



Cermet cathodes for strontium and magnesium-doped LaGaO₃-based solid oxide fuel cells

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ABSTRACT

To check the suitability of La_{0.9}Sr_{0.1}Ga_{0.85}Mg_{0.15}O_{3-δ}-Ag cermets as cathode material for solid oxide fuel cell (SOFC) with Sr- and Mg-doped LaGaO₃ electrolyte a series of cermets with different Ag contents were prepared by conventional sintering process. The chemical compatibility between La_{0.9}Sr_{0.1}Ga_{0.85}Mg_{0.15}O_{3-δ} (LSGM) and Ag was investigated by X-ray diffraction, scanning electron microscopy, and X-ray photoelectron spectroscopy. Thermal expansion coefficient of the cermets was measured as a function of Ag content and was found to increase with increasing metallic content. Oxygen adsorption at the surface of the cermets could be detected but no reaction or solid solubility between LSGM and Ag was found. It was noticed that a minimum of 30 wt.% Ag is needed to form a cermet with percolating network. From impedance spectroscopy measurement activation energy for the polarization conductance was found to be around 110 kJ mol⁻¹.

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1. Introduction

Solid oxide fuel cells (SOFC) have offered an alternative source of producing electricity with the potential usage in a variety of commercial and industrial applications because of its high efficiency, emission of low pollutants, low noise and potential for cogeneration. Oxygen ion conducting electrolyte materials are the key components of a SOFC. Among the solid electrolytes yttria-stabilized zirconia (YSZ) has been most extensively studied. However, YSZ requires operation temperature as high as about 1000 °C, which is associated with problems like expensive constructional and interconnect materials. This has led to the development of intermediate temperature SOFC operation at 600–800 °C. A plethora of research activities focus the reduction of the operation temperature of the SOFC below 800 °C without reducing the efficiency of SOFC. Perovskite LaGaO₃ doped with Sr²⁺ and Mg²⁺ at the A- and B-site, respectively (LSGM) is the most promising material for the intermediate temperature operation of SOFC because of its higher ionic conductivity as compared to YSZ [1,2].

However, to tap the full potential of this electrolyte proper electrode materials need to be provided, because lowering the temperature increases the overpotential of the electrodes [3]. A fundamental requirement for the successful operation of SOFC is the thermodynamic stability between the cathode and the electrolyte [4].

Normally used cathode material for high temperature operation La_{1-x}Sr_xMnO₃ (LSM) suffers from very low ionic conductivity [5]. In order to increase the efficiency of the cell other materials with mixed conductivity should be chosen so that the oxygen reaction can be extended over a larger surface of the cathode rather than limiting it only at the triple phase boundary area. La_{1-x}Sr_xCoO₃ (LSC) satisfies the criterion of having higher oxygen ion conductivity and therefore a higher rate of surface oxygen exchange but it has higher thermal expansion coefficient (TEC) as compared to the electrolyte. Moreover, the ionic conductivity of this material drops rapidly with decreasing temperature necessitating the need of composite cathode for the operation of intermediate temperature SOFC [6].

The performance of La(Sr)MnO₃ (LSM)-YSZ composite cathode material for SOFC operating temperatures above about 800 °C was reported to be improved due to the suppression of the growth of LSM particles by YSZ particles thereby maintaining the porosity and increasing the triple phase boundary length (TPBL) [7,8]. Tanner et al. [9] using a model reported the effect of porous composite electrodes on the overall charge-transfer process and predicted that composite electrodes can significantly improve the performance of

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fuel cells. Indeed, the overall polarization of the cathode is reported to be decreased in composite cathodes [10]. Not only that the oxygen permeability of composite cathode materials is found to be higher than that of pure oxides [11,12].

