Principles and applications of high temperature ion conducting ceramic in power generation - fuel cells and oxygen membranes

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Abstract

High temperature membranes can be used in numerous applications including ceramic filters, selective sieves, removal of impurities, oxygen and hydrogen separation, electrochemical devices such as solid oxide fuel cells and solid oxide electrolysers. The fabrication process is oriented at achieving desired properties of the final product, including proper conductivity, size and density of pores, tortuosity, mechanical stability in high operating temperatures and others. Among the mentioned applications, solid oxide fuel cells and oxygen separation membranes represent materials with mixed ionic and electronic conductivity (MIEC) which will be further discussed in the lecture. Such material are often referred as membranes designed specifically for transport of ions and electrons.

Keywords: high temperature membranes, solid oxide fuel cells, oxygen transport membranes

1. Solid oxide fuel cells

The general concept of a fuel cell has been known since year 1838 when Christian Friedrich Schönbein described the principles of operation in Philosophical Magazine [1]. Based on this publication, the first unit was constructed and reported (Fig. 1) by Sir William Robert Grove in 1839 [2], and later referred as a gaseous voltaic battery [3]. In 1887 Walther Hermann Nernst proposed the mathematical description of a fuel cell governing laws [4] in a form known today as the Nernst equation (discussed later).

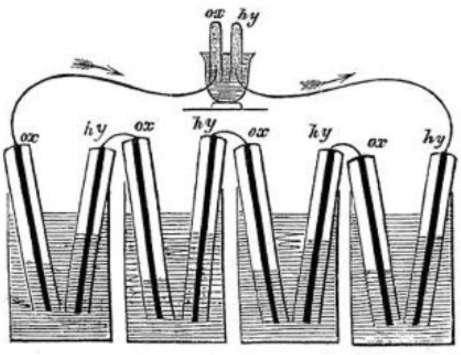

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Fig. 1 The very first scheme of a fuel cell by Grove (1839).

Over the years, different types of fuel cells emerged including so-called high temperature fuel cells which employ solid oxide electrolyte separating the positive and negative electrode (SOFC). These fuel cells are made of ceramic materials, and the operating principle correspond to the transport through ceramic membranes.

Solid oxide electrolytes make one of the three key layers of a fuels cells, and are in fact the ceramic membranes which are engineered to allow for efficient transport of ions. The working principle of a solid oxide fuel cell is shown in Fig. 2

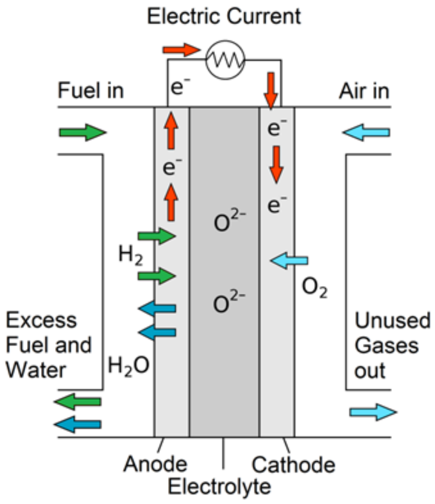

Fig. 2 Working principle of a solid oxide fuel cell

1.1 Principles of SOFC

The main difference between a fuel cell and the thermodynamic Carno cycle is the fact that an electrochemical device such as fuel cell directly converts chemical energy of fuel into electricity. Fuel cell operates continuously as long as the fuel and oxidant are supplied to the anode and the cathode, respectively. In the simplest configuration, fuel cell comprises three layers, the anode and cathode separated by electrolyte (Fig. 3).

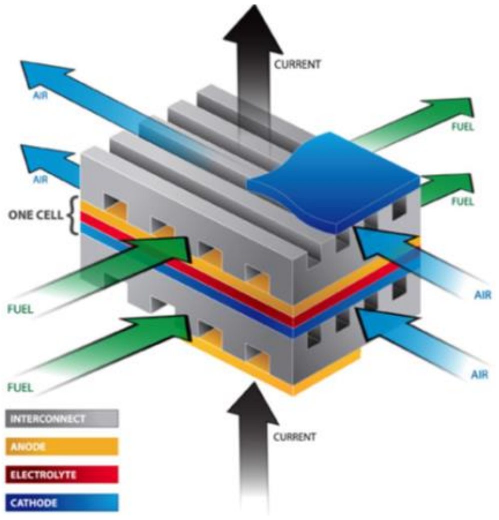

Fig.3 Simple scheme showing design of planar cross-flow SOFC. Source: NETL [5]

Oxidation of fuel takes place at the anode, while reduction occurs at the cathode.

