



Achievements in nanomaterials for solid oxide fuel cells for clean and sustainable energy

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Abstract

The energy need in the world is increasing each year, but the fossil fuel reserves that meet this need are decreasing much faster. Between 2030 and 2050, it is predicted that fossil fuel reserves will be depleted to a large extent or will not be able to meet the need. In addition, the accumulation of greenhouse gases in the atmosphere increases due to the continuous emission of gases namely CO₂, CO, CH₄, nitrogen oxides, and sulfur dioxide with the burning of fossil fuels. Due to all these economic and environmental factors, countries have turned to renewable energy sources in recent years. Hydrogen energy, which is one of the renewable energy sources, is preferred because it is more efficient than fossil fuels and is not harmful to the environment. Fuel cells convert a variety of fuels directly into electricity, including hydrogen, hydrocarbons and methanol. Solid oxide fuel cells (SOFC) have attracted much attention of researchers due to their fuel flexibility, high efficiency and good reaction kinetics. SOFCs, consisting of anode, cathode and electrolyte layers, show different performances depending on the type of each layer and the production conditions. The cathode electrode is the layer where oxygen is reduced. The cathode electrode must have high conductivity as well as high catalytic activity. The purpose of this study is to specify achievements in nanomaterials for cathode electrode.

Introduction

Fuel cells are new generation devices that allow electricity to be produced by an electrochemical reaction. It can basically continuously convert the chemical energy of a fuel and an oxidizer directly into electricity and heat [1]. Basically, the system has three main components: two electrodes (anode and cathode) with a porous structure and an electrolyte layer between these electrodes. A fuel cell is usually supplied with hydrogen gas as fuel from the anode section. On the other hand, from the cathode part, oxygen is supplied to the cell in the air. An electrical voltage is generated between within the electrodes, resulting from the chemical potential differences of hydrogen and oxygen. This voltage creates the electron transition from anode to cathode once the circuit is closed [2]. In general, fuel cells are assorted with respect to electrolyte type for instance, alkaline fuel cells (AFC), proton exchange membrane fuel cells (PEMFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) [3].

In SOFCs, dense electrolyte is placed between two porous anode and cathode electrolytes, forming a sandwich structure. When oxygen gas is supplied to the cathode the oxygen reduction reaction takes place in the cathode layer. When fuel gas is supplied to the anode, an electromotive force is created in the two layers. This force is used for producing power by connecting the electrodes with an external circuit [4]. Cathodes must have many properties such as high electronic and ionic conductivity, high catalytic activity for oxygen reduction, and compatibility with other cell components. Besides, the material used as cathode and the electrolyte material should not react at cell production and high operating temperatures.

SOFCs generally operate at 800-1000°C. These high operating temperatures cause chemical and microstructural deterioration in SOFC components in long-term use and thus decrease the performance over time [5]. As an approach to prevent these performance losses, the development of new materials that will not cause a significant performance loss at temperatures lower than 700°C, which is the medium temperature (IT) value, is considered. However, lowering the operating temperature will also slow down the ionic conductivity in the electrolyte and the kinetics of the reactions at the electrodes. As can be seen in Figure 1, especially the cathode polarization resistances will increase rapidly as the temperature decreases [6-7]. Therefore, achieving high SOFC performance at low temperatures depends on the development of cathodes that can show low polarization resistance at these temperatures. For this reason, this study focused on SOFC cathodes that can operate at low temperatures.