Ideally, the use of porous mixtures of an electro-catalyst and electrolyte material as cathode material should improve the performance as a result of increase in the TPBL. In principle, platinum, gold, and palladium could be incorporated into electrode materials. While the cost of these metals is prohibitive for commercial applications, silver is much less expensive and sufficiently active for oxygen reduction [13]. BaCe_{0.8}Gd_{0.2}O₃ (BCG)–silver composites were reported to be promising cathode materials for intermediate temperature SOFC using BaCeO₃-based electrolytes [14,15]. Results indicated that the electrochemical properties of these composites are quite sensitive to the composition and microstructure of the electrodes. Wang and Barnett [16] reported that the resistivity of the composite cathodes like Ag–La(Sr)CoO₃ and Ag–LSM decreases with increasing Ag content and the performance of the composites is superior to that of pure silver. Other authors [17–21] also reported encouraging results with silver–electrolyte composite cathodes.

In this work, the possibility of using LSGM–Ag cermet as cathode material is explored as it satisfies all the conditions necessary to be a cathode material. Oxygen permeation in a composite is realized by the means of oxygen transport through the oxide phase and of electron migration through the metal phase. Silver is chosen as it is reported to be catalytically active towards surface oxygen exchange, which is one of the most important requirements that must be met by the metal phase.

One of the most important criteria for successful operation of the fuel cell is the compatibility between the cathode material and the electrolyte. Any chemical reaction or inter-diffusion between the ceramic and the metallic phase would shrink the triple phase boundary area, which is the preferable cathode reaction site, and this in turn would adversely affect the performance of the SOFC.

The chemical compatibility between LSGM and Ag has been investigated by means of scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS). TEC of LSGM–Ag cermets as a function of Ag content has also been determined. The reported electrical and electrochemical characteristics behaviour of the cermets has been measured by dc four probe and ac impedance spectroscopy.

2. Experimental procedure

Samples with overall nominal composition of La_{0.90}Sr_{0.10}Ga_{0.85}Mg_{0.15}O_{3-δ} were prepared by solid state synthesis starting from powders of La₂O₃ (99.99%, Sigma–Aldrich, Steinheim, Germany) SrCO₃ (98%+, Sigma–Aldrich, Steinheim, Germany), Ga₂O₃ (99.99%, Sigma–Aldrich, Steinheim, Germany) and MgO (98%+, Merck, Darmstadt, Germany). Detailed sample preparation procedure is given in another report [22]. Along with the obtained LSGM powder with a particle size of few microns varying amounts of silver powder (10–50 wt.%) were mixed separately and milled in a WC ball mill (average particle size <160 μm) for 10 min to get a homogenize mixture. The powder mixtures were then isostatically cold pressed at 625 MPa for 60 s into rectangular compacts with the dimension of 15 mm × 5 mm × 5 mm. The pressed samples were then annealed at different temperatures starting from 600 to 900 °C for durations of 20–100 h in static air atmosphere. Heating rate for all cases was 5 °C min^{−1} and all samples were furnace cooled to room temperature.

The phase distribution of the calcined powders as well as sintered samples was studied by powder X-ray diffraction analysis (XRD) using Cu Kα1+2 radiation with 40 kV acceleration voltage, 25 mA filament current (D5000, Kristalloflex, Siemens, Germany). Crushing and grinding of the compacts was performed in an agate mortar. Fine grained powder, was sprayed evenly on a substrate. Diffraction data were smoothened and the background and Cu Kα2 component were removed using the Siemens software package, DiffracAT, EVA5.0 rev.1.

Microstructural characterization was performed by a scanning electron microscope (SEM Model REM S200, Cambridge Instruments, UK) using a Tungsten anode with an acceleration voltage of 20 kV. Chemical analysis was carried out by a built-in EDX spectrometer (Model AN10000 pentafect detector, Link Systems, High Wycombe, UK). Specimens for SEM were embedded in a carbon containing epoxy

polymer and polished with 1 μm diamond suspension on a soft polishing cloth (DP-NAP, Struers, Copenhagen, Denmark).

The density of the sintered samples was measured by Helium Pycnometry (Micromeritics, AccuPyc 1330, Australia), whereas the porosity was measured by conventional mercury porosimetry (Denver Instrument GmbH, Göttingen, Germany).

