

Solid Oxide Fuel Cells Materials and Prospects

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Abstract: The paper summarizes and discusses the basic properties of solid oxide fuel cell (SOFC) components (electrode materials and electrolyte) from the point of view of their essential functional parameters such as chemical stability, transport, catalytic and thermomechanical properties under operational conditions in a SOFC. An interrelation between the defect structure of these materials related to oxygen nonstoichiometry and their electronic properties and catalytic activity was shown. Single-chamber fuel cell concept was also presented.

Key words: Solid oxide fuel cells, SOFC, Electrode materials, Electrolyte

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1 Introduction

The fuel cell technology, due to the possibility of direct conversion of energy stored in the hydrogen-containing fuels into electrical energy, becomes very attractive alternative to traditional heat engines. The relatively simple construction of a fuel cell and high efficiency of electricity generation, noise-free operation due to a lack of mobile parts, a low level of waste products make this technology to be the most prospective for future electrical energy sources. The rate of charging (fuel refill) and the potential reversibility of this process (storage of instantaneous energy excess in the form of chemical energy) are the additional benefits. In the large group of fuel cells special attention is paid to the Solid Oxide Fuel Cells (SOFC)^[1-4]. Their commercial importance is connected with the construction of stationary generators with the power of at least 1 MW.

Wide application of this technology is hindered by some properties of the electrode materials and the electrolyte as well as the high-temperature reaction conditions. The presently used yttrium-stabilized zirconia (YSZ) with a low ionic conductivity must oper-

ate at about 1 000 °C. This implies short service life of the cell (thermal degradation of materials) and requires expensive and toxic materials, like LaCrO₃, for interconnectors, raises problems with miniaturization and safety and increases the costs. Lowering of service temperature to 600 °C, considered as a strategic goal for the technological development of the SOFC's, calls for the application of a suitable solid electrolyte, which at that temperature would have purely ionic conductivity of 10⁻² Scm⁻¹ and would be stable within the oxygen pressure range 10⁵ ~ 10⁻¹⁵ Pa.

2 Electrical, Catalytic and Thermomechanical Properties of Materials used in SOFC

In Fig 1 the structure and functions of the basic SOFC components are schematically presented. Some different aspects must be considered in the functioning of each component of the whole system (i.e., transport and catalytic properties as well as structural and thermomechanical properties).

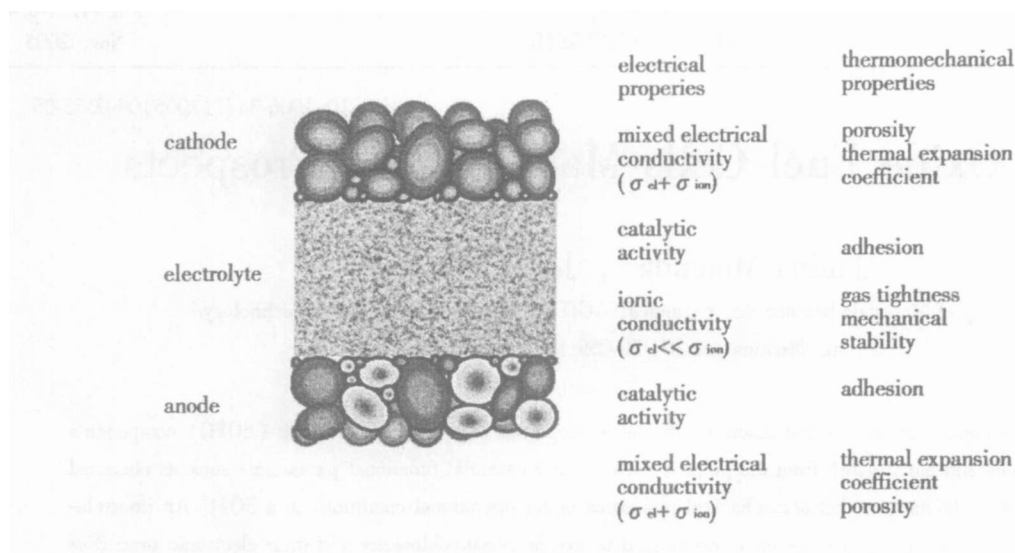


Fig 1 The structure of a SOFC cell and required electrical and thermomechanical properties of its components

