Lanthanum Chromite as an Anode Material for Solid Oxide Fuel Cells

P. Vernoux
Laboratoire d'Electrochimie et de Physicochimie des Matériaux et des Interfaces (INPG, UJF and CNRS), F-38402 St. Martin d'Hères Cedex, France

Abstract. The electrochemical behavior of pure lanthanum chromite and strontium doped-lanthanum chromite was studied by impedance spectroscopy under H2/H2O, CO/CO2, and CH4/H2O. Results show that the electrochemical oxidation of H2 is faster than that of CO or CH4. Strontium doping enhances the anodic activity of the material.

The impedance diagrams are composed of two semi-circles. The high frequency one does not appear to be related to a chemical or electrochemical reaction. The low frequency one is linked to the nature and concentration of the electroactive species.

1. Introduction

Solid oxide fuel cells (SOFC's) show great promises for the production of electricity from natural gas. A major drawback of these fuel cells is the reformer which is costly and voluminous. It can be eliminated by internal reforming. Recent pre-industrial applications exhibit good performances at 1000 °C with YSZ (Yttria Stabilized Zirconia) as an electrolyte, LSM (Lanthanum Strontium Manganite) as a cathode and a Ni-YSZ cermet as an anode. With such an anode, a high water content in the fuel gas (with H2O/CH4 ratio close to 4) is necessary to avoid carbon deposition [1 - 4]. The handling of these large quantities of water is costly.

To overcome these difficulties, we are working only with materials which are not prone to cracking. The idea is to use an anode material for the hydrogen electrochemical oxidation and a catalyst material which will be coated on or impregnated in the first material for the reforming of methane.

We have selected lanthanum chromite LaCrO3 as an anode material because its compatibility with the SOFC operating conditions has already been demonstrated as interconnect material [5,6]. Lanthanum chromite shows a good chemical stability under reducing atmosphere and has a reasonable compatibility with YSZ. We have already demonstrated that lanthanum chromite is quite inert for the carbon deposition [7]. It is also inert for the steam reforming, even at 800 °C [7].

As a catalyst, ruthenium appears to be very effective. Ruthenium coated on lanthanum chromite is able to convert methane at 700 °C even with a ratio H2O/CH4 as low as 0.1 without carbon deposition [7]. When the H2O/CH4 ratio is smaller than 1, full conversion of steam is obtained.

The electrochemical behaviors of lanthanum chromite under different anodic atmospheres: H2/H2O, CO/CO2 and CH4/H2O are reported here.

The reaction rates of the electrochemical oxidation of hydrogen (H2 + O2 \rightarrow H2O + 2 e-) on different anode materials at elevated temperature have already been measured by Schouler and Isaacs [8]. The author gave the following quality order: Fe > Co > Ni > Mo > LaCrO3. Thus, lanthanum chromite appears to be a relatively poor electrocatalyst. Recently, Baker et al. [9] shows that potential anode materials exhibit fairly similar characteristic performances, in contrast to the cathode materials.

Mogensen and Lindegaard [16] have investigated the H2/H2O electrode reaction on a Ni/YSZ cermet at 1000 °C by impedance spectroscopy. They decomposed the diagram into two semi-circles. The high frequency one is assumed to be due to the proton transfer from Ni to YSZ (H+ad.Ni + O2-ysz \leftrightarrow OH-ysz) and the low frequency one to a
chemical reaction \(2 \text{OH}_{\text{YSZ}} \leftrightarrow \text{H}_2\text{O} + \text{O}^{2-}_{\text{YSZ}}\).

Impedance diagrams of ball shaped Ni electrode, reported by Guindet et al. [17], also show two arcs.

The reaction rates of the electrochemical oxidation of carbon monoxide \((\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{e}^-)\) measured on Ni-YSZ cermet [11] and Pt-electrodes with CeO\(_2\) [10] are slower than the \(\text{H}_2\text{O}\) reaction.

Studies [11,12] carried out on a Ni/YSZ cermet, under \(\text{CH}_4/\text{H}_2\text{O}\), were not conclusive because Ni acts as a cracking catalyst; carbon deposition gradually blocks the nickel electrocatalytic activity.

2. Experimental Aspects

We worked with cone-shaped micro-electrodes. Such micro-electrodes are gently pressed into contact with the surface of the solid electrolyte pellet under light weight (\(\approx 200\) g). This technique allows to minimise the influence of the electrode microstructure.

The rig we used is equipped with a temperature controlled gas humidifier. In the electrochemical cell (Fig. 1), three micro-electrodes can be studied simultaneously (and support the electrolyte pellet). Reference and auxiliary electrodes coated on the other side of the electrolyte pellet were made of platinum.

Except for steam, the gas compositions were controlled by mass flow meters (Brooks, accuracies better than 1\%). The overall gas flow rate was kept constant at 100 ml/min (± 1 ml/min). Gases were analysed before and after passing through the electrochemical cell by a chromatograph (Hewlett-Packard 6890). Three columns (3 and 6 feet long porapak Q 80/100 mesh and a 6 feet long molecular sieve 5Å, 80/100 mesh) enabled \(\text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}, \text{CO}_2\) and \(\text{O}_2\) to be separated. These were quantitatively analyzed by a thermal conductivity and a flame ionisation detector. The valve system was controlled by a PC (Hewlett Packard software). This PC also handled the data acquisition and processing.

The electrolyte was Yttria Stabilized Zirconia (TOSOH powder 99.99 %, average grain size: 0.3 μm, sintered at 1350 °C for 2 hours).

Oxide micro-electrodes were made of pure lanthanum chromite (LC) powder, purchased from CERAC (99.9 %, average grain size: 9.5 μm) and strontium-doped lanthanum chromite \(\text{La}_{0.83}\text{Sr}_{0.17}\text{CrO}_3\) (LSC) powder, purchased from Rhône-Poulenc (99.9 %, average grain size: 10.3 μm). Pellets which were prepared by uniaxial (1000 kg/cm\(^2\)) and isostatically (under 2500 bar) pressing. They were sintered at 1500 °C for 4 hours. The LC sample has a relative density of 70 % and the LSC one of 85 %. The cone-shaped electrodes were machined using diamond tools, polished on a rotary zirconia disc and cleaned in an ultrasonic sound bath.

Measurements were carried out in the 750-900 °C temperature domain: Note that this domain is not wide enough for getting accurate activation energies. The values given below should be regarded only as estimates.

The impedance measurement were carried out with an Autolab spectrometer (Eco Chemie B.V.) with a 50 mV signal amplitude for frequencies from \(10^{-4}\) to \(10^{-3}\) Hz and a HP 4192A impedancemeter (Hewlett Packard) with a 50 mV signal amplitude for frequencies form \(10^{-7}\) Hz to \(10^{-4}\) Hz.

Overpotential resistances \(R_n\) have been normalized by the length of the triple phase boundary (TPB) perimeter. Thus, the overpotential resistance \(R_n\), describing the reaction rate, is normalized by using the following relationship:

\[
R_n = R_n^0 (2\pi r)^{-1}
\]

where \(R_n^0\) is the normalized overpotential resistance and \(r\) the average radius of the electrode interface. \(r\) is calculated from the Newmans’s equation [13]: \(R_e = (4\pi\sigma)^{-1}\) where \(R_e\) is the electrolyte resistance of the investigated cell and \(\sigma\) the electrolyte conductivity.

Overpotential capacitances \(C_n\) have been normalized by the surface of the electrode interface:

\[
C_n = C_n^0 (\pi r^2)
\]