_3$.

Fig. 5 SEM photograph of La$_{0.7}$Sr$_{0.3}$MnO$_3$.

700°C×2h, 1350°C×4h

non-calcined, 1550°C×3h
Fig. 6 Electrical conductivity of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ as function of Sr content at different temperatures.

Fig. 7 $\log \sigma T$ versus reciprocal temperature.

Reciprocal temperature, $1000/T$ (K$^{-1}$)
Fig. 8 Activation energy for conduction versus Sr content