

REFERENCES

- [1] Fergus, J.W. Oxide anode materials for solid oxide fuel cells. *Solid State Ionics* 177(2006): 1529–1541.
- [2] Williams, M.C.; Dokiya, M.; Yamamoto, O.; Tagawa, H., and Singhal, S.C. The Electrochem. Soc. Proceedings Series, Pennington NJ, USA, 1995, p. 10.
- [3] Singhal S.C. and Iwahara, H. The Electrochem. Soc. Proceedings Series, Pennington NJ, USA, 1993, p. 665.
- [4] Blomen, L.J.M.J., and Mugerwa, M.N. *Fuel Cell Systems*, New York: Plenum Press, 1993.
- [5] University of Cambridge. Solid oxide fuel cells (SOFCs) [online]. (n.d.). Available from: www.doitpoms.ac.uk/tlplib/fuel-cells/figures/flat_plate_soft_sml.png [2008 August 1].
- [6] Lloyd, J. Perovskite [online]. (n.d.). Available from: <http://en.wikipedia.org/wiki/Perovskite> [2008, August 1].
- [7] Teraoka, Y.; Zhang, H.-M.; and Yamazoe, N. Oxygen sorption and catalytic properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ Perovskite-type oxides. *Journal of Catalysis* 121 (1990): 432–440.
- [8] Rao, C. N. R.; Gopalakrishnan, J.; Vidyasagar, K. Superstructure, ordered defects and nonstoichiometry in metal oxides of perovskite and related structure. *Indian Journal of Chemistry* 23A(1984): 265-284.
- [9] Teraoka, Y.; Nobunaga, T.; Yamazoe, N. Effect of cation substitution on the oxygen semipermeability of perovskite-type oxide. *Chemistry Letters* (1988): 503-506.
- [10] Tidrow, S. C.; Tauber, A.; Wilber, W. D.; Finnegan, R. D.; Eckart, D. W.; Drach, W.C. Dielectric Properties Of Perovskite Antimonates. *IEEE Trans. Appl. Supercond.* 7(1997): 1769-1771.

- [11] Kovalevsky, A.V.; Kharton, V.V.; Yaremchenko, A.A.; Pivak, Y.V.; Naumovich, E.N.; Frade, J.R. Stability and oxygen transport properties of $\text{Pr}_2\text{NiO}_{4+\delta}$ ceramics. *Journal of the European Ceramic Society* 27(2007): 4269–4272.
- [12] Yu, H-C.; Fung, K-Z.; Guo, T-C.; Chang, W-L. Syntheses of perovskite oxides nanoparticles $\text{La}_{1-x}\text{Sr}_x\text{MO}_{3-\delta}$ (M = Co and Cu) as anode electrocatalyst for direct methanol fuel cell. *Electrochimica Acta* 50(2004): 811–816.
- [13] Odier, P.; Allanion, Ch.; Bassat, J. M. Oxygen Exchange in $\text{Pr}_2\text{NiO}_{4+d}$ at High Temperature and Direct Formation of $\text{Pr}_4\text{Ni}_3\text{O}_{10-x}$. *Journal of Solid State Chemistry* 153(2000): 381-385.
- [14] Goodenough, J. B., and Longo J. M. *Crystallographic and Magnetic Properties of Perovskite and Perovskite-related Compounds*. Landholt-Bornstein Numerical Data and Functional Relationships in Science and Technology New Series Group III/vol. 4a, Springer-Verlag, Berlin-Heidelberg, 1970.
- [15] Yeyongchaiwat, J. *Synthesis and Characterization of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ Perovskite Membrane*. Doctoral dissertation, Department of Chemical Technology, Faculty of Science, Chulalongkorn University, 2002.
- [16] Fagg, D.P.; Kharton, V.V.; Kovalevsky, A.V.; Viskup, A.P.; Naumovich, E.N.; Frade, J.R. The stability and mixed conductivity in La and Fe doped SrTiO_3 in the search for potential SOFC anode materials. *Journal of the European Ceramic Society* 21(2001): 1831–1835.
- [17] Zha, S.; Tsang, P.; Cheng, Z.; Liu, M. Electrical properties and sulfur tolerance of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{1-x}\text{Mn}_x\text{O}_3$ under anodic conditions. *Journal of Solid State Chemistry* 178(2005): 1844–1850.
- [18] Tshipis, E.V.; Kharton, V.V.; Frade, J.R. Mixed conducting components of solid oxide fuel cell anodes *Journal of the European Ceramic Society* 25(2005): 2623–2626.

