Durable direct ethanol anode-supported solid oxide fuel cell

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HIGHLIGHTS

- Direct ethanol anode-supported SOFC stable for 600 h without water.
- High-performance SOFC exhibiting similar current output in both hydrogen and ethanol.
- Ceria-based catalytic layer ensures ethanol conversion and avoids carbon deposits.

ARTICLE INFO

ABSTRACT

Anode-supported solid oxide fuel cells accumulating more than 700 h of stable operation on dry ethanol with high current output are reported. A highly active ceria-based catalytic layer deposited onto the anode efficiently converts the primary fuel into hydrogen using the electrochemically generated steam. On the other hand, standard fuel cells without the catalytic layer collapse because of carbon deposit formation within the initial 5 h of operation with ethanol. The nanostructured ceria-based catalyst forms a continuous porous layer ($\sim$25 μm thick) over the Ni-based anode support that has no apparent influence on the fuel cell operation and prevents carbon deposit formation. Moreover, the catalytic layer promotes overall steam reforming reactions of ethanol that result in similar current outputs in both hydrogen and ethanol fuels. The stability of single cells, with relatively large active area (8 cm^2), confirms the feasibility of a catalytic layer for internal reforming of biofuels in solid oxide fuel cells. The experimental results provide a significant step towards the practical application of direct ethanol solid oxide fuel cells.

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1. Introduction

The greenhouse gas emissions resulting from the combustion of fossil fuel have been directly related to the measured temperature rise around the planet. In this scenario, the historical combination of oil-derived fuels and combustion engines requires urgent alternatives to meet the 2 °C global warming limit recently defined [1]. The development of more efficient and environmentally friendly energy sources has gained vital importance to avoid a legacy of irreversible environmental damage for future generations. In this context, fuel cells and the so-called hydrogen economy have attracted a great deal of attention as a promising evolution of energy systems to contribute for more efficient and clean energy production. Fuel cells are electrochemical converters not limited to the Carnot cycle, with theoretical efficiency exceeding 80%,

and water as the only residue released to the atmosphere when hydrogen is used. Among fuel cells, solid oxide fuel cells (SOFCs) are potentially the most efficient technology to convert chemical energy into electricity and thus could have a major impact on reducing fuel consumption and CO$_2$ emissions [2–5]. However, a critical issue is that hydrogen must be produced from other primary sources. Most of hydrogen is obtained from steam reforming of natural gas, requiring additional carbon capture technologies to ensure a complete carbon neutral cycle. Methane is the most studied alternative fuel for SOFCs due to availability and possible internal reforming [4,6–11].

Considerably less attention has been given to the use of renewable fuels in SOFCs, though the direct use of SOFCs with biofuels has been proposed as the most energy efficient means to use homegrown carbon neutral fuels [5,12–14]. Among available biofuels the most produced worldwide and probably the most advanced one is ethanol with notable application in transportation [14–16]. Bioethanol is efficiently produced from renewable bio-

mass and is an economically viable energy source for large-scale production, generating low emissions and bringing positive impact to the economy and the environment [14–16]. Nonetheless, as compared to methane, a limited number of studies is dedicated to ethanol SOFCs [17–20]. More recently, such a renewable and available liquid biofuel has gained increasing attention as a promising SOFC fuel, as reported in several studies [15–24]. Liquid fuels compensate the need of engineering optimization for fuel delivery with easier storage, handling and transportation than gas fuels. Such a trend has been confirmed by the announcement of an ethanol SOFC prototype vehicle by Nissan, expected to be commercialized in 2020 [25]. The e-bio fuel cell concept is the first to use ethanol for electric power generation with an SOFC for vehicular application. This carbon neutral vehicle brings together the advantages of a liquid and renewable biofuel to power electric cars and it is a perfect example of the applicability of ethanol SOFCs. It is interesting to notice that Nissan's prototype uses a pre-reformer, whereas our study aims at improving the technology to (direct) internal reforming of bioethanol.

The high operating temperatures of SOFCs allow the direct conversion of primary fuels (e.g., natural gas and ethanol) into electricity [2–11]. However, the stable operation of SOFCs running on fuels containing carbon is still a challenge because Ni, from the standard anode yttria-stabilized zirconia (YSZ)-Ni cermet, promotes the dehydrogenation of fuel. Such reactions result in carbon deposition on the surface of the anode, causing an irreversible degradation that has hampered a more widespread use of SOFCs [4–6]. Two main strategies have been developed to allow the use of such fuels in SOFC. The first one is the addition of an oxidizing agent to the fuel stream to prevent the thermodynamic conditions that favor carbon deposition [4,25]. Usually, water is the most common choice, but some studies have reported SOFCs running on methane by adding air or CO_2 [26]. Nonetheless, the addition of large amounts of water (or air) in the fuel stream reduces the overall efficiency and adds complexity to the system. The second strategy is to modify or substitute the traditional Ni-based cermet anode to allow stable operation of SOFCs without fuel dilution. Different materials have been reported, including various cermets and ceramic anodes [4,10,27]. However, such anodes usually exhibit either low electronic conductivity or low catalytic activity [4,6,10]. Finding a material (single phase or composite) that combines high catalytic activity and high conductivity along with other SOFC requirements (stability, compatibility, cost, etc.) is a hard task. Indeed, no alternative anode has shown performance equivalent to that of the standard Ni-YSZ running on hydrogen [4,10]. Therefore, preserving the Ni cermet and adding a catalyst tailored for a desired fuel is a promising strategy for SOFC anode design [12,13,19,20].

