Structural features of the magnetron sputtered CuO/GDC anodes for solid oxide fuel cells

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Abstract. The paper presents the results of the research of structure of a thin film CuO/Ce0.9Gd0.1O2−δ (CuO/GDC) anode for solid oxide fuel cells (SOFCs) prepared by magnetron sputtering. Cu-based anode materials of SOFCs are of great interest because they exhibit greater tolerance to sulfur-containing fuels than the widely used Ni-based composite anodes. After deposition, annealing in air and reducing atmospheres, the composition, microstructure and crystallinity of the films were characterized using energy dispersive X-Ray spectroscopy, scanning electron microscopy and X-ray diffractometry, respectively. The as-deposited film consists of cubic fluorite structures of GDC and Cu2O and has a dense, homogeneous structure, in which Cu is evenly distributed over the volume of the film. However, it was shown that, strong Cu segregation is observed in CuO/GDC films, after reduction in hydrogen at a temperature of 750 °C, with the formation of massive agglomerates on the surface. The influence of pre-calcination of the as-deposited films at 1000 °C and 1200 °C on their structure was studied. It is shown that annealing at a temperature of 1000 °C does not prevent the agglomeration of Cu in a reducing atmosphere, while Cu evaporation is observed if annealing temperature is 1200 °C.

1. Introduction
Solid oxide fuel cells (SOFCs) have received great attention due to their potential for providing a highly efficient and ecologically friendly method of generating electricity. The optimization of materials and of production processes are fundamental issues for the performance improvement of SOFCs. When hydrogen is used as a fuel in solid oxide fuel cells with Ni-based anodes, they experience relatively low degradation rates and fast electrochemical kinetics. But if synthesis gas is used as fuel, Ni could be easily poisoned by contaminants like sulfur or carbon [1, 2]. Carbon deposition reduces the cell performance by blocking the anode reaction sites and damaging the microstructure of Ni in the anode. In recent studies [3, 4], Cu has been suggested as an alternative to Ni as the electronic conductor in SOFC anodes. Recently, Cu/yttria stabilized zirconia (YSZ), Cu/samaria-doped ceria (SDC) and Cu/gadolinia-doped ceria (GDC) anodes [5–9] have been developed and tested, showing good electronic conductivity and tolerance towards sulfur-containing fuels [10]. However, Cu has a low catalytic activity for hydrogen or hydrocarbon electrochemical oxidation, and so doped ceria should be used instead of yttria stabilized zirconia in order to improve the cell performance.
Despite the advantages of Cu-based composite anodes, it is difficult to apply conventional ceramic processing methods to fabricate Cu-containing SOFCs due to the low melting point of Cu (that is 1085 °C). Presently they are manufactured using a multi-step wet ceramic technique that requires more processing and firing steps and not attractive for mass production. Furthermore, high sintering temperatures increase interdiffusion of elements between adjacent cell layers.

To avoid the treatment of copper oxide at high temperatures (sintering), several approaches have been proposed, such as infiltration of metal salt solutions in pre-sintered porous ceramic scaffolds [11], plasma spraying [12] and electroplating [13]. The low melting temperature of Cu also means that, once the oxide is reduced, the cell operating temperature must be limited to prevent copper phase coarsening, which would result again in decreased cell performance. Due to this fact, Cu-based anodes are suitable for operating temperatures lower than 700 °C.

CuO/ceria-based anodes fabricated by sintering were employed using Li-doped gadolinia-doped ceria electrolyte [14], reaching 200 mW·cm⁻² power density peak at 700 °C. A method applying co-pressing and ion impregnation was used to fabricate SOFCs with thin GDC electrolyte and Cu/GDC based anode [15]. When H₂ was used as fuel, the maximum power densities at 600 °C achieved 265 mW·cm⁻². Nevertheless, the overall performances are still far to be compared with those obtained using conventional Ni-based anodes [8]. Additional investigations are therefore required to optimize Cu/GDC-based anodes and point out their potential performances.

