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Lanthanum doped strontium titanate - ceria anodes: deconvolution of impedance spectra and relationship with composition and microstructure

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HIGHLIGHTS

- Differential EIS and microstructure analysis revealed 3 anode processes.
- None of the processes were assigned to gas diffusion impedance.
- The dominant low frequency process was attributed to chemical capacitance.
- CGO surface reactions is the kinetic limitation for the dominant anode process.
- 30 redox cycles did not induce degradation but even anode activation.

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ABSTRACT

Electrochemical performance of ceramic (Ni-free) SOFC anodes based on $La_{0.2}Sr_{0.7}TiO_{3-\delta}$ (LST) and $Gd_{0.1}Ce_{0.9}O_{1.95-\delta}$ (CGO) is thoroughly investigated. Microstructures and compositions are systematically varied around the percolation thresholds of both phases by modification of phase volume fractions, particle size distributions and firing temperature. Differential impedance spectroscopy was performed while varying gas composition, electrical potential and operating temperature, which allows determining four distinct electrode processes. Significant anode impedances are measured at low frequencies, which in contrast to the literature cannot be linked with gas concentration impedance. The dominant low frequency process (~1 Hz) is attributed to the chemical capacitance. Combined EIS and microstructure investigations show that the chemical capacitance correlates inversely with the available surface area of CGO, indicating CGO surface reactions as the kinetic limitation for the dominant anode process and for the associated chemical capacitance. In anodes with a fine-grained microstructure this limitation is significantly smaller, which results in an impressive power output as high as 0.34 Wcm^{-2}. The anodes show high redox stability by not only withstanding 30 isothermal redox cycles, but even improving the performance. Hence, compared to conventional Ni-cermet anodes the new LST-CGO material represents an interesting alternative with much improved redox-stability.

1. Introduction

1.1. Ceramic composites as an alternative to nickel based cermet anodes

Anodes for Solid Oxide Fuel Cells (SOFCs) and cathodes for Solid Oxide Electrolysis Cells (SOECs) that can withstand severe conditions and provide high performances are of great practical and scientific interest [1–5]. Whilst the state-of-the-art anode material Ni-YSZ provides an excellent catalytic activity and high power output, it is prone to various degradation phenomena due to the presence of nickel. For example, nickel tends to coarsen at high temperatures [6,7] and at high water vapour partial pressures [7,8]. The coarsening results in loss of phase contiguity and in a reduction of the electrochemically active three-phase boundary length (3PB). Nickel as a catalyst is sensitive to fuel impurities, whereby it shows harmful reactivity already at low ppm levels (H_2S, tetrahydrotiophene – THT, HCl etc.) [9–13]. Ni reactivity can sometimes also cause anode destruction due to the formation of a carbon filament [14–16]. However, the most detrimental problem of nickel is its poor redox stability due to the volume change associated with NiO formation at high oxygen partial pressures (redox) [17–23].

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The change of redox conditions can be caused either by a sealing failure, by internal and external gas delivery failure, by regular start-up and shut-down procedures or by working at low cell polarisations at high current densities. Microstructure modifications to improve the redox-stability of cermet anodes are among the most widely applied strategies to solve Ni stability issues. However the mentioned degradation phenomena cannot be completely suppressed, as long as Ni serves as primary electronic conductive phase, i.e. with Ni volume fraction above the percolation threshold [22]. Hence, new material concepts are required for the future SOFC anode technology whereby Ni is replaced by an electronic conducting phase with better redox-stability.

Over the past decade mixed ionic-electronic conductors (MIEC) based on ceria have been identified as potential anode material. Ceria is recognized to possess sufficient redox stability [24,25] and relatively high ionic conductivity. However, cerium oxides similarly to several other MIEC oxides such as La-Sr-Cr-Mn [26–28], Y(Sc)-Ti-Zr [29–31] and Sr-(Co, Mn)-Mo [31–33] exhibit insufficient electronic conductivity under anode atmosphere.

Another redox stable material which exhibits good electronic conductivity is donor doped (La,Nb)$SrTiO_3$, [34–38]. This type of perovskite can achieve also interesting for practical usage catalytic activity and ionic conductivity. However, all those properties are very sensitive to the crystal chemistry and chemical composition. It turns out that the synthesis of phase-pure titanate is a challenging task and that the formation of phase impurities and associated compositional changes can negatively affect the conductivity and other material properties [38,39]. Nevertheless, over the last years the authors have established synthesis routes that allow us to produce phase pure titanate-based perovskites with a relatively high electronic conductivity. For high performing SOFC anodes this perovskite material has to be combined with an additional phase that provides catalytic activity and ionic conductivity. In previous studies on composite anodes, the titanates were combined with zirconia (YSZ, SSZ) and with nickel (as catalyst, not as electric conductor, i.e. below percolation threshold). For those composites, reaction is facilitated by the nickel catalyst and takes place at the active three phase boundary (3PB) between electronic and ionic conducting phases. Literature reports show promising results [40–42], which encourage further investigations of such ceramic composites, which were so far only marginally addressed in literature. In particular, the influence of nanostructured microstructures on the electrochemical performance of titanate-based anodes has hardly been investigated, mainly due to experimental difficulties related to the fabrication of phase pure, nanoscaled titanates. For the present study we have synthesized ceramic anodes consisting of phase pure titanate and Gd-doped ceria (CGO) with varying microstructure and composition. Quantitative microstructure analysis is combined with detailed electrochemical characterization (impedance spectroscopy) in order to reveal the anode reaction mechanism and to understand the performance limitations associated with specific microstructure-property relationships.

