SOFC's Interconnects Materials Development

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Abstract

A short history of interconnects in high and intermediate temperature solide oxide fuel cells form those based on ceramics to those made of metals.

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1. Introduction

Last two decades have witnessed significant progress in the research and development of solid oxide fuel cells (SOFCs), driving them closer to the ultimate goal of commercialization. To accumulate the voltage output for practical applications, single cell is rarely utilized, instead, multiple cells are stacked in either electrical series or parallel or both where an interconnect is required for connecting the cells. In essence, interconnect, physically separates yet electrically connects the anode of one cell to the cathode of the other. Specifically, it provides electrical connection between anodes of one individual cell to the cathode of the neighboring one. It also acts as a physical barrier to separate and to seal the two compartments (i. e. cathode and anode) in order to prevent harmful gases mixing (e. g. oxygen and hydrogen) and to avoid the eventual reduction of the cathode or oxidation of the anode due to leakage. It is also important to not forget that interconnects have also a structural role to keep solid and transportable the stack.

As the interconnect is required to serve multiple roles in the SOFC stack, the material requirements for the SOFC interconnect are the most demanding among all cell components, so, in order to perform their intended functions, interconnects should have the following characteristics:

- Under the SOFC operating temperatures and atmospheres (oxidizing at cathode and reducing at anode), interconnect must exhibit excellent electrical conductivity with preferably nearly 100% electronic conduction. This implies that not only the electronic transference number should be high, but also the absolute magnitude of the electrical conductivity should be reasonably large. Ideally, the ohmic loss generated as a result of the introduction of interconnects is so small that the power density of a stack does not suffer a prominent drop as compared to an individual cell.
- Interconnect should demonstrate adequate stability in terms of dimension, microstructure, chemistry, and phase at operating temperature around 800 °C in both reducing and oxidizing atmospheres, considering that they are exposed to oxidant on one side and fuel on the other. Any dimensional change in the presence of oxidizing and reducing atmospheres is likely to cause mechanical

stresses whose magnitude may be large enough to initiate cracking or warping to the sealing, thus drastically degrading the overall stack performance. The microstructure of interconnect should remain relatively stable throughout the entire range of chemical potential gradient so that no appreciable variation of electrical conductivity develops during its expected lifetime service.

- It should have excellent imperviousness for oxygen and hydrogen to prevent direct combination of oxidant and fuel during fuel operation.
- Regarding ambient and operating temperatures, the thermal expansion coefficient of interconnect (TEC) should match well those of electrodes and electrolyte, so that the thermal stresses developed during stack startup and shutdown could be minimized.
- No reaction or inter diffusion between interconnect and its adjoining components, specifically, anode and cathode, is allowed to occur under operation conditions. The desired chemical compatibility is of extreme importance and constitutes a challenging task for SOFC stack.
- The interconnect should possess fairly good thermal conductivity: 5 W/(m.K) is considered to be an acceptable lower limit [1].
- Excellent oxidation, sulfidation and carburization resistances are requisite attributes for interconnect to qualify for application in SOFC-like environments.
- The interconnect should be easy to fabricate, which is a key point in determining the feasibility of large-scale manufacture. The costs of raw materials as well as fabrication processes for the interconnect are also desired to be as low as possible so that they will not present major obstacles to commercialization.
- The interconnect should also exhibit adequate strength and creep resistance at elevated temperatures. This requirement is of special relevance to the planar SOFC where the interconnect serves as a structural support.

