CHAPTER IV

CONCLUSIONS

4.1 Conclusions

The perovskite ABO_3–type oxide $La_{0.7}Sr_{0.3}FeO_3$ doped with various compositions of Cu, Ni, Al and Mn ions at the B site were synthesized by the modified citrate method. XRD patterns of $La_{0.7}Sr_{0.3}FeO_3$, Cu–, Al– and Mn–doped $La_{0.7}Sr_{0.3}FeO_3$ showed single and homogeneous phase with cubic perovskite–type structure whereas the Ni–doped $La_{0.7}Sr_{0.3}FeO_3$ showed single phase with tetragonal structure. Estimated from the XRD analysis, the lattice parameters of Cu– and Mn–doped $La_{0.7}Sr_{0.3}FeO_3$ did not change significantly in comparison with that of undoped $La_{0.7}Sr_{0.3}FeO_3$. On the other hand, the lattice parameters of Ni– and Al– doped $La_{0.7}Sr_{0.3}FeO_3$ gradually decreased when increasing the amount of the metal ions.

The morphologies of the perovskite membranes were characterized by SEM. The grain size slightly increased with the increasing content of Cu, but slightly decreased with the increasing content of Al. On the contrary, the increasing amount of Ni and Mn substituted at the Fe site had no effect on the grain size. The densities of Cu– and Ni–doped $La_{0.7}Sr_{0.3}FeO_3$ discs increased with the amounts of Cu and Ni.

When the composition of Cu changed from 10% to 20%, the reduction peaks of Cu–doped oxides shifted gradually to lower temperatures. It is evident that doping Cu at Fe site causes the perovskite oxide to be more easily reducible. The reduction peaks of Mn–doped $La_{0.7}Sr_{0.3}FeO_3$ gradually shifted to higher temperatures with the increasing amount of Mn, indicating that Mn made the oxides more hardly reducible. TPR peaks of Ni–doped oxide shifted to lower temperature (200°C) than that of undoped material suggesting that the Ni–substitution at Fe site might facilitate the reduction. The reduction profile of Al-doped $La_{0.7}Sr_{0.3}FeO_3$ should be ascribed to the reduction of Fe^{n+} ions, which is similar to that of $La_{0.7}Sr_{0.3}FeO_3$.

Form this work, the obtained conductivity values rank in the increasing order: Al0.4<Mn0.2<Al0.3<Mn0.1<Al0.2<Al0.1<**LSF**<Cu0.2<Ni0.1<Cu0.1<Ni0.2<Ni0.3, implying that the electrical conductivity of $La_{0.7}Sr_{0.3}FeO_3$ was improved by doping Cu and Ni at the Fe site. The values increased with the Ni content in the sample. However, the increase of Cu doping amount caused the decrease in the conductivity. At 750°C, the electrical conductivity of $La_{0.7}Sr_{0.3}Fe_{0.7}Ni_{0.3}O_3$ (650.5 S/cm) was about 3.8 times higher than that of undoped $La_{0.7}Sr_{0.3}FeO_3$ (170 S/cm). On the other hand, the conductivity property decreased with increasing the amounts of Al and Mn.

For the thermal expansion results, the thermal expansion coefficient (TEC) of $La_{0.7}Sr_{0.3}FeO_3$ was improved by doping Ni at the Fe site. As compared to $La_{0.7}Sr_{0.3}FeO_3$, the TEC of $La_{0.7}Sr_{0.3}Fe_{0.9}Cu_{0.1}O_3$ and $La_{0.7}Sr_{0.3}Fe_{0.8}Cu_{0.2}O_3$ did not change significantly and the TEC values of Ni^{2+} specimens were smaller than that of $La_{0.7}Sr_{0.3}FeO_3$. The TEC values of doping Ni at the B site increased with Ni contents.

The Experimental results of doping at the B site indicated that: (i) Cu doping at $La_{0.7}Sr_{0.3}FeO_3$ could improve the conductivity, but its TEC did not change significantly. $La_{0.7}Sr_{0.3}Fe_{0.9}Cu_{0.1}O_3$ (σ = 312.2 S/cm at 650°C, TEC = 15.2 x $10^{-6}K^{-1}$) showed better property than $La_{0.7}Sr_{0.3}Fe_{0.8}Cu_{0.2}O_3$ (σ = 218.5 S/cm at 750°C, TEC = 15.3 x $10^{-6}K^{-1}$); (ii) Ni–doped $La_{0.7}Sr_{0.3}FeO_3$ oxide can improve both the conductivity and TEC values; $La_{0.7}Sr_{0.3}Fe_{0.7}Ni_{0.3}O_3$ (σ = 650.5 S/cm at 750°C, TEC = 15.1 x $10^{-6}K^{-1}$), $La_{0.7}Sr_{0.3}Fe_{0.8}Ni_{0.2}O_3$ (σ = 601.4 S/cm at 800°C, TEC = 15.0 x $10^{-6}K^{-1}$) and $La_{0.7}Sr_{0.3}Fe_{0.9}Ni_{0.1}O_3$ (σ = 257.2 S/cm at 750°C, TEC = 14.9 x $10^{-6}K^{-1}$); (iii) Al– and Mn–doped $La_{0.7}Sr_{0.3}FeO_3$ exhibited lower conductivity than $La_{0.7}Sr_{0.3}FeO_3$. The conductivity property decreased with the increase Al and Mn amounts, implying improper property for anode materials. Lastly, all metals doped–perovskite samples have shown no improvement of reduction property.

In conclusion, $La_{0.7}Sr_{0.3}Fe_{0.8}Ni_{0.2}O_3$ (electrical conductivity is 601.4 S/cm at 800°C and the TEC value is 15.0 x $10^{-6}K^{-1}$) and $La_{0.7}Sr_{0.3}Fe_{0.7}Ni_{0.3}O_3$ (electrical conductivity is 650.5 S/cm at 750°C and the TEC value is 15.1 x $10^{-6}K^{-1}$) can be potential candidate for SOFC anode material.

4.2 Suggestions

From experiment results, the future work should be focused on the following:

(i) improving the reducibility and TEC of the samples by doping anti–reduction metal; and

(ii) determination of sample electrical conductivity under condition H_2 by DC 4–probes technique for fuel cell application.