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Infiltration of ionic-, electronic- and mixed-conducting nano particles into $La_{0.75}Sr_{0.25}MnO_3$–$Y_{0.16}Zr_{0.84}O_2$ cathodes – A comparative study of performance enhancement and stability at different temperatures

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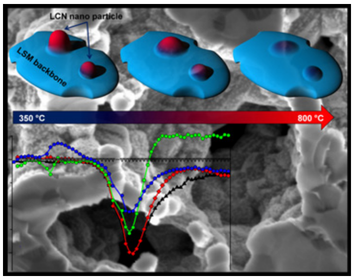
HIGHLIGHTS

- ► In situ formation of nano particles leads to performance increase.
- ► Polarization resistance R_p decreased by more than 70%.
- ► The performance increase strongly differs with temperature and type of infiltrate.
- ► Mechanism of the performance increase independent from electrochemical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The microstructure and electrochemical performance of LSM–YSZ composite electrodes infiltrated with $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) as an electronic conductor, $LaCo_{0.6}Ni_{0.4}O_{3-\delta}$ (LCN) as a mixed conductor and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) as an ionic conductor, were compared in the temperature range 550–800 °C. All three infiltrates resulted in improved electrochemical performance. Impedance analysis suggested dissociative adsorption and transfer of species to the triple phase boundary as the main mechanism responsible for the performance enhancement in all cases, attributed to the increase in surface area and triple phase boundary upon infiltration. LCN showed the most pronounced improvement at 550 °C, but its performance degraded drastically with increasing temperature. LSM and CGO infiltrated electrodes degraded less upon heating up to 800 °C. Infiltrated CGO electrodes showed the smallest degradation rate upon long term testing at 750 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that produce electricity directly from various fuels e.g. hydrogen, bioethanol or hydrocarbons [1–3]. Compared to traditional technologies, SOFCs exhibit high energy conversion efficiency, low noise level and reduced CO_2 emissions. Furthermore, the excellent load following capability makes it ideal for playing an important role in future decentralized, intelligent power grids, if current challenges of high price, limited life time and insufficient performance are overcome.

State-of-the-art SOFCs typically utilise yttria stabilized zirconia (YSZ) as electrolyte and a Ni-YSZ cermet anode [4]. The most commonly used cathode material is a composite of YSZ and strontium doped lanthanum manganite ($La_{1-x}Sr_xMnO_{3-\delta}$ (LSM)) [5]. The operating temperature is in the range 800–1000 °C. Reduction of the operating temperature range to 550–750 °C (intermediate temperature (IT)) is currently a topic of much

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research and development. IT-SOFCs can be economically favorable, as thermally activated degradation phenomena are minimized at lower temperatures, thereby increasing the life time. Furthermore, reducing the operating temperature allows the use of cheap materials for auxiliary components [6,7].

However, reduction of the operating temperature increases the ohmic and electrode polarization losses, the relative contribution of the cathode becoming the most significant due to its larger activation energy. Mixed ionic and electronic conducting (MIEC) materials, such as LSCF ($La_xSr_{1-x}Co_yFe_{1-y}O_3$), LCN ($LaCo_{0.6}Ni_{0.4}O_3$) and LSC ($La_xSr_{1-x}CoO_3$) [8,9] are considered as cathodes for IT-SOFCs, due to their superior performance in comparison to LSM, but require a costly barrier layer (usually CGO) between the YSZ electrolyte and the cathode layers to prevent formation of electrical insulating secondary phases. A promising alternative is to improve the state-of-the-art and thermodynamically more stable LSM–YSZ cathode by introduction of (electro) catalytically active nanomaterials into the porous cathode structure.

A way to obtain such nano-structured cathodes is the so called infiltration or impregnation process [10–23]. Here, nano particles are deposited into a pre-sintered backbone via an aqueous solution of metal salts. Low firing temperatures between 500 and 750 °C (compared to more than 1100 °C for sintering a LSM–YSZ composite) are sufficient to (in-situ) form and deposit the nano particles. These low firing temperatures have the advantage that a) the high catalytic activity and large triple phase boundary (TPB) areas, typical for nano sized particles, persist and b) that e.g. reaction between the MIEC material and the electrolyte, with the formation of electrical insulting secondary phases, can be minimized.

The infiltration of different materials into LSM–YSZ backbone structures has been reported in the literature [10–12,14–16,20,21] and an improved performance has been demonstrated for several materials. In these articles the main research focus is on finding the optimum particle loading to maximize the performance gain, and often highly concentrated solutions and/or a large number of repeated infiltration cycles are used to obtain a high density of particles along with an improved performance. However, studies comparing the effect of nano particles with different electrochemical properties on the performance, which could help determine the reaction mechanism, are still missing.