During operation of a fuel cell, different irreversible losses occur. There are three phenomena responsible for these voltage losses often called the overpotentials or polarizations, namely:

- activation polarization η_a
- ohmic polarization η_{ohm}
- concentration polarization η_C

Activation polarization is related to the activation energy of the electrochemical reactions at the electrodes. It depends on the electro-catalyst material and microstructure, reactant activities, and weakly on the current density.

Ohmic losses are caused by ionic resistance in the electrolyte and electrodes, electronic resistance in the electrodes, current collectors and interconnects, and contact resistances. Ohmic losses are proportional to the current density, depend on materials selection, cell geometry, and on temperature.

Concentration polarization results from finite mass transport limitations rates of the reactants and depend strongly on the current density, reactant activity, and electrode structure [6]. The three overpotentials are defined by the material properties of the membranes making the fuel cell.

Actual cell voltage E_{SOFC} corresponds to the theoretical thermodynamic voltage of an open cell E_{OCV} reduced by the mentioned losses:

$$E_{SOFC} = E_{OCV} - \eta_a - \eta_{ohm} - \eta_C \qquad (1)$$

This can be graphically presented by comparing the ideal cell exhibiting no losses with the real cell (Fig. 4).

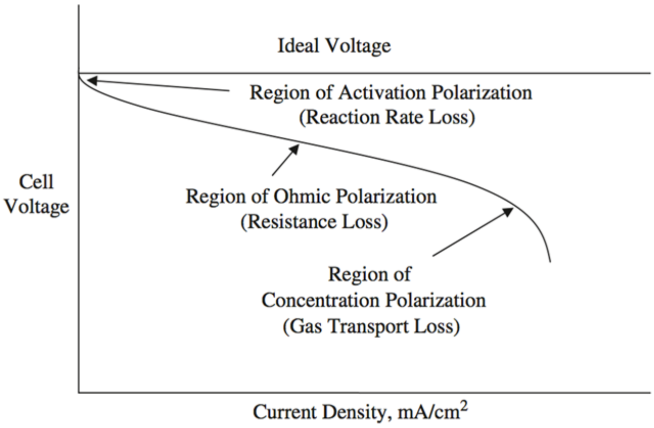

Fig. 4 Ideal and real fuel cell characteristics

Ideal voltage (usually referred as open circuit voltage or OCV) can be calculated using Nernst equation, which for hydrogen-fuelled cell can be written in the form [7]:

$$E_{OCV,H2} = \frac{1}{2}\left[\Delta G(T) + RT\ln\frac{p_{H_2}\cdot p_{O_2}{}^{1/2}}{p_{H_2O}}\right] \qquad (2)$$

Overpotentials can be found according to the following equations [8]:

$$\eta_a = \left(\frac{RT}{n\alpha_a F}\right)\ln\left(\frac{j}{j_{0a}}\right) - \left(\frac{RT}{n\alpha_c F}\right)\ln\left(\frac{j}{j_{0c}}\right) \qquad (3)$$

$$\eta_{ohm} = j \cdot ASR_{ohm} \qquad (4)$$

$$\eta_C = c\ln\frac{j_L}{j_L - j} \text{ while } c = \frac{RT}{nF}\left(1 + \frac{1}{\alpha_i}\right) \qquad (5)$$

where α_a and α_c are the charge transfer coefficients of reactions occurring on the anode and cathode, respectively. Constant c is calculated using the limiting current density j_L. R is the universal gas constant of 8.3145 J K^{-1} mol^{-1}, n is the number of electrons taking part in an electrochemical reaction, F is the Faraday's constant of 96485 C mol^{-1}, j - net cell current and j_{0a}, j_{0c} - the anode and cathode exchange current densities, respectively. According to equation (2) temperature and partial pressures of oxidant and fuel have strong effect on the cell voltage.

