

## CHAPTER I

### INTRODUCTION

Today energy is mainly used for three purposes, electricity, heat and transportation. Most of the world's energy comes from fossil fuels like coal, oil and natural gas. However, fossil fuels are not an inexhaustible resource. To keep the global progress and prosperity, a change to a more sustainable and clean energy system is needed. Therefore, worldwide interests in building a decentralized, hydrogen-based energy economy have been focusing on solid oxide fuel cells (SOFCs) as it can potentially offer a clean, low-pollution technology to electrochemically generate electricity at high efficiencies. These fuel cells provide many advantages over traditional energy conversion systems including high efficiency, reliability, modularity, fuel adaptability, and very low levels of NO<sub>x</sub> and SO<sub>x</sub> emissions. Quiet, vibration-free operation of SOFCs also eliminates noise usually associated with conventional power generation systems [Singhal, S.C., 2004; Minh, N.Q., 1993].

Firstly, SOFCs were being developed for operation primarily in the temperature range of 900-1000°C with the capability of internally reforming hydrocarbon fuels (e.g. natural gas), such high temperature SOFCs provide high quality exhaust heat for cogeneration. Thus, reduction of the SOFC operating temperature by 200°C or more allows the use of a broader set of materials. The lower operating temperature can impose less-demanding requirements on the seals and the balance-of-plant components, simplifies thermal management, aids in faster start up and cool down, and results in less degradation of cell and stack components [Ormerod, R.M., 2003; Singhal, S.C., 2007]. However, at lower temperatures, electrolyte conductivity and electrode kinetics decrease significantly; to overcome these drawbacks, alternative cell materials and designs are being extensively investigated [Ralph, J.M. *et al.*, 2001]. Studies of intermediate temperature SOFCs (IT-SOFCs) have been focused on electrodes in the development of cathode, because oxygen reduction is generally more difficult to operate at intermediate temperature

range of 400-800°C [Routbort, J.L. *et al.*, 1996; Chiba, R. *et al.*, 1999; Jiang, S.P. *et al.*, 2005; Amow, G. *et al.*, 2006].

Materials with mixed ionic and electronic conducting properties (MIECs) have attracted much attention for electrochemical applications, especially IT-SOFCs cathode. Perovskite ( $ABO_3$ ) and Ruddlesden-Popper ( $A_2BO_4$ ) structures are the important MIECs materials which are currently studied. Perovskite materials have shown to be one of the most highly flexible structures because the elements of the periodic table can be accommodated in the A and/or B sites resulting in wide range of properties. Both A and B site substituted perovskite structures such as  $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$  (LSCF) have been studied [Tai, L.-W. *et al.* 1995; Sekido, S. *et al.*, 1990; Jiang, S.P., 2002; Wang, S. *et al.*, 2003; Ji, Y. *et al.*, 2005]. However, at the intermediate temperature range (400-800°C), these perovskite materials do not satisfy all cathode requirements, especially mechanical compatibility with other cell components and conductivity [Chiba, R. *et al.*, 1999]. Therefore, materials with the Ruddlesden-Popper structure which is comprised of alternating perovskite blocks with a rock-salt have attracted much interest recently due to their mixed conducting properties while maintaining high electrical conductivity in the targeted temperature range [Greenblatt, M., 1997; Vashook, V.V. *et al.*, 1999; Tang, J.P. *et al.*, 2000; Hui, Z. *et al.*, 2011]. The  $La_2NiO_{4+\delta}$  structure is made up of sheets of  $(NiO_6)$  corner sharing octahedra, interleaved with  $La_2O_2$  layers in which the additional oxygen could be localized. The compound is therefore able to accept oxygen overstoichiometry that leads to potentially high oxygen diffusivity compared to that of the common cathode materials [Routbort, J.L. *et al.*, 1996; Greenblatt, M., 1997; Boehm, E. *et al.*, 2003; Darcovich, K. *et al.*, 2005; Amow, G. *et al.*, 2006]. However, due to insufficient electrical conductivity, 10-70 S/cm [Vashook, V.V. *et al.*, 1999] in  $La_2NiO_{4+\delta}$ , attempts to improve such properties which have been conducted through substitution of the A-site with alkaline-earth ions. Ca and Sr are the most popular dopants due to their compatible ionic radii. However, Ca has been found to have little effect on electrical conductivity, while the replacement of La by Sr leads to a much larger improvement [Tang, J.P. *et al.*, 2000; Hui, Z. *et al.*, 2011; Aguadero, A. *et al.*, 2006; Fontaine, M. L. *et al.*, 2006]. It is not only A-site

substitution on  $\text{La}_2\text{NiO}_{4+\delta}$  materials, but the higher ordering of the B-site in perovskite materials known as double perovskite also become interesting. Because the unit cell in  $\text{ABO}_3$  perovskite type materials can be seen like a three-dimensional corner-sharing network of  $\text{BO}_6$  octahedra, with a large A cation occupying the 12 coordinate position between 8  $\text{BO}_6$  octahedra. If two atoms, B' and B'', are placed on two crystallographic different B sites, a double perovskite is formed with the general formula  $\text{A}_2\text{B}'\text{B}''\text{O}_6$  or  $\text{A}_3\text{B}'_2\text{B}''\text{O}_9$  [Fuentes, V.C. *et al.*, 2011]. Ordering can be in a rock salt pattern, with different cations occupying alternating  $\text{BO}_6$  octahedra, it can form layers of alternating B cations. Therefore, the B-site ordered perovskites is believed to be similar to the relatively open structural framework afforded by the rock-salt intergrowth in Ruddlesden-Popper structure which allows for the accommodation of hyperstoichiometric oxide-ions in the rock-salt layer resulting improvement of ion conductivity.

To obtain the materials with appropriate properties for IT-SOFCs cathode, two attempts have been used including A and B site substitutions. Thus, this work is focused on synthesis of Sr substitution on  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  ( $x = 0 - 0.8$ ) and the new family of  $\text{La}_3\text{Ni}_2\text{MO}_9$  ( $M = \text{Nb}$  and  $\text{Ta}$ ) by via sol-gel process and solid state reaction. The effects of synthesis routes and A-site (Sr) and B-site (Nb and Ta) substitution on phase, morphology, electrical conductivity and ionic transport property were investigated.