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Redox behaviour, chemical compatibility and electrochemical performance of $Sr_2MgMoO_{6-\delta}$ as SOFC anode

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ABSTRACT

The double perovskite $Sr_2MgMoO_{6-\delta}$ (SMM) has been proposed as a potential anode material for direct hydrocarbon oxidation in solid oxide fuel cells (SOFCs). The oxygen nonstoichiometry and electrical conductivity dependence of $Sr_2MgMoO_{6-\delta}$ have been determined as a function of the oxygen partial pressure by coulometric titration and impedance spectroscopy techniques. The chemical compatibility of $Sr_2MgMoO_{6-\delta}$ with most of the typical electrolytes commonly used in SOFCs i.e. $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM), $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) and $Zr_{0.84}Y_{0.16}O_{2-\delta}$ (YSZ), was investigated. Reactivity between SMM and all these electrolytes has been found above 1000 °C, although the reaction is most severe with ZrO_2-based electrolytes. Area-specific polarisation resistance of the SMM/LSGM/SMM symmetrical cells indicates that the polarisation resistance increases with the firing temperature of the electrodes due to chemical interaction between LSGM and SMM layers. A CGO buffer layer between the anode and electrolyte was also used to prevent an excessive interdiffusion of ionic species between these components, resulting in better performance. Power densities of 330 and 270 mW cm^{-2} were reached at 800 °C for SMM/CGO/LSGM/LSCF and SMM/LSGM/LSCF electrolyte-supported cells, respectively; with 600-μm-thick LSGM electrolyte, using humidified H_2 as fuel and air as oxidant. XPS and XRPD studies on SMM powders annealed in air and diluted CH_4 atmospheres showed that the surface of SMM powders is mainly formed by $SrMoO_4$ and metal carbonates.

1. Introduction

Fuel cells are efficient electrochemical devices for the conversion of a fuel directly into electrical power. Such devices render theoretical efficiencies significantly higher than those based on the combustion of fossil fuels [1–3]. Among the different fuel cell types, polymer electrolyte membrane fuel cell (PEMFC) and solid oxide fuel cell (SOFC) are the most studied in last few years. However, SOFCs have several advantages compared to low temperature fuel cells, such as the possibility to operate directly with hydrocarbon fuels, greater tolerance to sulphur species in the fuel, and additionally they do not contain any precious metal, which significantly decreases the cost of these devices [1–3]. Different strategies have been investigated to enhance the efficiency and to reduce the operating temperature of SOFCs. New oxide ion conductors with higher ionic conductivity than the state-of-the-art YSZ at lower temperature have been investigated, e.g. doped ceria and doped lanthanum gallate [4,5]. Several cathode materials operating at rather low temperature as 600 °C have been identified, e.g. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $GdBaCo_2O_{5+\delta}$ [6–9], whereas Ni-YSZ cermet is still the most widely-used SOFC anode, possessing high performance with pure H_2 as fuel. However, there are certain disadvantages related to the use of Ni-cermets in direct reforming SOFCs; in particular those related to carbon deposition, sulphur poisoning, agglomeration of Ni particles and volume instability upon redox cycling [10]. In this sense, several approaches have been proposed to overcome these issues such as the development of alternative cermets and mixed oxides [11,12]. Cermets based on ceria are effective to prevent carbon formation and have good tolerance to sulphur [13]. In addition, mixed oxides with high redox stability and catalytic activity for hydrocarbon oxidation have been also studied as alternative anodes to Ni-YSZ cermets, most of them based on perovskite-type structures, e.g. chromium manganites derived from $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ [14,15] and titanates based on $SrTiO_{3-\delta}$ [16]. Despite the fact that chromium–manganites exhibit comparable performance to Ni-based cermets in H_2 their performance for hydrocarbon oxidation is somewhat modest. Activated titanates have limitations as low reduction kinetics and low electronic conductivity.

The double perovskite Sr_2MgMoO_6 (SMM) was recently proposed as an efficient SOFC anode using directly methane and natural gas

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fuels. A high electronic, redox stability and tolerance to sulphur species were reported for this anode material [17,18]. Although a recent study suggests a limited redox stability at temperatures above 900 °C [19]. On the other hand, modification of the double perovskite Sr_2MgMoO_6 by La^{3+} substitution has been reported to improve the electrocatalytic properties for fuel oxidation [20]. However these substituted SMM phases are not stable in oxidising atmosphere, limiting its possible application in a SOFC device [21]. Sr_2MgMoO_6 exhibits also a second order structural phase transition at 275 °C from triclinic (space group $I\bar{1}$) to cubic (space group $Fm\bar{3}m$) symmetry at high temperature [21]. In this case, the continuous character of the phase transition is not a limiting factor for the application of this material in SOFCs.

The performance of SMM was initially evaluated with 300-µm-thick $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{3-\delta}$ electrolyte, using a thin buffer layer of $La_{0.6}Ce_{0.4}O_{2-\delta}$ to prevent possible cation diffusion between the cell components [18]. It has to be considered that the chemical compatibility between SMM and different electrolyte materials has not been studied yet. Thus, further studies on several issues as the phase stability under oxidising/reducing atmospheres, redox behaviour and chemical reactivity between the cell components are required for a better characterisation of this potential anode material for SOFCs.

In the present work, the dependence of the electronic conductivity and oxygen nonstoichiometry of $Sr_2MgMoO_{6-\delta}$ on the temperature and the oxygen partial pressure are studied by a combination of coulometric titration and impedance spectroscopy measurements. A chemical compatibility study between $Sr_2MgMoO_{6-\delta}$ and the electrolytes commonly used in SOFCs is also reported. In addition, the influence of the firing temperature on the electrochemical performance of $Sr_2MgMoO_{6-\delta}$ using LSGM electrolyte is evaluated by area-specific polarisation resistance and fuel cell test measurements.