The aim of the present study is to contribute to fill this gap. Here, we compare how the performance of a standard LSM–YSZ composite electrode is influenced by the addition of three infiltrates with mainly different electrical conduction properties: a) $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) as an electronic conductor; b) $LaCo_{0.6}Ni_{0.4}O_{3-\delta}$ (LCN) as a mixed conductor and c) $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO) as an ionic conductor. All materials were infiltrated via nitrate precursor solution into the LSM–YSZ backbone. The used infiltration process, temperature treatments and electrochemical test protocols were identical to allow comparison. Solutions with a relative low concentration of 0.3 M were used to favor the formation of isolated nano particles, which is useful for such fundamental studies. Additionally, a 3 M CGO solution was included in the test matrix to evaluate concentration effects of an ionic conductor. The changes in the microstructure and the electrochemical performance of the impregnated half cells were investigated in the temperature range from 550 °C to 800 °C. Impedance analysis was used to characterize losses and assign changes of the cell components and the electrochemical processes.

2. Experimental

Approximately 200 μm thick 8YSZ tapes (~4 cm × 4 cm) which have been prepared "in house" were used as electrolyte layer. On both sides of these tapes, an ink consisting of 50/50 wt.% of $La_{0.75}Sr_{0.25}Mn_{1.05}O_{3\pm\delta}$ (LSM25) and $Y_{0.16}Zr_{0.84}O_{1.92}$ (8YSZ) was screen printed. After sintering above 1000 °C, the tapes were cut into small pieces of about 6 × 6 mm. The latter were used for the impregnation with nano particles and represent the not-impregnated reference materials [14]. The following solutions were used for infiltration: $La_{0.8}Sr_{0.2}MnO_3$ (LSM) (0.3 M), $LaCo_{0.6}Ni_{0.4}O_3$ (LCN) (0.3 M) $Ce_{0.8}Gd_{0.2}O_2$ (CGO) (3 M and 0.3 M). In each case an aqueous solution containing the metal nitrates in the appropriate ratio and the surfactant Pluoronic® P123 (BASF Cooperation) (0.5 mg ml^{-1}) was prepared. The following nitrates were used: $La(NO_3)_3\cdot 6H_2O$ (Alfa Aesar, 99.9%), $Sr(NO_3)_2$ (Alfa Aesar, 99%), $Mn(NO_3)_2\cdot 4H_2O$(Alfa Aesar, 98%), $Ni(NO_3)_2\cdot 4H_2O$ (Sigma Aldrich 98.5%), $Co(NO_3)_2\cdot 6H_2O$(Sigma Aldrich 98%), $Gd(NO_3)_3\cdot 6H_2O$(Sigma Aldrich 99.9%) and $Ce(NO_3)_3\cdot 6H_2O$(Sigma Aldrich 99.9%). The nitrate solution was then dropped onto the LSM–YSZ cathode and infiltrated into the pores by capillary forces. Afterward the samples were placed under vacuum to remove air pockets and enhance the penetration of the solution into the backbone, ensuring an even particle distribution throughout the complete porous electrode. The impregnated samples were dried at 350 °C before being used for electrochemical impedance spectroscopy (EIS) measurements. Prior to the EIS measurements, Pt paste was applied onto the symmetrical cells. Each cell was placed between Pt-grids connected to the electrochemical measurement equipment. The sample holder is placed in a furnace and EIS measurements were performed in compressed air flow. Two different temperature profiles were applied during EIS measurements: (a) EIS spectra were recorded at different temperatures starting from 550 °C with increasing the temperature in steps of 50 °C. The maximum temperature was 800 °C. After that, impedance spectra were recorded every 50 °C during cooling down to 550 °C. A last EIS measurement was performed at 750 °C. The various temperatures were kept constant for 2 h before the data collection. (b) Electrochemical impedance spectra were recorded at a constant temperature of 750 °C over approximately one week to determine electrochemical performance of the impregnated cells as a function of time. For the impedance measurements a Hioki frequency response analyzer was used. Open circuit conditions (OCV) were applied, using a 50 mV amplitude AC signal over a frequency range of 0.08 Hz–100 kHz with 10 points per decade. The impedance spectra were corrected for the inductance originating from the equipment such as wires etc. and normalized with the area of the symmetrical cells. 2–4 samples were made with each infiltrate to assure reproducibility. Polarization resistance values presented and discussed here are average values. The spread of these resistance values was below 15% for the impregnated cells showing a good reproducibility. Impedance data were analyzed using ZSimpWin 3.21, a program commercially available from EChem Software and applying the equivalent circuit $LR_s(RQ)(RQ)$ in Boukamp notation. For clarity and easier comparison the data in the Nyquist plots are presented after subtraction of the serial resistance (R_s).

Micrographs of the symmetrical cells and EDS spectra were recorded on a Zeiss Supra 35 scanning electron microscope (SEM) equipped with a field emission gun and an EDS detector.

3. Results and discussion

3.1. Microstructure of infiltrated LSM–YSZ (SEM/EDS)

To investigate temperature induced structural changes, SEM images from infiltrated samples annealed at 350, 550 and 750 °C (Fig. 1a–i) were compared. In all four infiltrated samples the in-situ formed nano particles are clearly observable in the SEM images for