2. Ceramic Interconnects

Ceramic interconnects based upon complex ceramic oxides with perovskite structure have been subject of intensive study over the past several decades. It was found that only a few such oxide systems can fulfill the rigorous requirements for the interconnect materials in SOFC. Lanthanum chromite ($LaCrO_3$) is currently the most common candidate material since it demonstrates reasonably high electronic conductivity in both fuel and oxidant atmospheres, moderate stability in the fuel cell environments as well as fairly good compatibility with other cell components in terms of phase, microstructure and thermal expansion. In order to improve the electrical conductivity as well as to modify the TEC, $LaCrO_3$ is often doped at lanthanum or chromium or both sites of the perovskite block unit for practical applications. Given the wide spectrum of oxygen partial pressures the interconnect is exposed to in SOFC environments, the implications for the dependence of the compensation mechanism on the oxygen partial pressure is of particular significance when doped $LaCrO_3$ is utilized as interconnect. Under oxidizing atmosphere such as oxygen or air at the cathode where the oxygen partial pressure is relatively high (10^{-7} to 10^{-4} atm), conductivity is noticeably promoted due to the induced Cr^{3+} to Cr^{4+} transition via the electronic compensation mechanism. On the other hand, in reducing environments such as fuel gases at the anode where the oxygen partial pressure is low (10^{-8} to 10^{-18} atm), the conductivity is considerably retarded because of the occurrence of oxygen vacancies via the ionic compensation mechanism [2]. It naturally turns out that the electrical conductivity of the doped $LaCrO_3$ in reducing atmosphere like hydrogen is significantly lower than that in oxidizing atmosphere like air [3]. Under such condition, a conductivity gradient across the doped $LaCrO_3$ is established that serves as an interconnect in the SOFC environments, considering that it is exposed to fuel on one side and oxidant on the other. Fortunately, the overall conductivity of the doped $LaCrO_3$ is still sufficient for that the operating temperature is above 800 °C [4]. As the temperature drops below 800 °C, the electrical conductivity of the doped $LaCrO_3$ is reported to experience a substantial decline [5]. This restriction renders it virtually useless for intermediate temperature SOFCs operating in the temperature range of 600-800 °C. Study of effects of many dopants incorporated into the $LaCrO_3$ ceramic on both TECs and electrical conductivities showed that:

- cobalt doping significantly increases the electrical conductivity, unfortunately, the TEC also exhibits considerable increase [6, 7];
- iron doping slightly improves the electrical conductivity while lowering TEC [8];
- nickel doping results in a drastic increase in electronic conductivity and a transition to a metallic conductor typical for $LaNiO_3$, but, the stability and solid solution limit are considerably lower than cobalt and iron counterparts [9];
- magnesium doping enhances electrical conductivity, while the TEC is hardly influenced [10];
- copper doping promotes both electrical conductivity and TEC [11];
- strontium and calcium doping remarkably enhance electrical conductivity, while TEC is also considerably increased [12-14];
- vanadium increases donor doping at the chromium site to reduce overall acceptor concentration. It is not surprising that both electrical conductivity and TEC decline as a result of vanadium doping [15];
- double acceptor doping at both lanthanum and chromium sites generally brings about significant enhancement in electrical conductivity, but the concomitant increase in TEC is unfavorably large. One major obstacle to mass production of ceramic interconnects like LaCrO3 or doped LaCrO3 is their extremely inferior sintering behavior in air due to the easy volatilization of Cr (VI) species. The poor sinterability of $LaCrO_3$-based ceramics has been attributed primarily to the development of a thin layer of Cr_20_3 at the inter-particle neck at the initial stages of firing [16]. It was also noted that chromium evaporation resulting in chromium deficient composition impedes sintering. Beside this, ceramic interconnects have high cost and warping. The warping issue is related to a tendency to partially reduce at the interface between the fuel gas and interconnect causing the component to warp and the peripheral seal to break.

3. Metallic Interconnects

To address the acute problems associated with ceramic interconnects, metal materials were initially envisaged to replace them as interconnects for electrolyte-supported planar SOFC. The invention of anode-supported planar SOFC design that has progressed considerably over the past several years is a major impetus behind the innovation in interconnect. Obviously, there are many advantages in preparing the interconnect from a metallic material instead of a ceramic material. Since the electrical conductivity of metallic materials is realized via the migration of valence electrons, their electrical conductivities are generally several orders of magnitude larger than those of acceptor- doped $LaCrO_3$ ceramics. Hence, the ohmic losses in the metallic interconnect are small enough to be neglected. More importantly, unlike the ceramic interconnect, the electrical conductivity of metallic interconnect is independent of oxygen partial pressure that typical stretches over a wide range for SOFC. In particular, metallic interconnect is favored over the ceramic one because of their low cost, easy manufacture, and good workability. It is really important considering that an oxide layer inevitably develops on the surface of metals exposed for a long time to oxidizing environment, it is imperative that the prospective metallic interconnects display exceptionally slow growth of scale over the projected service lifetime (40000 h) of the SOFC. Most importantly, the oxide scale formed should exhibit sufficiently high electronic conductivity so that the ohmic losses do not constitute a major source of stack performance degradation. The oxides should also be chemically stable, dense, free of defects, and strongly adherent to the metal on the scale/substrate interface. Another technical problem to be handled is the thermal expansion mismatch between metallic interconnect and the rest of the ceramic SOFC components. In particular, when it comes to the rapid heating and cooling frequently encountered in such applications as auxiliary power unit for automotive and portable power sources for laptops, the requirement for thermal compatibility is more rigorous. As metallic materials usually have inherently higher thermal expansion coefficients than ceramic ones, any measure to reduce the thermal expansion and shrinkage from the alloy design standpoint is acceptable provided that other critical properties are not compromised. All the above problems of metallic interconnect are due to the high operating temperature of the SOFC, and can be partially or entirely mitigated by lowering its working temperature. Therefore, in parallel with the attempt to replace $LaCrO_3$ with metal, there is also a concerted effort to reduce the operating temperatures of SOFC, preferably to between 600 °C and 800 °C. Currently, there are no commercially available alloys that fulfill all the criteria to be viable interconnects for SOFC. It is possible to divide suitable metallic materials in the following groups:

