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THE ROLE OF THIN FUNCTIONAL LAYERS IN SOLID OXIDE FUEL CELLS

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Widespread commercialization of solid oxide fuel cells requires lowering its cost. It is generally accepted that to lower the cost of solid oxide fuel cells it is necessary to use metal alloys as interconnectors and, consequently, lower its operating temperature to slow down interconnectors degradation. As a result the area specific resistance of the cathodes should be lowered to sustain the performance of the cells. In order to slow the interconnectors degradation (due to corrosion and interdiffusion with the anode) and improve the performance of the cathodes, novel functional layers are introduced to the structure of the fuel cells. In this paper, results related to three kinds of functional layers will be presented: a thin cathode layer between the porous cathode layer and the electrolyte to improve the cathode performance, a buffer layer between the electrolyte and the cathode to slow down inter-diffusion of atoms and thin and dense interconnector coatings to slow down interconnectors degradation. The investigated layers are deposited by cost effective spin coating and spray pyrolysis methods. Introduction of the layers show positive and promising results.

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1. Introduction

Lowering the operation temperature of Solid Oxide Fuel Cells from the current 800 °C to about 750 °C (and ultimately 700 °C) seems important to achieve low degradation rate allowing long term operation and thus viability of the technology. By lowering working temperature lower degradation, for example slower corrosion of the interconnectors (ICs) can be realized. To maintain power output at lowered temperatures, new materials must be sought. It has been reported that for state of the art fuel cells, the limiting factor in performance is the cathode overpotential [1]. For cells tested at 700 °C cathode overpotential contributed by ~55%, anode ~25%, electrolyte ~15% (remaining being concentration polarization). Therefore the largest improvement can be obtained by improving the cathode. This can be obtained either by looking for new materials or new cathode structures.

Usually cathodes that are electrochemically very active also react chemically with the yttria stabilized zirconia (YSZ) electrolytes [2]. Therefore, a barrier layer between the YSZ electrolyte and the cathode material is needed. Its fabrication and quality is very important in order to mitigate Sr and La diffusion [3,4]. Typically the barrier layer is made of cerium gadolinium oxide (CGO), which does not react with most of the cathode materials. It does, however, react with YSZ at temperatures exceeding 1200 °C, therefore its low temperature fabrication can be beneficial.

Another important issue with the degradation of fuel cells is the presence of the steel interconnector used to separate gas compartments of adjoining cells. Whereas coatings for the oxygen side are well developed [5–7], reports about coatings for the hydrogen side are scarce and need to be developed further [8].

Successful development of new functional layers is therefore crucial in order to lower operation temperature of the cells maintaining their performance. Deposition methods used in this study, comprising spin coating and spray pyrolysis of liquid precursors offer possibility to form thin (<1 μm) ceramic coatings with nanocrystalline grain size at low temperatures. Ceramic layers can be formed at temperatures not exceeding ~600 °C. Typically, cathodes, barrier layers or interconnector coatings are sintered at much higher temperatures, where initial degradation phenomena are introduced [2]. Therefore, using spin coating or spray pyrolysis offers the possibility to study ceramic layers prepared at relatively low temperatures.

There is no standardized nomenclature for naming of the new functional layers introduced into the fuel cell structure. Typically,

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anode functional layers and cathode functional layers were used to describe electrode layers with a tailored microstructure, enhancing triple phase boundaries for electrochemical reactions [9]. However depending on the research group, different naming can be used [10–12]. As in the case of fuel cells developed at Gdansk University of Technology (GUT), the oxygen side electrode is a single layer structure. Therefore a newly developed layer has been named in this study “cathode thin functional layer”. It serves a similar electrochemical role but is differentiated by having a small thickness, below 1 μm (~single grain thickness), whereas traditional functional cathode layers have a thickness of ~10 μm and thickness of the whole cathode (including current collector layer) is around 50 μm.