The main advantage of SOFC is the widely discussed fuel flexibility. Possibility of generating hydrogen rich gas from different fuels was extensively studied for different resources including natural gas, biogas, different hydrocarbons [9,10] carbon monoxide [9], DME, and other fuels like jet oil (or JP-8) [10]. For a reference hydrogen fuel, electrochemical reactions of a solid oxide fuel cell are the following: at the anode of SOFC:

$$H_2 + 2O_2{}^- \rightarrow 2H_2O + 4e^- \qquad (6)$$

and at the cathode of SOFC:

$$O_2 + 4e^- \rightarrow 2O_2{}^- \qquad (7)$$

hence, the overall cell reaction is:

$$O_2 + 2H_2 \rightarrow 2H_2O \qquad (8)$$

1.2 Fully functional solid oxide fuel cells

A fuel cell presented in section 1.2 in fact requires several additional layers to create a fully functional electrochemical device. The added components are the contact and protective layers, gaskets (or sealing), current collectors, and others. Depending of the materials selected for the key functional layers, including the membrane making the electrolyte, alternative configurations are realized. In principle, thin ceramic membranes are exposed to high operating temperature (typically above 700°C), complex gas mixtures, pressure gradients, and fluctuations of the three earlier mentioned parameters. For that reason one layer is selected as a so-called support, providing the mechanical stability during steady-state and dynamic operation. The support layer is usually the thickest and in case of the planar SOFC either the electrolyte, anode or cathode can be chosen. Optionally, a metallic support can be introduced. All four options are presented in Fig. 5. Additionally, other designs are developed, including metallic supported cells, and thin films based on thin substrates. Schematic drawings of all types of supports are presented.

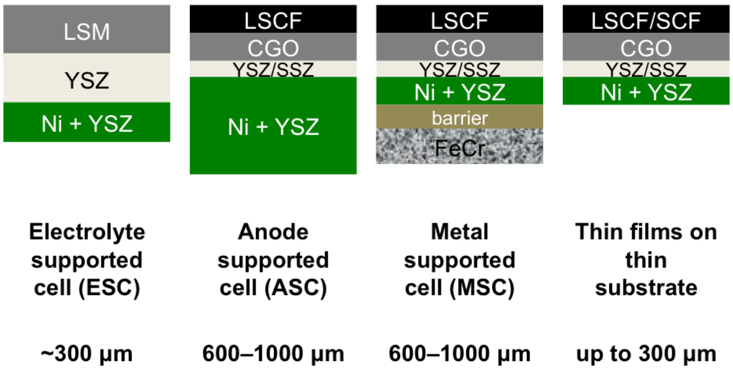

Fig. 5 Comparison of four types of solid oxide fuel cell supports. Based on [11]

Typical materials used in configurations shown in Fig. 5 are presented in Table 1.

Table 1. Summary of materials for alternative supports in SOFC [12]

Type of support	**Electrolyte**	**Electrodes**	**Operating temperature [°C]**
ES-SOFC	Solid ceramic: $Zr(Y, Sc, Ca)O_2Ce(Gd, Sm)O_2$	Anode- $NiO + Zr(Y, Sc, Ca)O_2$, $Ce(Gd, Sm)O_2$ Cathode- perovskite material (La,Sr,Mn,O)	900 - 1000
AS-SOFC			600 - 800
CS-SOFC			
MS-SOFC			600 - 800

Beside the type of support, SOFCs can be fabricated as rectangular, square and circular cells of different dimensions. Rectangular cells are shown in Fig. 6 and 7.

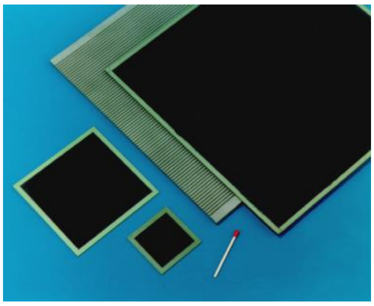

Fig. 6 Planar solid oxide fuel cells with area up to 20 x 20 cm^2 [11]