- [19] Ishihara, T.; Yan, J.; Shinagawa, M.; Matsumoto, H. Ni–Fe bimetallic anode as an active anode for intermediate temperature SOFC using LaGaO₃ based electrolyte film. *Electrochimica Acta* 52(2006): 1645–1650.
- [20] Plint, S.M.; Paul, A.C.; Shanwen, T.; Irvine, T.S. Electronic transport in the novel SOFC anode material La_{1-x}Sr_xCr_{0.5}Mn_{0.5}O_{3±δ}. *Solid State Ionics* 177(2006): 2005–2008.
- [21] Wang, Z.; Qian, J.; Cao, J.; Wang, S.; Wen, T. A study of multilayer tape casting method for anode-supported planar type solid oxide fuel cells (SOFCs). *Journal of Alloys and Compounds* 437(2007): 264–268.
- [22] Bao, W.; Guan, H.; Cheng, J. A new anode material for intermediate solid oxide fuel cells. *Journal of Power Sources* 175(2007): 232–237.
- [23] Huang, B.; Wang, S.R.; Liu, R.Z.; Ye, X.F.; Nie, H.W.; Sun, X.F.; Wen, T.L. Performance of La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ} perovskite-structure anode material at lanthanum gallate electrolyte for IT-SOFC running on ethanol fuel. *Journal of Power Sources* 167(2007): 39–46.
- [24] Chen, X.J.; Liu, Q.L.; Khor, K.A.; Chan, S.H. High-performance (La,Sr)(Cr,Mn)O₃/ (Gd,Ce)O_{2-δ} composite anode for direct oxidation of methane. *Journal of Power Sources* 165(2007): 34–40.
- [25] Mulders, J. J. L. An in-situ four-point probe method for the electrical characterization of beam induced depositions [Online]. (n.d.). Available from: http://www.nanotechnik.com/fileadmin/public/publications/in-situ_four-point-probe.pdf [2008, January 24].
- [26] Rodríguez-Martínez, L. M.; Vidal, K.; Ortega-San-Martín, L.; Díez-Linaza, E.; N6, M. L.; Rojo, T.; Laresgoiti, A.; Arriortua, M. I. Isolating the effect of doping in the structure and conductivity of (Ln_{1-x}M_x)FeO_{3-δ} perovskites. *Solid State Ionics* 178(2007): 1310–1316.
- [27] Kharton, V.V.; Shaulo, A.L.; Viskup, A.P.; Avdeev, M.; Yaremchenko, A.A.; Patrakeevev, M.V.; Kurbakov, A.I.; Naumovich, E.N.; Marques, F.M.B. Perovskite-like system (Sr,La)(Fe,Ga)O_{3-δ}: structure and ionic transport under oxidizing conditions. *Solid State Ionics* 150(2002): 229–243.
- [28] Pai, M.R.; Wani, B.N.; Sreedhar, B.; Singh, S.; Gupta, N.M. Catalytic and redox properties of nano-sized La_{0.8}Sr_{0.2}Mn_{1-x}Fe_xO_{3-δ} mixed oxides