1.1. Cathode thin functional layer

In recent years thin cathode layer between porous cathode layer and electrolyte became one of the promising functional layers. It is deposited on the surface of the electrolyte (possibly including barrier layer) on the oxygen electrode side, prior to deposition of the porous cathode. Its thickness is below 1 μm. It was shown by Hildenbrand et al. [12] that a 200 nm $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) layer prepared by a pulsed lased deposition (PLD) method between the actual, porous LSCF electrode (sintered at 1100 °C) and the electrolyte lowers the LSCF cathode area specific resistance (ASR) by 40% at 800 °C and 69% at 600 °C. Despite the fact that the PLD provides high quality ceramic layers, its high level of technical sophistication and high cost make it difficult to use in large-scale production. Further research into possible use of spin-coating of polymeric precursors to obtain dense layers was conducted by Dumaisnil et al. [13] and Chrzan et al. [14]. It was shown that 700 nm thick $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ functional layer lowers LSCF cathode ASR by 27% at 700 °C and 32% at 600 °C [13]. In another study, thin functional layers made of three different perovskites, $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (LNF), $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ (STF) and LSCF with various thicknesses (~30 nm to ~440 nm) were deposited to improve LNF cathode performance [14]. The highest, 29% improvement was shown for the 160 nm thick LSCF layer, while 27% for the 150 nm thick LNF layer. It proved that the enhancement of cathode performance is, to a certain extent, independent of the level of the thin layer’s ionic conductivity [14]. Additionally, it was shown that a thin functional layer largely improves the reproducibility of the cathode preparation, which was manifested by the significantly lower ASR’s standard deviation in comparison to the samples without thin layers. The exact nature of the cathode performance improvement is not yet fully understood. However, it was observed that the thin layer enhances the adherence of the porous cathode. It may enhance the oxygen transfer mechanism without visible change in oxygen reduction reaction mechanism, even if the thin layer is more catalytically active then the porous cathode (due to smaller grains). It is worth noticing that due to cathode sintering temperature of 1100 °C performed after the deposition of the thin functional layer, the deposited layer becomes porous [14] due to the coalescence of thin films. At this temperature, due to the grain growth, the grains become globular in shape with their size exceeding initial layer thickness. The influence of the layer microstructure on the fuel cell properties is yet to be tested. None of the studies published so far included a fuel cell performance investigation.

1.2. Diffusion barrier layer

One of the more promising cathode materials to lower SOFCs’ cathode overpotential is $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF). It is characterized by high ionic-electronic (mixed) conductivity and high catalytic activity [15] and thermal expansion coefficient similar to the most popular electrolyte – yttria stabilized zirconia (YSZ) [16]. Unfortunately, at sintering and operating temperatures of the cathode, a diffusion of atoms between the electrolyte and the cathode occurs. This diffusion can lead to formation of parasitic phases, namely $La_2Zr_2O_7$ and $SrZrO_3$, in the vicinity of electrolyte – electrode interface [17,18] or diffusion of Zr into the LSF cathode [18,19]. These phases have lower conductivity then LSF and they lower the triple phase boundary length for an oxygen reduction. In consequence the fuel cell performance is decreased [18]. The parasitic phases formation also concerns the other perovskite containing especially lanthanum and strontium, such as (La,Sr)(Co, Fe)O_3 family [20,21]. The solution to the problem is to employ diffusion barrier to separate electrolyte and cathode materials. To fulfill its role properly, diffusion barrier layer must be dense, tight and have a good ionic conductivity and of course do not react both with the electrolyte and cathode materials. Simultaneously it must be thin enough to do not introduce additional resistance to the electrolyte. One of the appropriate candidate for such diffusion barrier is cerium oxide doped with samarium oxide (CSO or SDC) or gadolinium oxide (CGO).

1.3. Interconnect coating

Another important application area of ceramic functional layers is connected to protective coatings of fuel cells’ metallic interconnectors. Metallic alloys, primarily based on stainless steels, undergo high temperature corrosion phenomena when operated at temperatures higher than 500 °C both in air and humidified hydrogen. Dense stainless steels are the current state of the art materials for construction of interconnectors in fuel cell/electrolysis stacks. For the uncoated alloys, reported corrosion rates indicate, that in order to achieve the desired lifetime of the stack (~40000 hours for stationary applications) surface of the alloy needs to be modified in order to lower the corrosion rate. Alternatively, operation temperature can be lowered by 50 °C–100 °C. However, even if the temperature is lowered and the oxide growth (and chromium depletion) is no longer the limiting factor, chromium poisoning of the oxygen electrode [22,23] and nickel, iron and chromium interdiffusion on the hydrogen side will still occur [24,25]. Therefore protective coatings are still required. Many different protective coating materials and techniques have been evaluated so far. In our group we have been developing coatings based on reactive elements (e.g. Ce, Gd, La, Y) deposited by spin coating [26]. These allow to lower corrosion rate of the Crofer 22 APU alloy by around one order of magnitude. Both the spin coating of polymeric precursors [27] and spray pyrolysis [28] deposition methods can be effectively used with metallic substrates. These offer unique opportunity to form novel thin nanocrystalline protective films on the steel surface. In this work we focus on deposition of pure ceria (CeO_2) coatings by spray pyrolysis method. Ceria has already been shown as a successful protective material in the form of thin [29,30] and thick coatings [8]. Ceria, as an n-type electronic conductor is especially promising for use in reducing atmospheres, where its electrical conductivity is relatively high [31,32].

In this study, selected aspects of the development of thin functional layers are presented. Namely, original results related to the fabrication of thin and dense cathode layers between the porous cathode layer and the electrolyte, to the buffer layer between the electrolyte and the cathode and to the thin and dense interconnector coatings are presented.

In the case of the thin cathode layer between the porous cathode layer and the electrolyte, it is shown that a thin LNF layer spin-coated from polymeric precursor lowers the polarization resistance of the symmetrical cells and improves fuel cell maximum power density. The porous LNF cathode is sintered at

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