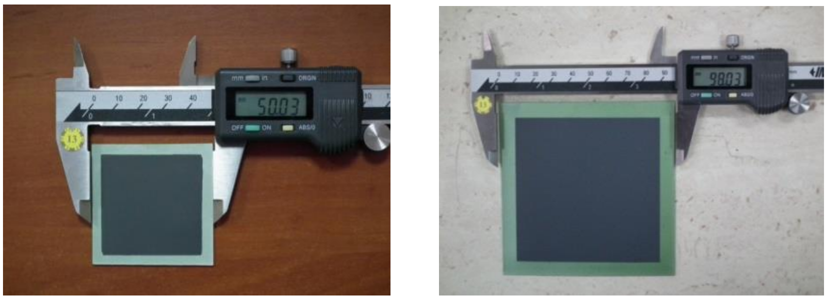

Fig. 7 Square SOFC cells fabricated in the Ceramic Department (CEREL) of the Institute of Power Engineering: 50 cm x 50 cm (left) and 100 mm x 100 mm (right) [13]

Optimization of the materials, manufacturing methods, geometries and working conditions is done using several experimental and numerical techniques which have to address multiple processes taking place during operation of a solid oxide fuel cells.

1.3 Degradation of fuel cells

Solid oxide fuel cells offer a great promise as highly efficient energy conversion devices with significant environmental benefits. Regrettably, fragile ceramic materials making the cell and stack are prone to performance degradation. Stability of fuel cells is a limiting factor in their market penetration, with the required reliability and lifetime of at least 40 000 hours for stationary applications. Cell performance can be deteriorated in number of different ways. Among those, effects of impurities, rupture of the structure, and formation of compounds limiting electrochemical reaction are the mostly evident. Combination of two or three of listed phenomena can also occur leading to even faster drop of a cell performance. Degradation mechanisms recently observed, include the decrease of the intrinsic electrical conductivity of the electrolyte [15], coarsening of nickel particles, formation and deposition of carbon and other compounds in the anode compartments [16,17]. Moreover, increase of cathode-electrolyte and cathode-current collector interface resistivity can be a major issue [18-20].

2. Oxygen separation membranes

Among several competing technologies, cryogenic process, mixed ionic electronic conducting membranes (MIEC) and oxygen enriched air membranes (OEA), such as polymeric membranes, are consider to be the most promising. The permeation selectivity of over 20 (O_2 over N_2) is targeted for a membrane based approach to become competitive with cryogenic techniques for hybrid CO_2 capture systems [21]. The MIEC membranes offer close to 100% pure oxygen steam. The choice of a specific membrane composition depends on the membrane design architecture and operating conditions of the membrane [22]. The over 20 years progress in development of ceramic membranes for oxygen separation from air is targeting replacement of the energy intensive, conventional air separation technologies [23]. The chemical and physical stability of the membrane and high permeation rates of oxygen are the most important selection factors.

2.1 Most commonly used oxygen transport membranes

Dense and thick ceramic MIEC membranes, such as LSCF and BSCF perovskites, exhibiting oxygen permeation of over 2.5 Nml/(cm^2 min) at 1123K [24], are currently considered as candidates for the oxy-combustion process. A significant potential for the order of magnitude increase in the O_2 permeation rates has already been shown, using porous support and thin membrane approach [25]. Typical OTM membranes, such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF), $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) have limitations for the operation under large O_2 chemical potential gradients and in contact with CO_2/H_2O atmosphere. Alternative membrane materials such as $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (CGO) are investigated, showing up to a 100-fold increase in the O_2 permeation rate when methane-rich fuel stream is supplied to the permeate side of the membrane [27].

In general, dense ceramic membranes are often considered as a potential source of high purity (over 99.5%) oxygen. Membranes made of BSCF perovskites are mixed ionic and electronic conductors [28]. They operate at elevated temperature, often exceeding 800°C [29]. Oxygen permeation for a circular membrane is defined by Eq. 9, which correlates oxygen permeation rate J_{O2}[Nml cm^{-2} min^{-1}] with ionic and electronic conductivities (σ_i *and* σ_e), Faraday's constant (F), universal gas constant (R), characteristic and actual thickness (L_C and L), diameter (d), operating temperature (T) and partial pressure of oxygen in the feed and permeate sides:

$$J_{O_2} = -\frac{1}{1+\left(\frac{2L_C}{L}\right)}\frac{RT}{4F^2L}\int_{\ln p^{I}_{O_2}}^{\ln p^{II}_{O_2}}\frac{\sigma_{el}\sigma_i}{\sigma_{el}+\sigma_i}\,d\ln\left(p_{O_2}\right) \qquad (9)$$

Formula 9 is known as the modified Wagner equation.