- synthesized by different routes. *Journal of Molecular Catalysis A: Chemical* 246(2006): 128–135.
- [29] Varma, S.; Wani, B.N.; Gupta, N.M. Redox behavior and catalytic activity of La-Fe-V-O mixed oxide. *Applied Catalysis A: General* 241(2003): 341–348.
- [30] Ciambelli, P.; Cimino, S.; Lisi, L.; Faticanti, M.; Minelli, G.; Pettiti, I.; Porta, P. La, Ca and Fe oxide perovskites: preparation, characterization and catalytic properties for methane combustion. *Applied Catalysis B: Environmental* 33(2001): 193–203.
- [31] Porta, P.; Cimino, S.; Rossi, S.; Faticanti, M.; Minelli, G.; Pettiti, I. AFeO_3 (A=La, Nd, Sm) and $\text{LaFe}_{1-x}\text{Mg}_x\text{O}_3$ perovskites: structural and redox properties. *Mater. Chem. Phys.* 71(2001): 165–173.
- [32] Zhang, R.; Villanueva, A.; Alamdari, H.; Kaliaguine, S. Cu- and Pd-substituted nanoscale Fe-based perovskites for selective catalytic reduction of NO by propene. *Journal of Catalysis* 237(2006): 368–380.
- [33] González, O.; Lujano, J.; Pietri, E.; Goldwasser, R.M. New Co-Ni catalyst systems used for methane dry reforming based on supported catalysts over an INT-MM1 mesoporous material and a perovskite-like oxide precursor $\text{LaCo}_{0.4}\text{Ni}_{0.6}\text{O}_3$. *Catalysis Today* 107–108(2005): 436–443.
- [34] Vidal, K.; Rodríguez-Martínez, L. M.; Ortega-San-Martín, L.; Díez-Linaza, E.; Nó, M. L.; Rojo, T.; Laresgoiti, A.; Arriortua, M. I. Isolating the effect of doping in the structure and conductivity of $(\text{Ln}_{1-x}\text{M}_x)\text{FeO}_{3-\delta}$ perovskites. *Solid State Ionics* 178(2007): 1310–1316.
- [35] Tao, S.; Irvine, J.T.S. Phase Transition in Perovskite Oxide $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ Observed by in Situ High-Temperature Neutron Powder Diffraction. *Chem. Mater.* 18(2006): 5453–5460.
- [36] Tao, S.; Irvine, J.T.S. Structural and electrochemical properties of the perovskite oxide $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$. *Solid State Ionics* 179 (2008): 725–731.

- [37] Kharton, V.V.; Tsipis, E.V.; Marozau, I.P.; Viskup, A.P.; Frade, J.R.; Irvine, J.T.S. Mixed conductivity and electrochemical behavior of $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$. *Solid State Ionics* 178(2007): 101–113.
- [38] Kindermann, L.; Poulsen, F.W.; Larsen, P.H.; Nickel, H.; Hilpert, K. Forum on SOFC, Proceedings 3rd ed., Europe, 1998, pp. 123–132.
- [39] Ullmann, H.; Trofimenko, N.; Tietz, F.; Stöver, D.; Ahmad-Khanlou, A. Correlation between thermal expansion and oxide ion transport in mixed conducting perovskite-type oxides for SOFC cathodes. *Solid State Ionics* 138 (2000): 79-90.
- [40] Julian, A.; Juste, E.; Chartier, T.; Del Gallo, P.; Richet, N. Catalytic Membrane Reactor: Multilayer membranes elaboration, 10th International Conference of the European Ceramic Society, Germany, 2007, pp. 718-722.
- [41] Tsipis, E.V.; Kiselev, E.A.; Kolotygin, V.A.; Waerenborgh, J.C.; Cherepanov, V.A.; Kharton, V.V. Mixed conductivity, Mössbauer spectra and thermal expansion of $(\text{La,Sr})(\text{Fe,Ni})\text{O}_{3-\delta}$ perovskites. *Solid State Ionics* 179(2008): 2170–2180.
- [42] Tai, L. W.; Nasrallah, M. M.; Anderson, H. U.; Sparlin, D. M.; Sehlin, S. R. Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. Part 1. The system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$. *Solid State Ionics* 76(1995): 259-271.
- [43] Li, S.; Lü, Z.; Huang, X.; Su, W. Thermal, electrical, and electrochemical properties of Nd-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as a cathode material for SOFC. *Solid State Ionics* 178(2008): 1853–1858.
- [44] Shao, Z.; Xiong, G.; Tong, J.; Dong, H.; Yang, W. Ba effect in doped $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ on the phase structure and oxygen permeation properties of the dense ceramic membranes. *Separation and Purification Technology* 25(2001): 419–429.
- [45] Runduo, Z.; Adrian, V.; Houshang, A.; Serge, K. Cu- and Pd-substituted nanoscale Fe-based perovskites for selective catalytic reduction of NO by propene. *Journal of Catalysis* 237(2006): 368–380.