2.1 Transport and Catalytic Properties

The cathode made of LiMeO_3 type oxides (Me = Mn, Fe, Co, Ni) with a perovskite structure is a mixed ionic-electronic conductor. The ionic conductivity is related to oxygen nonstoichiometry (oxygen vacancies), while the electronic conductivity to the mixed valency of cations, $\text{Me}^{3+}/\text{Me}^{4+}$, and depends on the extent of oxygen nonstoichiometry and the amount and type of dopants. The cathode material plays a role of a catalyst for the reduction of oxygen. As it operates in air or in oxygen, the stability of the oxides is not a problem.

The solid electrolyte (YSZ, $\text{CeO}_2(\text{Gd}, \text{Sm})$) as a purely ionic conductor with oxygen vacancies as carriers, is stable over a wide range of oxygen pressures ($10^5 \sim 10^{-15}$ Pa), because near the cathode it operates in the highly oxidizing conditions and near the anode (fuel supply) in highly reducing conditions. The ionic conductivity at the service temperature should be about $10^{-2} \text{ S} \cdot \text{cm}^{-1}$. So far, no real system has been found to satisfy both mentioned requirements.

The anode (Ni/YSZ or $\text{Ni}/\text{CeO}_2(\text{Gd}, \text{Sm})$ cermet) is an ionic-electronic conductor. Its ionic conductivity is related to oxygen vacancies in YSZ or in $\text{CeO}_2(\text{Gd}, \text{Sm})$. The electronic conductivity results

from the existence of a conductive percolation path at 30% Ni concentration in the anode material. Nickel catalyzes the oxidation of fuel. The highly reducing atmosphere is not detrimental for the anode material, furthermore it improves its effectiveness (maintains the catalytic activity of nickel and raises the electrical conductivity of CeO_2).

2.2 Structural and Thermomechanical Properties

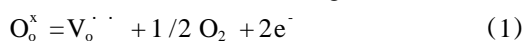
The cathode and anode materials should be porous to allow penetration of gases. However, in the layers close to the electrolyte, porosity should be possibly low to intensify the lattice diffusion of oxygen. Electrolyte is a gas-tight sinter with high strength preventing non-productive combustion of the fuel. All the cell components should be chemically and thermally compatible.

3 Electrolytes in IT-SOFC (IT-intermediate Temperature)

It seems that some improvements of the properties of solid electrolyte based on ZrO_2 are still technologically feasible. This especially refers to electrical conductivity, which might be increased by doping. It has been shown^[5] that scandium dopant in zirconia can raise the conductivity by two orders of magnitude,

but the scarce occurrence in the earth crust and high price exclude this element from practical applications. Another possibility of improving the electrical conductivity of zirconia-base electrolyte is to develop the technology of thicker than 1 mm, gas-tight YSZ layers, and to modify the microstructure of zirconia (nanocrystalline layers, dispersed composite electrolyte $Y_2O_3-ZrO_2-Al_2O_3$ ^[6,7]). Electrolytes based on bismuth oxide, Bi_2O_3 , exhibit high ionic conductivity but they undergo reduction to metallic bismuth at low pressures of oxygen. Investigation were also doing for some oxides with the perovskite structure showing proton conductivity (e.g. $SrCe_{0.95}Yb_{0.05}O_{3-y}$, $CaZr_{0.96}Y_{0.04}O_{3-y}$ ^[8]).