In this context, using a bi-layer anode has the advantage of using the best-known anode (Ni-YSZ) for hydrogen along with a suitable catalyst. Latest generation of SOFCs is a multilayer device in which several elaborated functional layers were incorporated to the initial anode/electrolyte/cathode arrangement. Two marked examples of layers incorporated to SOFC to enhance both performance and durability are: (i) gadolinia-doped ceria (CGO) diffusion barrier to avoid undesired reactions between the cobalt-iron lanthanum perovskite (LSCF) cathodes and YSZ electrolyte; and (ii) Cr-poisoning has been reduced by coating metallic interconnectors with spinels. Therefore, it's reasonable that a similar strategy is being used on the anode side to allow the operation of SOFCs on alternative fuels [12,13].

In general, direct ethanol SOFC tests revealed that switching fuel from H_2 to ethanol decreases the overall performance of the fuel cell and most of the reported results use some additional oxidant agent (usually water) [16,19–21]. More importantly, studies demonstrating long-term stability tests on ethanol are seldom reported. Thus, in the present study, to ensure the stability of the studied fuel cells we have investigated the SOFC operation on ethanol in harsh dry conditions (without adding water), inspired by the gradual internal reforming (GIR) [4,28]. The main idea of GIR is that the fuel is progressively reformed along the anode (the reactor) with only an initial addition of a small amount of water [4]. Such small amount of water is needed at the fuel inlet of the anode (reactor) to initiate the reforming activity [4,28]. Water plays partly the role of controlling the activity, making both catalytic and electrochemical functions intimately mixed together. Conceptually differently, the results here presented were obtained by separating catalytic and electrochemical reactions in two different layers of the anode [29–32].

The reactions of the direct ethanol single cell with catalytic layer are depicted in Fig. 1.

The role of the catalytic layer is to convert most of the fuel into H_2 and CO_2 by steam reforming before reaching the Ni-YSZ anode, thus preventing carbon deposition at the cermet. The catalytic reaction needs water to proceed. Water is provided by the electrochemical reactions at the cermet while the catalytic reforming reaction provides H_2 for the cermet. The global reaction for ethanol steam reforming results in six molecules of hydrogen, which are ideally converted to 12 electrons by the electrochemical oxidation of H_2 reaction at the anode/electrolyte interface. Thus, dry ethanol theoretically results in a number of electrons six times higher than that of the reaction of pure hydrogen. Moreover, water produced in the anode is in excess for the stoichiometric steam reforming. This operating procedure was previously demonstrated for electrolyte-supported button cells running with dry fuels such as methane and ethanol [22,29,31]. The catalytic layer was composed of $Ce_{0.9}Gd_{0.1}O_{2-x}$ promoted with Ir in trace amounts (Ir-CGO). This catalyst was shown to be active in both methane and ethanol reforming while being highly resistant to carbon deposition in water deficient conditions (conditions thermodynamically favorable to carbon formation). Two main aspects were investigated in previous reports: the catalytic activity for fuel conversion in SOFCs, and short-term stability [22,29–32]. Nonetheless, fuel cell performance in such previous studies was limited by a relatively low current output due to thick electrolyte supports [22,29–32]. As compared to electrolyte-supported cells, the anode-supported ones exhibit both higher Ni content and higher reaction rates that could favor carbon deposition. Additionally, mass transport of reactants and reaction products through the electrode must be preserved when the active layer is added to the anode support. Such features are potentially detrimental for the performance of anode-supported SOFCs with a catalytic layer. Therefore, validating the concept of a bilayer anode in high-performance direct-ethanol SOFC is paramount for
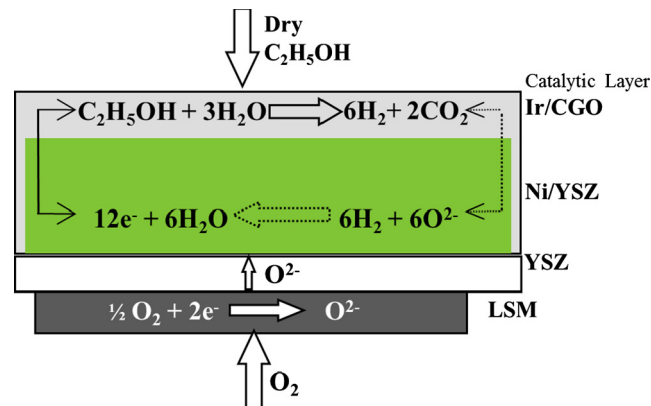

Fig. 1. Schematics of the anode supported cell (not in scale) and the theoretical reactions taking place in each component.