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Impregnation versus exsolution: Using metal catalysts to improve electrocatalytic properties of LSCM-based anodes operating at 600 °C

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ARTICLE INFO

Article history:

Received 21 March 2016

Received in revised form

2 June 2016

Accepted 7 June 2016

Available online 28 June 2016

Keywords:

SOFC

LSCM

Exsolution

Impregnation

Ni nanoparticles

EIS

ABSTRACT

Impregnation and exsolution methods were used to improve electrocatalytic properties of LSCM towards direct oxidation of fuel at 600 °C. The electrochemical performances of three electrode materials, LSCM, nickel-doped LSCM and Ni-impregnated LSCM were compared. Electrolyte-supported symmetrical cells using $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ as electrolyte were characterized by electrochemical impedance spectroscopy. Nickel doping or impregnation leads to a reduction of polarisation phenomena, essentially related to a decreasing of gas adsorption resistance. Under hydrogen and in comparison to impregnation approach, exsolution does not offer significant advantages with regard to the polarization phenomena. The only noticeable difference concerns the electrode microstructure. Therefore, exsolution method produces a dispersion of nanoparticles firmly anchored to grain surface which minimizes nanoparticles agglomeration during ageing.

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Introduction

In order to facilitate large-scale commercialization of solid oxide fuel cells (SOFC), one strategy consists in designing devices which could operate directly with carbonaceous fuel in the temperature range 400–600 °C. This purpose firstly requires developing new electrolytes with a high level of ionic conductivity at low temperature. Gadolinium-doped ceria $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) appears as a good candidate for such an application since it presents at 600 °C the same level of

conductivity as the benchmark electrolyte YSZ at 900 °C [1,2]. However, the decrease of operating temperature maximizes the influence of the electrode polarization phenomena on final device performances. Therefore, it seems necessary to identify new anode materials exhibiting good electrocatalytic properties towards direct oxidation of fuel at 400–600 °C. Cermets Ni/CGO were tested with fairly good results for operation under hydrogen [3], but the use of carbon-based fuels seems difficult because nickel catalyses coking. Since oxides catalyse less hydrocarbon cracking reactions, anodes based exclusively on ceramic mixed ionic–electronic

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<http://dx.doi.org/10.1016/j.ijhydene.2016.06.088>

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conductors (MIECs) have been extensively studied in the literature. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ (LSCM), for instance, was reported to be a promising anode material to replace Ni–YSZ cermet. It reveals good performances at high temperature for direct oxidation of methane while minimizing coking phenomenon [4,5]. Unfortunately, its electrocatalytic properties are poorer at 400–600 °C range.

Electrochemical characteristics of ceramic electrodes can be enhanced by adding a small amount of metallic nanoparticles (Ni, Ru), generally obtained by impregnation of a porous electrode with a metallic salt or a nanopowder suspension [6–9]. Nevertheless, the use of this approach in high temperature operating systems, can sometimes lead to an inhomogeneous distribution of the metallic particles as well as to their coarsening. Instead of adding metallic nanoparticles as a separate phase, it is possible to dissolve metals in their oxidized form (e.g. Ni^{2+} for Ni) into the electrode material phase. Then, upon heating under reducing atmosphere [10], metal nanoparticles can precipitate from bulk. This approach, highlighted by J.T.S Irvine's group, is cited in the literature as “redox exsolution” and has been a subject of interest in the last years [10–25]. By this method, a stronger interaction between support (electrode) and metallic nanoparticles is expected which could prevent coarsening [23]. Unfortunately, this interaction can also lead to the passivation of the nanoparticles, sometimes surrounded by an oxide layer [26,27]. Moreover in some cases, metal exsolution from bulk could induce a detrimental modification on the electrical properties of the electrode.

In a previous work, we used the exsolution method to improve the electrocatalytic properties of LSCM with Ni nanoparticles. Compounds with formula $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5-x}\text{Ni}_x\text{O}_{3-\delta}$ were prepared. A partial exsolution of Ni was obtained by reduction of nickel-substituted compounds. $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ (called $\text{LSCMn}_{0.3}\text{Ni}_{0.2}$) was identified as a good candidate for anode application since it supports total oxidation of methane for all oxygen stoichiometries studied [27]. Symmetrical cells $\text{LSCMn}_{0.3}\text{Ni}_{0.2}/\text{YSZ}/\text{LSCMn}_{0.3}\text{Ni}_{0.2}$ were studied by electrochemical impedance spectroscopy (EIS) under wet 5% H_2/Ar at 800 °C [28]. The ASR value obtained is comparable to the best results reported in the literature for LSCM although the total conductivity of $\text{LSCMn}_{0.3}\text{Ni}_{0.2}$ under reducing atmosphere (0.8 S cm^{-1}) is significantly lower than that of LSCM.