Among many oxide conductors studied, cerium dioxide, CeO_2 , stabilized with the rare-earth oxides (i.e. samarium or gadolinium) is mostly quoted as a candidate for IT-SOFC. This electrolyte has the electrical conductivity higher and the activation energy of conductivity lower than the ZrO_2 -based electrolyte. The $Ce_{0.8}Sm_{0.2}O_2$ solid electrolytes (referred to as SDC) and $Ce_{0.9}Gd_{0.1}O_2$ (GDC) have, so far, the highest oxide-ion conductivity reaching about $10^{-1} S \cdot cm^{-1}$ at 800 °C^[9]. An important benefit of the CeO_2 base electrolytes compared to ZrO_2 is their chemical and thermal compatibility with the new generation of the cathode materials, $LaMO_3$ ($M = Mn, Co, Fe, Ni$), with a perovskite structure and thermal expansion coefficient very close to that of interconnectors made of high-chromium ferritic steels. The most troublesome deficiency of the electrolyte based on CeO_2 in commercial use is that its oxygen nonstoichiometry increases at high temperatures and low oxygen pressures, $p_{O_2} < 10^{-9}$ Pa (reducing conditions near the anode), which gives rise to an undesirable electronic conduction related to the following reaction:

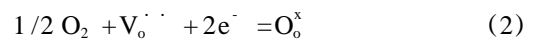


The elimination of electronic conduction and widening of the oxygen pressure range to 10^{-15} Pa, where the transport number of oxygen ions equals 1, remains one of the essential problems to be solved. This can be done by doping of the cerium sublattice with selected ions having valency different from that of

cerium. A challenging task for the solid state chemistry is to assess the interrelations between the types of point defects connected with oxygen nonstoichiometry and foreign atoms of dopants, their concentrations, crystal structure and transport properties.

4 Cathode Materials in IT-SOFC

The cathode materials in IT-SOFC must satisfy the following requirements: mixed ionic-electronic conductivity, thermal and chemical stability at high temperatures in air and good chemical and thermo-mechanical compatibility with the electrolyte. The cathode material also plays a role of a catalyst in the reduction of oxygen:



The mixed ionic-electronic conductivity and the significant open porosity enable oxygen reduction not only on the surface but in the whole volume of the electrode.

The candidate materials for the cathodes in IT-SOFC are searched in two groups of compounds with perovskite structures: $Ln_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (where: $Ln = La, Sm, Nd, Gd, Dy$) - referred to as LSCF and $Ln_{1-x}A_xM_{1-y}Mn_yO_3$ (where: $Ln = La, Nd, Pr, A = Ca, Sr$; $M = 3d$ metal other than manganese)^[10-11]. Recently also compounds like $(La, Sr)Ni_{1-y}Fe_yO_3$ ^[12] or $LaNi_{1-y}Co_yO_3$ ^[13] are under investigation.

The basic problem concerning the $LaMO_3$ ($M = Mn, Fe, Co, Ni$) cathode materials is insufficient rate of the oxygen-ion transport at 600 °C. Moreover, depending on oxygen partial pressure, the type of dominating defects may change from oxygen excess ($LaMO_{3+y}$) to oxygen deficiency ($LaMO_{3-y}$). For the cathode material the most advantageous defects are oxygen vacancies. However, these defects are often formed at oxygen partial pressures $p_{O_2} < 10^2 \sim 10$ Pa, while the cathode operates in air. One of the important research tasks is to shift the stability range of oxygen vacancies to higher oxygen pressures (2.1×10^4 Pa). It has been reported^[4] that strontium-doped (50%) $La_{1-x}Sr_xMnO_3$ changes the conduction mechanism at high temperatures from the small polaron mechanism to the metallic conduction, which

is a very desirable behavior in SOFC. Metallic conduction can be obtained also in the group of oxides with the formulas: $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ^[14].