APPENDIX

Appendix A

Activation Energy (E_a)

Arrhenius plot of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ is given in Figure 3.16 (b). The linear part can be described by the small polaron conduction mechanism, following the formula:

$$\sigma = (A/T) \exp(-E_a/kT) \quad (\text{B.1})$$

$$\sigma T = A \exp(-E_a/kT)$$

$$\ln \sigma T = -E_a/kT + \ln A \quad (\text{B.2})$$

A is material constant including the carrier concentration term,

E_a the activation energy

k the Boltzmann's constant

T is the absolute temperature.

From Equation B.2 Arrhenius plot of $\ln \sigma T$ versus $1000/T$ gives a straight line, whose slope and intercept can be used to determine E_a and A .

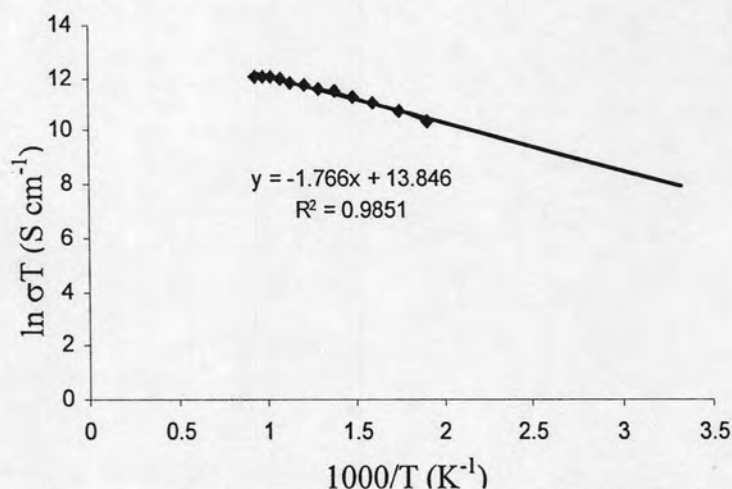


Figure A.1 Arrhenius plot of the electrical conductivity of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$.

The activation energy calculated from the slope of the straight line of figure A.1 For example, the activation energy (E_a) of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$, was calculated as below:

$$\text{Slope} = -E_a/k$$

$$\text{Slope} = -E_a / 8.314472$$

$$E_a = -\text{slope} \times 8.314472$$

$$E_a = -(-1.766) \times 8.314472$$

$$E_a = 14.68 \text{ kJ/mol}$$

Appendix B

Relative density

Relative density of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ is given in Figure 3.6. It was calculated following the formula:

$$\begin{aligned}\rho &= m / V \\ &= w / (\pi \times r^2 \times h)\end{aligned}$$

$$\rho_0 = M / N (a \times b \times c)$$

$$\text{Relative density} = (\rho / \rho_0) \times 100\%$$

Where;

ρ	= density
ρ_0	= theory density
w	= weight of perovskite membrane
r	= radius
h	= thickness
M	= molecular weight of perovskite
N	= Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$)
a, b and c	= lattice parameter

For example, relative density of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$, was calculated as below:

$$\begin{aligned}\rho &= 1.7498 \text{ g} / (\pi \times 0.804^2 \text{ cm}^2 \times 1.46 \text{ mm}) \\ &= 5.90 \text{ g/cm}^3 \\ \rho_0 &= 227.37 \text{ gmol}^{-1} / (6.02 \times 10^{23} \text{ mol}^{-1})(3.90 \text{ \AA})^3 \\ &= 6.37 \text{ g/cm}^3\end{aligned}$$

$$\begin{aligned}\text{So; Relative density} &= (5.90 / 6.37) \times 100\% \\ &= 92.7 \%\end{aligned}$$

VITAE

Miss Nantiwat Virattayanon was born on August 5, 1984 in Bangkok, Thailand. She graduated with Bachelor's Degree in Petrochemicals and Polymeric materials from Faculty of Engineering and Industrial Technology, Silpakorn University in 2006. She continued her study in Petrochemistry and Polymer Science Program, Faculty of Science, Chulalongkorn University in 2006 and completed in 2009.

Her present address is 59/7 Soi Puttabucha 12, Puttabucha Rd., Bangmod, Jomtong and Bangkok, Thailand 10150.