Linear TEC of the samples was measured after annealing at 600 °C for 100 h. The measurement was carried out using a bar of sapphire of the dimension of 10 mm × 4 mm × 4 mm in air atmosphere using a push rod type differential dilatometer (Model 802, Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) in the temperature range from room temperature to 900 °C.

For the dc four probe measurements electrolyte samples were prepared in the form of 10 mm × 4 mm × 4 mm pellets. Two current electrodes (porous Pt) were made by painting porous Pt on the two opposite faces of the samples. The potential probes were made of Pt wires (0.2 mm diameter) spooled around the sample. Potential probes were smeared with Pt paste in order to provide better electrical contact with the sample. Resistance of an electrolyte was calculated by means of Ohm law:

$$R = \frac{U_+ + U_-}{I_+ + I_-},$$

where U_+ and U_- are absolute values of the voltages, which were measured when current was passed in forward (I_+) and reverse (I_-) directions through the sample. Specific conductivity of electrolyte was calculated by equation:

$$\sigma = \left(\frac{L}{S}\right) \times R^{-1},$$

where L is the distance between the potential probes; S is the cross-section area of the sample. Experimental error of this method mainly depends on the precision of measurements of geometrical parameters of the sample and the distance between measuring probes, and it was not more than 5%.

For the impedance spectroscopy measurements the sintered LSGM pellets were 1 mm thick and 18 mm in diameter. LSGM–Ag powders along with around 5 wt.% Bi₂O₃ were thoroughly mixed in ethyl alcohol with polyvinyl butyral as binder to make a paste. The electrode paste was painted smoothly on both the surfaces of LSGM electrolyte. The pellets were first air-dried. Then they were fired in air at 900 °C for 1 h. Bi₂O₃ was added as sintering additive and adhesion of the electrode to electrolyte was good. Ag meshes were attached to both electrodes and co-sintered with them so as to act as current collectors. Lead wires of Pt were used to connect the Ag mesh current collectors to the ac impedance spectrometer (IM6, Zahner Elektrik). Electrochemical measurements were carried out in a frequency range 1 Hz to 100 kHz with an applied variable voltage of 10 mV. All the measurements were taken in air atmosphere in a temperature range of 450–800 °C.

The electrochemical cell was connected to impedance meter by the two-electrode four-wire mode that allowed to exclude the impedance of current carrying leads from a total impedance of the system. Specific values of polarization conductivity were calculated by the formula:

$$\sigma_p = 2[S(R_{dc} - R_{hf})]^{-1},$$

where S is the area of an electrode, R_{dc} is the total resistance of an electrochemical cell to a direct current and R_{hf} is the resistance determined by extrapolation of a high-frequency part of impedance hodograph on real axis, which corresponds to resistance of an electrolyte.

XPS technique was employed to identify minute reactions between the ceramic phase and Ag. The XPS analysis was performed with a Thermo VG Thetaprobe system operating in the parallel data acquisition mode using monochromatic Al Kα ($h\nu = 1486.68$ eV; spot size 400 μm). Experimental detail is given elsewhere [23].

3. Results

3.1. XRD and SEM study

LSGM–Ag powder mixtures compacted and annealed at various temperatures. Fig. 1 shows the XRD patterns of the LSGM–Ag cermets after annealing at 600 °C for 100 h. The LSGM parent phase, which has a perovskite structure, is marked as p in the pattern. Ag is also indexed. In addition to the peaks of these two phases some small ones are also visible which are indexed as LaSrGa₃O₇ (JCPDS 45–637) and LaSrGaO₄ (JCPDS 24–1208). A typical SEM picture of LSGM–50Ag after 100 h of annealing is shown in Fig. 2. The percolation of Ag phase in the LSGM is clearly visible. Through EDX analysis the dark phase is identified as LSGM and the bright one is Ag. No trace of Ag in the LSGM matrix or any of the constituent elements of LSGM in Ag is found. It is noted here that purpose of doing SEM was to find out the different phases present in the picture and

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