Recently, oxides with the perovskite structure have been a subject of extensive studies^[15, 16] but the main research activities concentrate on useful properties, i.e. a possible application of these materials as cathodes in SOFC. Fundamental studies that might contribute to better understanding of relations between crystallographic structure, ionic and electronic defects resulting from nonstoichiometry, doping level, electronic structure and transport properties or reactivity of perovskite oxides versus oxygen are lacking. These issues are still of a great importance. It has been found^[4] that kinetics of the cathode reaction (oxygen reduction) may restrict the electrochemical effectiveness of SOFC. The process of catalytic reduction of oxygen on perovskites is not yet sufficiently clarified. It is known that the rate of oxygen absorption by the cathode material depends on both the concentration of oxygen vacancies and quasi-free electrons in the cathode material. Oxygen vacancies are donor centers, which provide the quasi-free electrons on ionization. So, the oxygen nonstoichiometry and foreign dopants affect the location of the Fermi level in the cathode material^[17], which according to Volkenstein's theory controls the catalytic activity of the cathode material. The extent of oxygen nonstoichiometry (dependent on the synthesis conditions, i.e. temperature and oxygen pressure) as well as the type and concentration of dopant (which also affects the oxygen nonstoichiometry)^[18, 19] can control the Fermi level and the catalytic activity of the cathode material.

5 Anode Materials in IT-SOFC

The anode material in the high-temperature SOFC is Ni/YSZ cement whereas in IT-SOFC it is Ni/CeO₂ (Sm, Gd)^[20]. The anode material, similarly as the cathode material should be an ionic-electronic conductor. The ionic conductivity is associated with the oxygen ion transport via oxygen vacancies in YSZ or in CeO₂ (Sm, Gd). The electronic conductivity

originates from the presence of metallic nickel in the anode material. For a nickel concentration of 30% a percolation path is formed, which manifests itself by macroscopic metallic properties of the anode material. The metallic nickel additionally plays a role of a catalyst in the oxidation of fuel.

Investigations of the Ni/YSZ system under the operating conditions of the cell^[21] indicate that the optimization of its microstructure is necessary. Current flow brings about nickel agglomeration in the anode/electrode system, which to a significant extent lowers the electrochemical efficiency of the anode.

6 Single-chamber Cell Concept

The concept of a single-chamber cell, a new and very promising one, put forward by Hibino^[22-24], overcomes many difficult problems unresolved so far. In this cell the cathode and the anode, both with selective electrocatalytic properties for oxygen and hydrogen, respectively, are mounted in a common space filled with a mixture of fuel and oxidant. The electrocatalytic properties of the anode in this system must be sufficient to eliminate the need of preliminary conversion of the natural fuel. The ionic current in the cell depends on a difference between the catalytic activities of the electrodes. It becomes pointless to separate the gases around the anode and cathode (simple design of batteries). The electrolyte can be porous and permeable for gases, which eliminates the technologically difficult problems connected with the manufacturing of thin plates of ceramic electrolytes with high strength. As the oxygen pressure in the reaction chamber of this cell is relatively high (fuel/air mixture) compared to the oxygen pressure in the anode space of the classical cell, the instability of some oxide electrolytes, which have competitively high electrical conductivity (e.g. bismuth oxide) is no more a problem. The optimum operating temperature of a single-chamber cell is 600°C, for higher temperatures both electrodes catalyze non-productive combustion of the fuel. It should be stressed that the materials earlier selected for characterization and application in the classical IT-SOFC, electrolytes

(based on CeO_2) and electrode materials (cathode based on the perovskite type oxides LnMO_3 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$), anode- Ni/CeO_2 (Gd) cement), are also suitable for the single-chamber cells. In the development of materials for the single-chamber cells, special attention should be paid to the catalytic selectivity and activity of both electrodes.

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固体氧化物燃料电池 —— 材料与前瞻

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摘要: 本文依据固体氧化物燃料电池 (SOFC) 于运作条件下的基本性能, 诸如化学稳定性、电迁移、催化和热机械性能等评述 SOFC 组成部分 (电极材料和电解质) 的基本性质. 示明由氧偏离化学计量比引起的电极材料结构缺陷与其电子性质及催化活性之间的相互关系, 提出单室燃料电池概念.

关键词: 固体氧化物燃料电池; SOFC; 电极材料; 电解质