However, at the end of this work some questions remained. Is it possible to get same results by adding catalysts by impregnation? Can this approach also be used to improve electrocatalytic properties of LSCM towards direct oxidation of hydrogen or methane a lower operating temperature (e.g. 600 °C)? Is there any influence of the method used to add catalysts on the final electrode performances? In fact, few electrochemical studies in the literature concern the comparison between impregnation and exsolution methods, especially at low temperature.

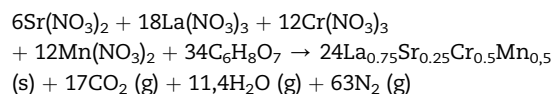
The aim of this work is therefore to provide some answers to these questions through a comparative study of the electrochemical performance of three electrode materials: LSCM, $\text{LSCMn}_{0.3}\text{Ni}_{0.2}$ and LSCM pre-coated with metallic Ni by impregnation, further named LSCMimpNi. For this purpose, three electrolyte-supported symmetrical cells using

$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) as electrolyte material have been fabricated. The polarisation resistances (R_p) of the electrodes were characterized by electrochemical impedance spectroscopy (EIS) at 600 °C under hydrogen and methane. An ageing study was also performed.

Experimental

$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.3}\text{Ni}_{0.2}\text{O}_{3-\delta}$ compound ($\text{LSCM}_{0.3}\text{Ni}_{0.2}$) was prepared by solid-state reaction according to an experimental protocol described elsewhere [27,28]. In order to induce partial nickel exsolution from bulk, $\text{LSCM}_{0.3}\text{Ni}_{0.2}$ was reduced under Ar/H_2 (5%) at 800 °C during 12 h.

Ni pre-coated LSCM (LSCMimpNi) was synthesized by incipient wetness impregnation method from a LSCM precursor prepared by self-combustion synthesis [29]. For combustion reaction, the citric acid ($\text{C}_6\text{H}_8\text{O}_7$) from Alfa Aesar (99.5%) was used as fuel and complexing agent. Metal nitrates $\text{La}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from Alfa Aesar (99%) were used as metal precursors and oxidizing agents. The method of Jain et al. [29] was used to calculate the combustion ratio (fuel/oxidant) needed to achieve stoichiometric combustion (i.e. full oxidation of organic fuel). The global reaction between metal nitrates and citric acid used in this work can be written as follows:



Metal nitrates were mixed with citric acid in water. After evaporation and self-combustion, the powder obtained was calcined at 800 °C during 2 h, ground and heated at 1000 °C for 12 h to obtain LSCM compound. Subsequently, incipient wetness impregnation was used to impregnate LSCM powders. In this technique, a metal-containing solution is added to a catalyst support containing the same pore volume as the volume of the solution added. Capillary action draws the solution into the pores. In this work, a pellet of LSCM was used as catalyst support. Its mass m_p and volume V_p were measured and used to calculate the amount of $\text{Ni}(\text{NO}_3)_2$ (m_{Ni}) dissolved in water (V_w), needed to fill pellet porosity:

$$V_w = \left(1 - \frac{m_p}{V_p \times \rho_{\text{LSCM}}}\right) \times V_p$$

$$m_{\text{Ni}} = x_{\text{Ni}} \times M(\text{Ni}(\text{NO}_3)_2) \times \frac{m_p}{M(\text{LSCM})}$$

where $M(\text{LSCM})$ and $M(\text{Ni}(\text{NO}_3)_2)$ correspond to molar mass of LSCM and $\text{Ni}(\text{NO}_3)_2$ respectively, ρ_{LSCM} symbolize LSCM density and $x_{\text{Ni}} = n_{\text{Ni}}/n_{\text{LSCM}}$ is the Ni molar ratio in the electrode. In this work, the molar ratio x_{Ni} was chosen equal to 0.2.

Afterwards, the pellet was dried and calcined at 700 °C.

$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte was also synthesized by a self-combustion method using citric acid as fuel. $\text{Ce}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ from Alfa Aesar (99%) were used as metals precursors. A fine powder (crystallites size less than 60 nm) was obtained, pressed into a pellet and sintered at 1550 °C. Sintered pellet was cut into 200–300 μm slices using a

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