2. Experimental

2.1. Synthesis and powder characterisation

Submicron sized particles of Sr_2MgMoO_6 with an average diameter of 0.3 µm and BET specific area of 3.1 m^2/g were prepared via a freeze-dried precursor route and final thermal treatment at 1000 °C under a 5%H_2–Ar flow for 10 h. The experimental details are reported elsewhere [22]. This material is thermally stable in air and 5%H_2–Ar mixture up to 1200 °C, exhibiting the same structure and lattice cell parameters in both atmospheres [22]. The perovskite $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ used as cathode material in the fuel cell tests was prepared by a modified citrate sol–gel method using high purity metal nitrates and citric acid as complex agent in a ligand:metal molar ratio of 1:1 and 2:3 for trivalent and divalent cations respectively. After slow heating at 65 °C the dried-gel was fired at 900 °C for 5 h to obtain a single phase.

X-ray powder diffraction (XRPD) patterns were obtained using a PANalytical X'Pert Pro automated diffractometer, equipped with a Ge (111) primary monochromator and the X'Celerator detector. The scans were collected in the 2θ range (10–100°) with 0.016° step for 1 h.

XRPD studies were also performed to evaluate the chemical reactivity between SMM and different commercial electrolytes: $Zr_{0.84}Y_{0.16}O_{2-\delta}$ (YSZ, Tosoh), $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO, Pi-Kem) and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM, Praxair). SMM:electrolyte powders were mixed in a weight ratio 1:1. The powders were ground in an agate mortar and then fired in air between 800 and 1200 °C for 24 h. The powders were then cooled down to room temperature and examined by XRPD. Phase identification and quantification were performed with X'Pert HighScore Plus v.2.0a software using the ICSD database for the structural models [23,24].

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Physical Electronics PHI-5700 spectrometer equipped with Mg–K_α and Al–K_α X-ray sources and a hemispherical electron analyser. The data were analysed using XPSpeak 4.1 software [25]. The experimental peaks were deconvoluted into components using mixed Gaussian–Lorentzian functions.

2.2. Redox stability

Two different electrochemical cells were used to measure the oxygen stoichiometry and electrical conductivity of SMM as a function of oxygen partial pressure and temperature. These are shown schematically in Fig. 1A and B.

The cell illustrated in Fig. 1A was used to determine the temperature dependence of the oxygen stoichiometry of SMM powders as a function of the oxygen partial pressure. The electrochemical cell comprises a section of YSZ tube (length 12 mm and internal diameter of 9 mm) with symmetrical platinum electrodes and Pt wires connected to a dc source which acts as an oxygen pump. The oxygen partial pressure inside the cell was controlled by varying the applied voltage with an external dc source (V_B). Fine powders of SMM were placed into a small Pt crucible. The cell was then closed with two YSZ disks using a glass ceramic sealant thermally compatible with YSZ to ensure gas-tight conditions. The top YSZ disk was used as an oxygen sensor to measure the oxygen partial pressure (V_S) according to the Nernst law:

$$Po_2 = P_o \cdot \exp(-4FV_s / RT) \quad (1)$$

where P_o is oxygen partial pressure in atmospheric conditions (0.21 atm), F the Faraday constant and V_s the voltage read in the oxygen sensor.

The cell was placed in a vertical tubular furnace using an alumina cell with Pt wires for the corresponding electrical connections

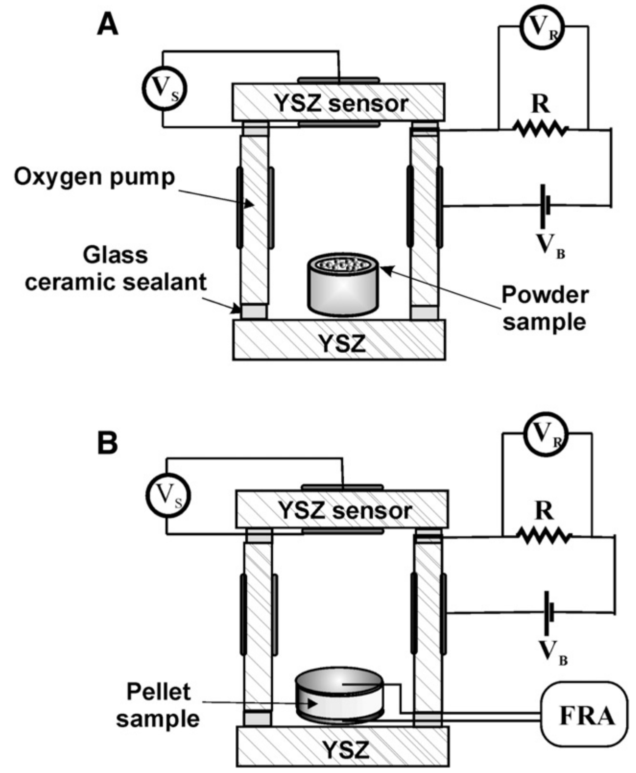

Fig. 1. Schematic drawing of the electrochemical cells for (A) coulometric titration measurements in powder samples and (B) a combination of coulometric titration and impedance spectroscopy measurements (B). V_B is a dc source, FRA a frequency response analyser and V_S and V_R the measured voltages in the oxygen sensor and in the external resistance in series with the oxygen electrochemical pump.