- Chromium based alloys: they were initially developed as a replacement of ceramic interconnects for electrolyte-supported planar SOFC. They are favored because of their moderate oxidation resistance and fairly good corrosion resistance provided by the formation of Cr_2O_3 scale in the presence of oxidant. In addition, the binary metal oxide Cr_2O_3 has comparatively large electronic conductivity [17]. Moreover, the thermal expansion behaviors of these alloys in the temperature range of 25 °C to 1000 °C exhibit considerable resemblance to that of the other ceramic components. The major drawback of chromium-based alloys as metallic interconnects is their unacceptably high oxidation rate and the formation of volatile gaseous Cr (VI) species at the fuel cell operating temperatures [18, 19]. These high valence Cr species such as CrO_3 (g) and $Cr(OH)_2O_2$ (g) develop literally simultaneously with the formation of Cr_2O_3 scale at the cathode side of the interconnect. Further oxidation of Cr_2O_3 scale usually takes place at the higher oxygen partial pressure end of the cathode prior to the electrochemical reduction of oxygen. Due to their unusually large vapor pressures, these species have been shown to diffuse into and interact with electrodes, leading to a change in the air electrode composition and formation of new phases [19]. The electrochemical performance of SOFCs is severely damaged due to the generation of volatile Cr species at the cathode of the fuel cell. Additionally, these species can interfere adversely with the oxygen reduction reaction by taking up electrons at the cathode, especially at the low end of oxygen partial pressure, resulting in the deposition of Cr_20_3 at the electrode/electrolyte interface.

- Iron based alloys: have some apparent advantages over chromium-based ones in terms of high ductility, easy machinability and low cost. Presently, two types of iron based alloys are being explored because of their relatively low TECs namely, Fe/Cr/Mn and Fe/Cr/W, chromium enhance the formation of corrosion-resistant Cr_2O_3 scale while manganese addition is intended to develop surface scales consisting of the spinel Cr_2MnO_4 or a spinel layer on the top of an inner Cr_2O_3 layer. Hence the problem of chromium volatilization encountered in chromium-based alloys also occurs in these alloys.
- Nickel based alloys: these alloys are resistant to high temperature and typically include nickel, chromium, iron and manganese. They are also attractive because of their slower oxidation kinetics than their stainless steel counterparts. The apparent disadvantage in their application as interconnect is their larger thermal expansion coefficients as compared to iron-based alloys.

In order to reduce the rate of scale growth on the surfaces of chromia-forming alloys, as well as prevent the chromium vaporization on the cathode side, coating with a perovskite or spinel ceramic layer has been suggested and currently is being extensively investigated. Another option is to coat these alloys with an oxide layer that subsequently reacts with chromia to form a chromite (or chromate). The resulting compound should exhibit better electrical conductivity as compared to chromia and be capable of retarding further oxidation of chromium and suppressing the volatilization of chromium.

Successful development of interconnect materials is vital to the large-scale commercialization of SOFCs technology. To address the challenge of excessively large contact resistance on short exposure to SOFC environments, new metallic interconnects should be developed based on a fundamental understanding of oxide growth kinetics and conductivity. This should be the focus of future study. Other recommended avenues of investigation include further lowering the operating temperature of SOFC to 700 °C or even 600 °C without compromising the fuel cell electrical efficiency. This essentially allows current commercially available stainless steels to be utilized directly as interconnects. Coating metallic interconnects with oxides of complex structure has proved to be an effective approach to reduce the contact resistance but this practice can be put into widespread application provided that costs of both coating materials and fabrication techniques are substantially curbed.

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