1.2. *The electrochemistry of ceria-based anodes*

In reducing atmosphere ceria is a MIEC, which also has excellent catalytic properties towards fuel oxidation because ceria acts as oxygen donor. The reaction mechanism of MIEC based electrodes is very different from composites with phases that have purely electronic (e.g. Ni) and purely ionic conductivities (e.g. YSZ). For the interpretation of the impedance spectra it is important to understand the specific properties of the MIEC phase and the associated reaction pathways.

Electronic properties of ceria (CeO_2) are enhanced by addition of trivalent dopants such as Gd^{3+}, which results in non-stochiometric Gd-doped ceria (CGO: $Ce^{4+}_{1\text{-}2\delta}\ Gd^{3+}_{2\delta}\ O^{2-}_{2-\delta}$). The active electronic species of CGO are thus the reduced Ce^{3+}cations, with relative negative charge compared to Ce^{4+} and which can be interpreted as an electrons, whereas the active ionic species are the oxygen vacancies (V_O). Under reducing atmosphere, some oxygen is released from CGO, which leads to an increase of the oxygen vacancy concentration (c_{ion}). The formation of oxygen vacancies is then coupled with the reduction of Ce^{4+} to Ce^{3+} (c_{eon}) in order to maintain charge neutrality. As a consequence, the electronic conductivity of CGO increases when lowering the pO_2 (e.g. upon reduction under anode conditions). [43] presented the following quantitative description for the pO_2-dependency of Ce^{3+}-concentration (c_{eon}):

$$c_{eon} = 2\delta c^0_{eon} = K_T\ pO_2^{-0.25} \tag{1}$$

where δ is the oxygen non-stochiometry and c^0 represents the Ce^{3+}concentration at standard conditions (1 atm pO_2). The combination of MIEC properties with catalytic activity makes CGO an interesting candidate for SOFC anodes. However, since the electronic conductivity of CGO is rather low (~0.1 S/cm @ 850 °C and $pO_2 = 10^{-18}$ bar), it is usually combined with Ni (~25′000 S/cm @ 850 °C) or with another electronic conducting phase. In the present study we use LST (1 - 20 S/cm @ 850 °C) [38] instead of Ni, in order to avoid the mentioned problems like Ni-oxidation, coking, S-poisoning etc. Nevertheless, for thin films and for so-called patterned electrodes that entirely consist of CGO (without any Ni or LST) excellent anode performances have been reported [44–46]. In these thin film anodes, transport distances are very short, and therefore eventual transport resistances associated with the low electronic conductivity of CGO are not relevant. The anode performance of CGO thin films is thus mainly controlled by the kinetics of the hydrogen oxidation reaction (HOR), which involves the following steps [44]:

a) adsorption and dissociation of hydrogen on the CGO surface (H_{ads}),
b) formation of adsorbed oxygen (O_{ads}) due to oxygen donation from CGO bulk,
c) formation of oxygen vacancy coupled with reduction of Ce^{4+} to Ce^{3+} (this step is directly linked with b),
d) first recombination of H_{ads} with O_{ads}, which produces OH_{ads},
e) second recombination of H_{ads} with OH_{ads}, which produces H_2O_{ads},
f) desorption of H_2O_{ads} from the CGO surface, which produces steam (H_2O_g).

Recently, experimental evidence was presented which suggests that the recombination reactions (d, e) represent the rate determining steps for hydrogen oxidation reaction (HOR) [44] in CGO thin film anodes. Other studies interpreted hydrogen adsorption as rate limiting step [47]. But of course, the HOR rate also depends on operating conditions and experimental parameters such as temperature and gas compositions such as pO_2, pH_2O or pH_2.

Characterization of CGO thin film anodes by impedance spectroscopy (EIS) typically reveals Nyquist plots with a single, dominant semicircle in the low frequency (LF) range with a peak frequency $f_{peak} = 0.1–1$ Hz [43]. Because diffusion is negligible in thin films, the frequency is mainly controlled by the kinetics of HOR, i.e. by adsorption (a) or by recombination steps (d, e) on the surface. The LF impedance is associated with a capacitance, which scales with the thickness of the CGO films [43].

In electrochemistry, capacitance (C) of electrodes is usually explained by the accumulation of charges (q) at interfaces (charged double layers) upon variation of an external potential (ϕ):

$$C = dq/d\phi \tag{2}$$

However, Chueh et al. [43] provided experimental evidence by in-situ XPS measurements during EIS analysis, which shows that the low frequency impedance of CGO anodes is not due to a surface capacitance, but rather due to a so-called chemical capacitance, which is caused by the accumulation of charges (z_i) and charge carrier concentrations (c_i) in the bulk of the CGO phase, which is described as follows: