

Chapter 2

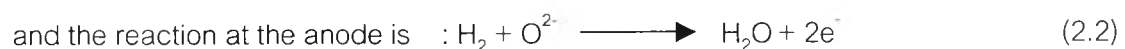
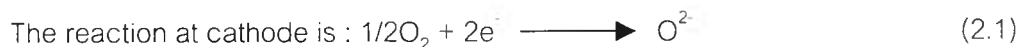
Literature review

2.1 Solid Oxide Fuel Cell (SOFC)

There are several advantages of SOFC as compared with other types such as use of nonprecious material electrodes and solid electrolyte. High operating temperature at 800-1000°C offers high-energy conversion efficiency and the waste heat produced by this cell can be used for co-generation system. Furthermore, SOFC can be fabricated in thin layers and cell component can be configured into its unique shape^(1,3). However, high operating temperature does limit the material selection for both electrode and electrolyte due to thermal expansion mismatch and chemical incompatibility of each component. From these reasons, there are many researchers trying to develop SOFC materials to used at a reduced operating temperature.

2.1.1 Fundamental operating of SOFC

Similar to other types of fuel cell, solid oxide fuel cell has two electrochemical reactions. An oxidant gas (air or O₂) is reduced at the cathode and fuel gas (H₂ or CO) is oxidized at the anode. The oxygen ions form at the cathode and move through the solid electrolyte and then combine with hydrogen or carbon monoxide at the anode side to produce water vapor or CO₂. The electrons produced from the anode site transport through the external circuit to maintain charge balance and consequently generate a direct current⁽¹⁾.



Fundamental reactions in the solid oxide fuel cell show in Fig. 2.1

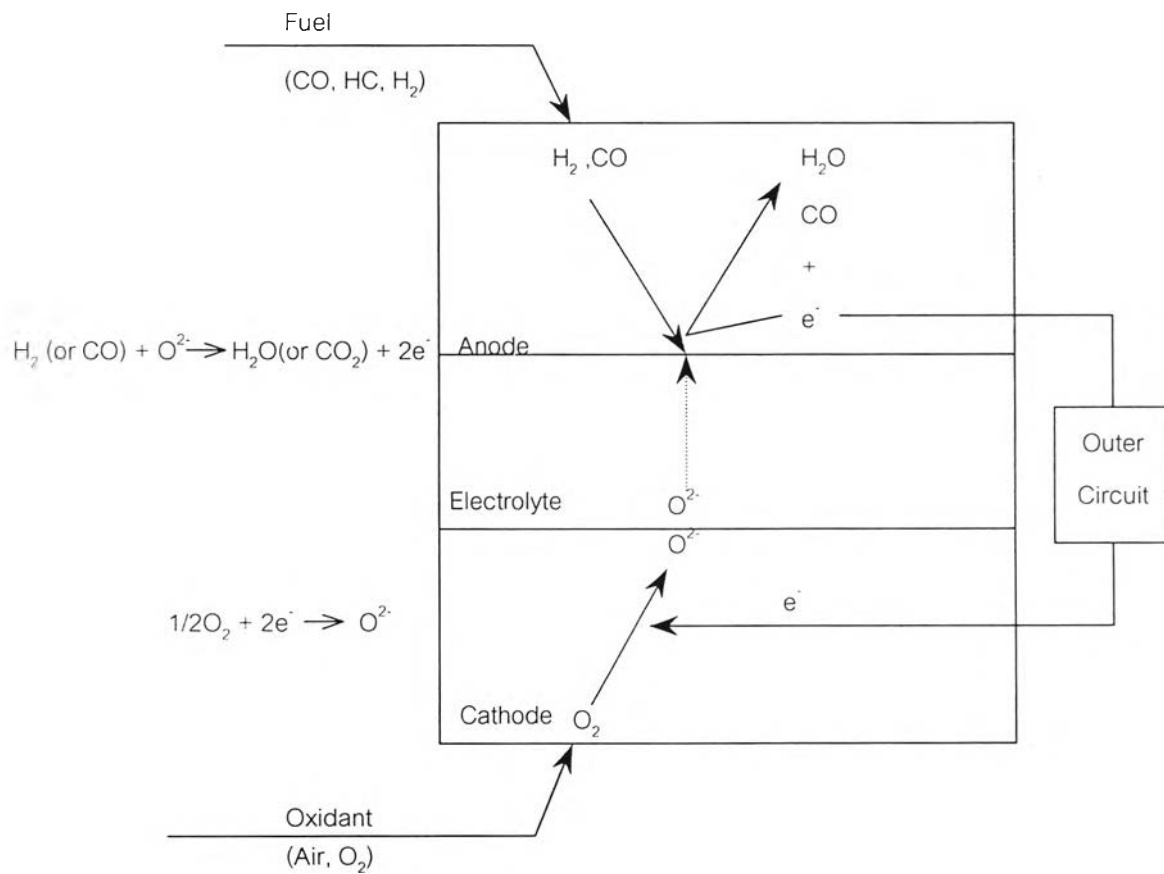


Fig. 2.1 Fundamental reactions in the solid oxide fuel cell ⁽³⁾.

2.1.2 Cell components and requirement

The major components of SOFC stack are the cathode, the anode, the electrolyte and the interconnect. Each component must have the proper stability (chemical, phase, morphological and dimensional) in oxidizing and/or reducing atmosphere, chemical compatibility with other components, and sufficient conductivity. Moreover, each component must have similar coefficients of thermal expansion to avoid separation or cracking during fabrication and operation at high temperature ^(1,2).

1. Cathode

The main function of the cathode is to provide reduction of the oxidant. Thus, the cathode operates in an oxidizing environment. The requirements of the cathode are ^(1,2):

- high electronic conductivity
- chemical stability under the oxidizing atmosphere
- sufficient catalytic activity for the oxidant gas reaction at the operating conditions
- chemical and thermal compatibility with the other components
- sufficient porosity to allow air or oxygen gas transport to the reaction sites

The most frequently used cathode material is doped lanthanum manganite (LaMnO_3). Besides, there are other materials such as doped LaFeO_3 , doped LaCoO_3 , and doped PrMnO_3 ⁽²⁾. However they have some disadvantages such as thermal expansion mismatch with other components and insufficient conductivity.

2. Anode

The main function of the anode is to provide oxidation of the fuel³. The requirements of the anode are ^(1,2):

- high electronic conductivity
- chemical stability under the reducing atmosphere
- sufficient catalytic activity
- chemical and thermal compatibility with the other components
- tolerance of contaminants in fuel gas
- sufficient porosity to allow fuel gas transport

Because of the reducing conditions of the fuel gas, only metals can be used as the anode material. Nickel is commonly used because of its low cost. To eliminate thermal mismatch with YSZ as an electrolyte and to maintain the porous structure, nickel metal is usually dispersed on the surface of the YSZ support to form a Ni-YSZ cermet. Recently, CeO_2 based material has been selected for intermediate temperature SOFC ^(1,2).

3. Electrolyte

The primary function of the SOFC electrolyte is to conduct ions between the anode and the cathode⁽¹⁾. Furthermore the electrolyte separates the fuel from the oxidant in the fuel cell. The key requirements for the electrolyte in the SOFC are discussed below^(1,2).

- a. It must possess adequate ionic conductivity in both reducing and oxidizing atmospheres.
- b. The electrolyte material must be stable in dual atmospheres.
- c. It must be chemically and thermally compatible with other components.
- d. The electrolyte must be dense to prevent gas cross leak and has high strength.

At present, the common material used as an electrolyte in SOFC is yttria stabilized zirconia (YSZ). Also, other materials have been developed, for example, doped CeO_2 , Bi_2O_3 and perovskite type oxide. These will be discussed later.

4. Interconnect

The primary function of the SOFC interconnect is to join the anode of the one cell to the cathode of the other cell⁽¹⁾. The choice of material must be^(1,2)

- stable in both reducing and oxidizing atmospheres
- impermeable to gases
- sufficiently conductive to support electron flow at the operating conditions
- chemically and thermally compatible with other components
- durable at high temperature

The most suitable materials are perovskite type ceramics based on LaCrO_3 .

2.2 Solid electrolyte

The solid electrolyte in SOFC requires high ionic conductivity. The electrical conductivity as a function of temperature for conventional oxide ionic conductors is shown in Fig. 2.2.

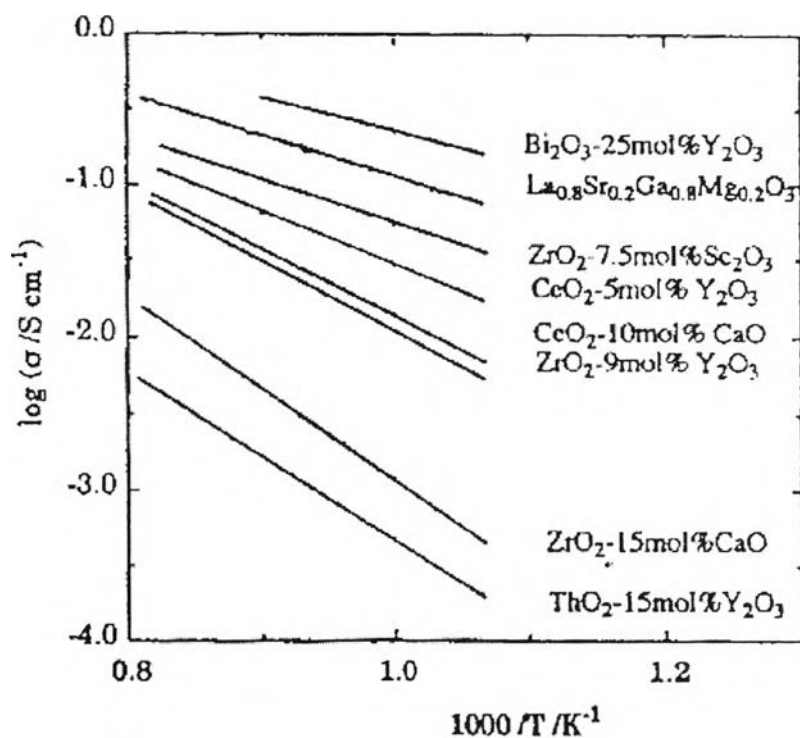


Fig.2.2 Arrhenius plots of conventional oxide ionic conductor⁽⁷⁾

2.2.1 Zirconia based

Stabilized zirconia is the most common electrolyte in SOFC because it has adequate ionic conductivity and exhibits desirable stability in both atmospheres. SOFC which uses zirconia based electrolyte is usually operated at 800-1000 °C. ZrO_2 itself has monoclinic form at room temperature and then changes to a tetragonal above 1170 °C. Above 2370 °C it transform to a cubic fluorite structure. An addition of some trivalent oxides can stabilize the cubic fluorite structure and simultaneously increase the concentration of oxygen vacancy resulting in high ionic conductivity⁽³⁾. Typically Y_2O_3 is used to stabilized ZrO_2 and, consequently, the oxygen vacancies can form due to

charge balance. The other dopants have been used with ZrO_2 including CaO , MgO , Sc_2O_3 and some rare earth oxides.

2.2.2 Ceria based

CeO_2 has cubic fluorite structure from room temperature to its melting point; therefore it does not require stabilizer. To promote ionic conductivity, however, some di- or tri- valent cations such as Gd_2O_3 , La_2O_3 , Nd_2O_3 , Sm_2O_3 , Yb_2O_3 and SrO are partially substituted into CeO_2 . Ceria based electrolyte can be at $450-700^\circ C$ ⁽¹⁾ and still exhibits higher conductivity than YSZ. Although doped CeO_2 electrolytes are superior to YSZ, their performance diminishes at elevated operating temperature due to electronic conductivity. This can be suppressed by doping with some cations and coating CeO_2 with YSZ layer. The stability of CeO_2 depends on the oxygen partial pressure at the interface of CeO_2/YSZ ^(1,3).