For the BSCF perovskites which exhibit much larger electronic than ionic conductivity equation (9) reduces to equation (10).

$$J_{O_2} = -\frac{1}{1+\left(\frac{2L_C}{L}\right)}\frac{RT}{4F^2L}\int_{\ln p_{O_2}^{I}}^{\ln p_{O_2}^{II}} \sigma_i \, d\ln\left(p_{O_2}\right) \qquad (10)$$

For the purpose of system-level studies, oxygen permeation can be expressed in a simplified form:

$$J_{O_2} = \frac{\sigma_i RT}{16LF^2}\ln\left(\frac{p_{O_2}^{I}}{p_{O_2}^{II}}\right) \qquad (11)$$

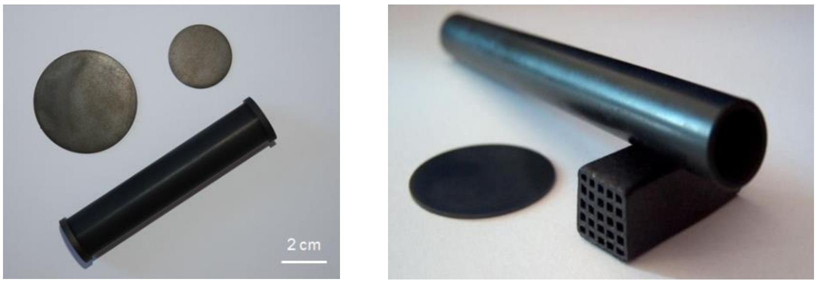

Fig. 8 Planar (circular), tubular and monolithic BSCF membranes fabricated by Institute of Power Engineering, Ceramic Department CEREL

Examples of dense circular, tubular and monolithic BSCF membranes fabricated by Ceramic Department (CEREL) of the Institute of Power Engineering are shown in Fig. 8.

A key parameter determining the applicability of oxygen transport membranes is the oxygen permeation rate. According to eq. (9), the permeation rate is correlated to the temperature and logarithm of the parti of partial pressure of oxygen in the feed and permeate sides. A pictorial representation of this relation is shown in Fig. 9.

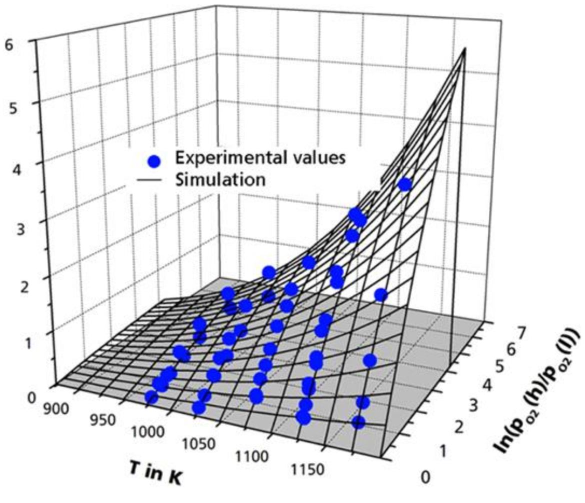

Fig. 9 Oxygen permeation rate as a function of temperature and partial pressure of oxgygen. Source: Fraunhofer IKTS

2.2 Selected applications of oxygen transport membranes

Currently discussed applications of oxygen transport membranes include stand-alone generation of high purity oxygen in for various processes [30], oxy-combustors in which the membrane is embedded in the combustion zone and various power systems in which either enriched air (with more than 21 mol-% O_2) or oxy-combustion is realized. Such systems offer several advantages and are mostly considered in carbon capture and sequestration (CCS) systems or so-called CCS-ready systems in which elimination of N_2 from the oxidant stream enables high concentration of CO_2 in the exhaust gases to allow for alternative methods for fixation of carbon dioxide. Numerous such concepts were evaluated for large and micro-power units [31].

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