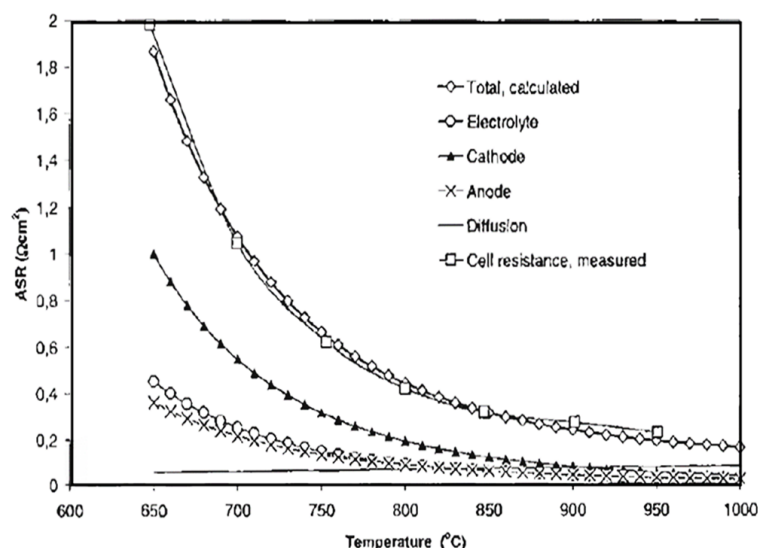


Figure 1. Polarization resistance variation graph in SOFC components [7]

Material and Method

Lanthanum strontium manganese oxide (LSM) perovskites are the most widely used cathode for SOFC application. It remains that the practical choice for operation is higher than 700°C. It is only possible to obtain high electrical conductivity, high electrochemical activity for the O₂ reduction reaction, high thermal stability and compatibility with electrolyte at high temperature for these cathode materials [8]. In many studies in the literature, different transition metals (Cr, Mn, Co, Fe, Ni) or their combinations have been substituted for B in the La_xSr_{1-x}BO₃ perovskite structure to obtain minimum ion transfer resistance and maximum electrical conduction. In Table 1, the electrical conductivity of the cathode materials is given which are developed for IT-SOFCs at different temperatures [9].

Table 1. Electrical conductivity of the cathode materials

Composition	σ_e/Scm^{-1}		
	900 °C	800 °C	600 °C
LaCoO _{3-δ}	1259	1122	1000
La _{0.8} Sr _{0.2} CoO _{3-δ}	1125	1221	1375
La _{0.8} Sr _{0.2} FeO _{3-δ}	84	87	90
LaCo _{0.2} Fe _{0.8} O _{3-δ}	9	4.2	
La _{0.8} Sr _{0.2} Co _{0.8} Fe _{0.2} O _{3-δ}	945	1000	1050
La _{0.8} Sr _{0.2} Co _{0.2} Fe _{0.8} O _{3-δ}	210	280	332

Since LSC cathode material show high electronic conductivity, it is promising to be used instead of LSM. However, the widespread use of this cathode is restricted because LSC reacts with the commonly used YSZ electrolyte, its thermal expansion coefficient is not compatible with YSZ, and it is toxic and expensive [10-11]. As seen in Table 1, LSCF has a high electrical conductivity (1050 Scm⁻¹ at 600 °C). This is much higher than the aforementioned LSM materials (~420 Scm⁻¹ at 600 °C).

Various synthesis methods can be used to produce nanostructure perovskite oxides. The synthesis parameters; chemical stoichiometry, temperature and etc. are important to improve the properties of cathode materials. Combustion, sol-gel, co-precipitation, solid-state reaction and mechanical alloying are some of the methods generally used. In the solid state reaction, the determined substance amounts are weighed after the necessary molar calculations are made. The weighed starting raw materials are regularly ground for a certain period of time in an agate mortar at room temperature to obtain a homogeneous mixture. The grinded mixture is placed in a platinum crucible and placed in the ash furnace. Annealing is carried out at the appropriate temperature and time. Solid state synthesis method has an advantage to increase the yield with reduced costs. Besides, it also decreases the amount of chemical wastes [12].

Discussion

This study focuses on the new generation nanostructured cathode materials and their production methods for IT-SOFCs. The cathode layer used in SOFCs is generally ABO_3 perovskite structure containing trivalent transition metal ions in the B region and a trivalent rare earth in the A region. LSM is used in commercial applications. However, corrosion and deterioration problems are seen due to its use at high temperatures. In the literature, there are intensive studies on the cathode material that can operate with higher performance at temperatures below 700 °C. Some of these studies are on synthesizing new cathode materials with alternative combinations in regions A and B as A (*La, Sr, Ca*) and B (*Cr, Mn, Co, Fe, Ni*) O_3 . Some studies are on synthesizing nano-structured cathode material by making changes in production methods or parameters. It is concluded that nanostructured LSCF cathode material shows promise in IT-SOFC applications.

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