As far as we know, magnetron sputtering has never before been used to form Cu/GDC anodes. Although it is known that magnetron sputtering allows the deposition of thin layers of nickel-containing anodes with a nanoporous structure, which are suitable to improve the efficiency of the SOFCs [16–20]. It was shown that Ni/YSZ and Ni/GDC thin-film anodes require post-annealing at high temperature (1200 °C) to stabilize their microstructure, because the nickel-containing anodes tend to Ni coarsening. The aim of the present work is to investigate the microstructural characteristics of magnetron sputtered CuO/GDC layers and their changes after reduction in hydrogen atmosphere and heat treatment.

2. Methodology and materials

CuO/GDC thin films were deposited by reactive magnetron co-sputtering of Cu (99.995% purity) and Ce₀.₉Gd₀.₁ targets with diameter of 75 mm. Sputtering was carried out in oxygen-argon atmosphere at working pressure of 0.2 Pa, using a pulse bipolar magnetron supply (APEL-M-BP, Applied Electronics Ltd.) at pulse repetition frequency of 80 kHz and positive pulse duration of 4 μs. The argon and oxygen flow rates were fixed at 26 and 33 sccm, respectively. Targets were positioned at 45° to the fixed substrate holder. The distance between the magnetron target center and substrate was 80 mm. Prior to film deposition, the substrates were heated to 450 °C. Afterward, the substrate surface was cleaned for 30 s by the ion beam generated by the ion source with a closed electron drift with 1000 V discharge voltage and 30 mA discharge current to improve the film adhesion. The zirconia co-doped with 10 mol% Sc and 1 mol% Ce (10Sc1CeSZ) electrolyte plates (NEVZ-CERAMICS) with a thickness of 250 μm were used as substrates. The discharge power of a Ce-Gd magnetron was 1 kW in all experiments. The discharge power of the Cu magnetron ranged from 100 to 700 W to control the volume content of CuO in the film. Some samples were annealed in an air atmosphere at temperatures of 1000–1200 °C for 1 hour. The heating/cooling rate was 300 °C·min⁻¹. After that, some samples were reduced in a hydrogen atmosphere at a temperature of 750 °C for 2 hours.

X-ray diffraction (XRD) analysis of the films was performed using a Shimadzu XRD-6000 diffractometer (Cu Kα radiation, with 40 kV and 30 mA) and PDF-4+ database. The scanning electron microscope (SEM; FEI Quanta 3D 200) imaging of the films was performed to observe the uniformity of their microstructure. Energy-dispersive X-ray spectroscopy (EDX, Pegasus 4000) was performed to determine the content of Cu in the films. Thickness of the deposited films was measured by MII-4 interference microscope (LOMO corp.).
3. Results and discussion

Figure 1 shows the dependences of CuO/GDC films deposition rate and Cu content in the films on discharge power of Cu magnetron. The copper content in the films was determined after films reduction in hydrogen. As expected, an increase in Cu target power results in an increase in the deposition rate and Cu content in the film. In the examined range of target power these parameters changed linearly with the applied power. This indicates that it is possible to quite simply control the Cu content in the film by changing the power of the Cu magnetron.

![Figure 1. The dependence of deposition rate of CuO/GDC films and the content of the Cu in the films on Cu magnetron power.](image1)

Figure 2a shows the surface SEM image of 2 µm thick CuO/GDC film deposited at power of Cu magnetron of 500 W. The as-deposited film has a dense, homogeneous structure with a Cu content of about 42 at. %. However, after reduction of CuO/GDC anode in a hydrogen atmosphere, Cu agglomeration occurs on the surface of the film, with the formation of massive agglomerates (figure 2b).

![Figure 2. Surface SEM images and results of EDX analysis of thin-film CuO/GDC anodes on 10Sc1CeSZ substrates: as-deposited (a) and after reduction in hydrogen (b).](image2)

As can be seen from the SEM image, Cu agglomeration occurs on the surface of the film, in analogy with what happens when nickel-containing thin films are reduced at high temperature [16, 19, 20]. This process caused the appearance of Ni granules on the surface of the film, which resulted in a decrease in the Ni content in the film volume and a change in its microstructure.

Garcia-Garcia et al [17, 18] proposed to use post-annealing in air (pre-calcination step) to solve the problem of Ni agglomeration in Ni/YSZ, Ni/GDC and Ni/YSZ/GDC thin-film anodes. The purpose of
this heat treatment is as follows. During heating in H₂, highly dispersed NiO in as-deposited film is rapidly reduced to Ni metal, which has a much less favorable interaction with the ceramic (YSZ or GDC). Moreover, hydrogen, even at modest temperatures and pressures, greatly enhances the mobility of Ni [21]. Both factors lead to growth of large metallic Ni particles which are expelled from the film volume rather than being incorporated in it.