2.2.3 Bismuth oxide based

At the intermediate temperature ($700-900^\circ C$), stabilized Bi_2O_3 shows higher ionic conductivity than any other oxygen ion conductors. However, the main drawback of this oxide is the optimum conductivity can be obtained only in the short range of oxygen partial pressure. Below this certain range, it is easily reduced and decomposes into bismuth metal; consequently, its ionic conductivity decreases.

2.2.4 Perovskite oxide based

Recently, there have been many developments of other materials, especially those possessing sufficient ionic conductivity at the intermediate temperature. Several doped perovskite (ABO_3) for solid electrolytes can replace YSZ in a reduced temperature application, therefore the limitation of material selection is not a serious problem. In addition, that can improve cell reliability during working period. Early studies have shown that some doped perovskite oxides such as $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$

exhibits high ionic conductivity in 600-800°C and they are stable in a wide range of oxygen partial pressure^(3-5,7-9,11-13).

2.3 Ionic Conductivity in Perovskite-type Oxide

Perovskite-type oxide ABO_3 , where A is di- or tri- valent cation and B is tetra- or tri- valent cation. When the cation A or B is partially substituted with the cation of lower valency, oxygen vacancies are created to maintain charge balance in the composition.

2.3.1 Perovskite structure

The ideal cubic perovskite has shown in Fig 2.3¹⁶. From this figure, both the larger A cation and oxygen form an FCC lattice. The octahedral sites in this FCC array are occupied by the smaller B cation that has only oxygen as its nearest neighbor. The perovskite structure is observed for many compounds such as $CaTiO_3$, $BaTiO_3$, $SrTiO_3$, $LaGaO_3$, $LaAlO_3$ and $YAlO_3$.

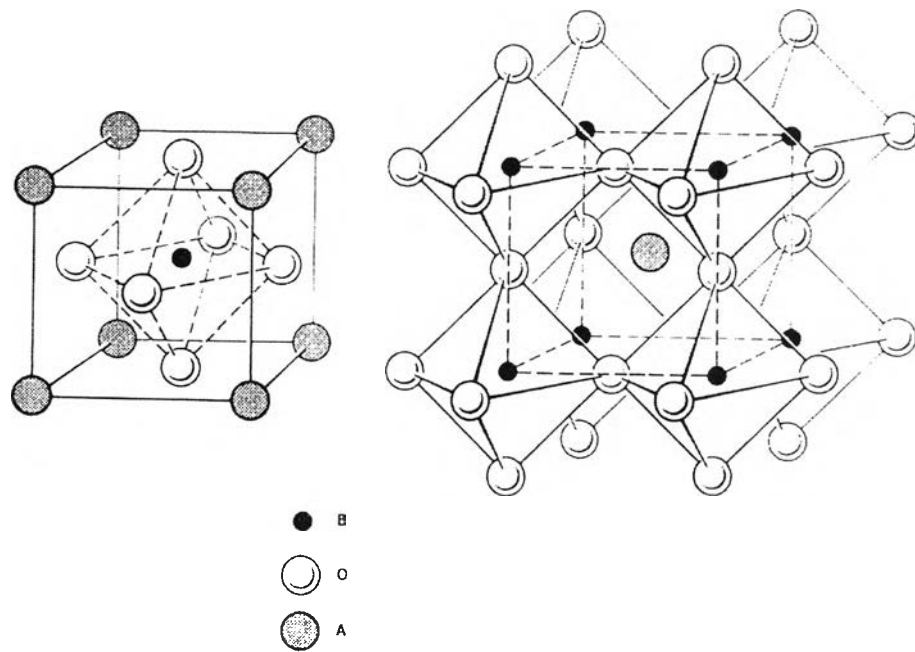


Fig 2.3 Ideal perovskite structure ⁽¹⁶⁾.

The tolerance factor (t) is obtained from ionic radii of each component as

$$t = (r_A + r_O) / \sqrt{2} (r_B + r_O) \quad (2.4)$$

where r_A , r_B and r_O are the ionic radii of A, B and oxygen ions respectively ^(8,14).

The perovskite structure is stable when tolerance factor is in the range of 0.75-1. When the value is 0.95, it may be cubic or small distortions to rhombohedral structure. The ideal perovskite is the cubic structure with the tolerance factor of 1.0. Increasing in lattice distortion requires the higher activation energy for oxygen ion to transport. As a result, the ionic conductivity decreases. H. Huyashi et al. ⁽¹⁴⁾ have studied the electrical conductivity as a function of tolerance factor and concluded that the maximum electrical conductivity was obtained from the tolerance factor around 0.96. Similarly, T. Ishihara and coworker ⁽⁷⁾ have stated that the reduction of electrical conductivity results from the decrease in geometrical symmetry of the lattice.

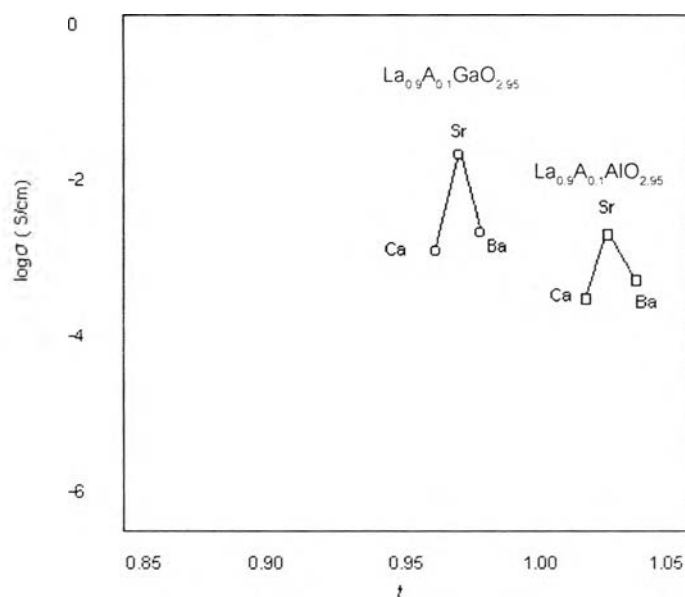


Fig 2.4 Effect of dopant ion in A site on the electrical conductivity¹¹⁴

The electrical conductivity as a function of the tolerance factor in LaMO_3 ($M=\text{Al}, \text{Ga}$) was shown in Fig 2.4. From this figure, when La^{-3} is partially substituted by Sr^{-2} , its electrical conductivity is the largest whether B cation is Ga or Al. In addition, the optimum content of Sr dopant to obtain the highest conductivity is not reported. Several studies have reported the different suitable concentration of Sr dopant in range of 10 to 20 mole percent^(8,9). An inappropriate amount of Sr causes the formation of impurity phase such as La_4SrO_7 .

Undoped LaAlO_3 and Sr modified LaAlO_3 have lower electrical conductivity than that of LaGaO_3 . That may be caused by rather high tolerance factor (>1) of LaAlO_3 base compound⁽¹⁴⁾. Although many researchers studied on the electrical properties of divalent dopants on La and Al sites, the substitution of cation into both La and Al sites of LaAlO_3 has never been reported.

2.3.2 Ionic conductivity

High ionic conductivity usually occurs in solid electrolytes, superionic conductor or fast ionic conductor. The structural requirements for them suppose to have empty sites available for ions to hop into. In other word, vacancies should be created from either the dopants or atmosphere. Also the energy barrier for ion hopping between sites should be small enough to overcome. This strongly depends on non-stoichiometry of the composition. Oxygen ion conduction occurs in solid electrolyte of SOFC when cation is substituted with lower valency, resulting in the formation of oxygen vacancies. The equation for the ionic conductivity usually applied to doped oxide conductor, i.e. ⁽¹⁾

$$\sigma T = A \exp (-E_a/kT) \quad (2.5)$$

where σ is the ionic conductivity,
 T is the absolute temperature,
 E_a is the activation energy,
 k is Boltzmann constant and
 A is a pre-exponential constant.

From this equation, it is clear that in order to obtain high conductivities at low temperature, E_a should be minimum.

In general, the selected dopants can provide the higher ionic conductivity, depending on their concentration and type of cation. Although the numbers of oxygen vacancies increase with an addition of the dopant, the conductivity may decrease resulting from the present of second phase, if exceeding the limit of solid solution.

2.4 AC impedance spectroscopy

The ionic conductivity of polycrystalline ceramics depends on the microstructure. A complex impedance method is commonly used to determine the ionic conductivity of the materials. Fig 2.5 represents the resistance of grain interior (R_b), grain boundary (R_{gb}) and electrode-electrolyte interface (R_e) connecting in the series. Different regions of a ceramic sample are modeled by a resistance and a capacitance usually placed in parallel. From this figure, each parallel RC element gives rise to a semicircle (ideally) from which the component R and C values may be determined. R values are obtained from the intercepts on the z' axis. The high-frequency semicircle provide the bulk resistance; the intermediate-frequency semicircle provides the grain boundary resistance; and the low-frequency semicircle provides information on the oxygen ion transport at the electrodes. Usually R_e is rarely obtained due to the limitation of equipment. The conductivity of the grain boundary may vary depending on temperature so that the number and size of semicircles may vary with temperature

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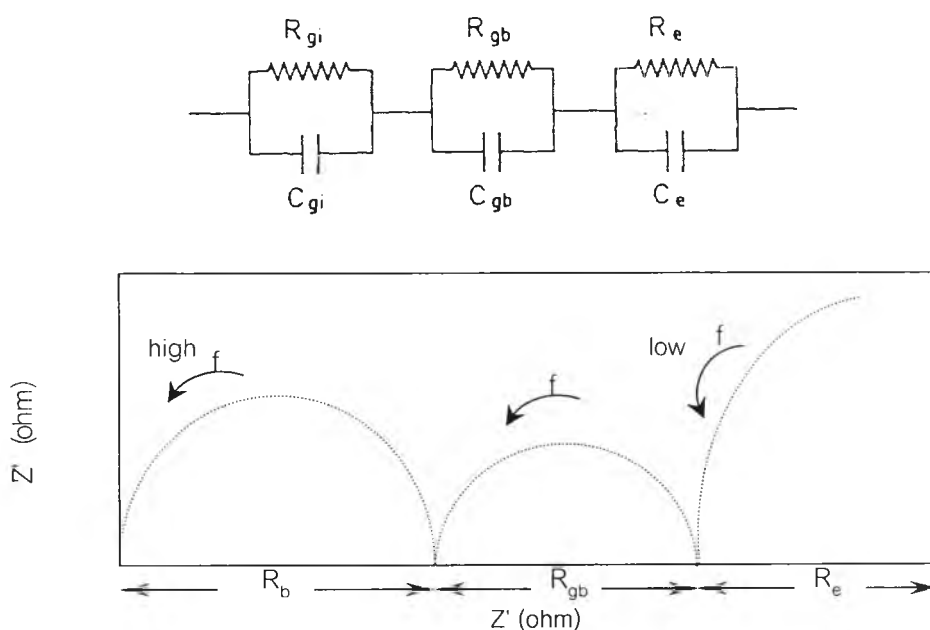


Fig 2.5 The AC impedance plot ⁽¹⁾