After pre-calcination of the as-deposited film the highly dispersed NiO component undergo particle growth, resulting in formation of crystalline NiO grains distributed over the YSZ or GDC matrix. NiO adheres well to the second component due to a favorable oxide-oxide interfacial interaction. During subsequent H₂ treatment, the NiO crystallites act as fixed nucleation centers that undergo conversion to metallic Ni particles uniformly distributed within the ceramic structure.

Therefore, we used this approach in fabricating the CuO/GDC thin-film composite anode, and the influence of the annealing temperature on its structural and morphological properties was investigated. The annealing temperature was 1000 and 1200 °C. After annealing, the samples were reduced in hydrogen.

After annealing at 1000 °C the CuO/GDC anode acquires a fine-grained porous structure (300 nm grain size) with large particles (1–3 µm) on the surface (figure 3a). On some of the larger particles, crystallographic facets can be observed. After the reduction of this film in hydrogen, isolated oblong Cu particles are formed on its surface with characteristic dimensions approximately in the range 0.5–4 µm (figure 3b). But the amount of copper segregated on the film surface is significantly less than on the film reduced without prior annealing (see figure 2b).

Figure 3. Surface SEM images and results of EDX analysis of thin CuO/GDC films: annealed at a temperature of 1000°C (a) and after reduction in hydrogen (b).

From the microphotographs of the surface of the CuO/GDC anode annealed at 1200°C, it can be concluded that anode film acquires a granular structure consisting of GDC grains with size of 2–2.5 µm (figure 4a). The GDC grain size increased from 300 nm to 2–2.5 µm with an increase in the annealing temperature from 1000 to 1200 °C. Agglomerate formation on the surface of the film is not observed. After the reduction in hydrogen the film changes insignificantly and consists of sintered GDC grains with clear boundaries. Chemical analysis showed that Cu in both the annealed and reduced films is absent. Therefore, the structure of the film changes insignificantly after reduction.

According to the published data, the vapor pressure of CuO at a temperature of 1000 °C is approximately 1.3·10⁻² Pa [22]. For comparison, for nickel oxide, even at a higher temperature (1165 °C), the saturated vapor pressure is two orders of magnitude smaller and amounts to 2·10⁻⁴ Pa [23]. This means that the annealing temperatures used for nickel-based thin-film anodes are not suitable for Cu-based anodes.
X-ray phase analysis showed that after deposition the film consists of cubic fluorite structures GDC and cuprite (Cu$_2$O) (figure 5, curve 1). It infers that sputtered Cu atoms reacted with oxygen in plasma which formed Cu$_2$O. Formation of cuprite indicates a deficit of oxygen atoms in the film. The lattice parameters corresponding to the GDC and Cu$_2$O phases were calculated from the XRD pattern using PowderCell 2.4 computer program, and the values are found to be 5.4952 and 4.2982 Å for GDC and Cu$_2$O, respectively. The Debye-Scherer relation was used to calculate the crystallite sizes of CuO/GDC films from the obtained XRD patterns. The crystallite sizes are 43 and 50 nm for GDC and Cu$_2$O phases, respectively.

![Figure 4. Surface SEM images and results of EDX analysis of thin CuO/GDC films: annealed at a temperature of 1200 °C (a) and after reduction in hydrogen (b).](image)

After annealing at 1000 °C, the film is saturated with oxygen and Cu$_2$O phase is transformed into CuO (figure 5, curve 2). The intensity of the reflexes of both phases GDC and CuO after annealing increases, indicating an improvement in the crystallinity of the film. The formation of CuO phase can be understood by the following reaction, Cu$_2$O + $\frac{1}{2}$O$_2$ $\rightarrow$ 2CuO. Lattice parameter of GDC decreased to 5.4130 Å. It means the unit cell became more closely packed. The shift of GDC reflexes to higher 2θ values after annealing is due to the fact that the Ce in the as-deposited CuO/GDC film is partially in the reduced Ce$^{3+}$ state. However during the annealing the Ce$^{3+}$ oxidizes back to Ce$^{4+}$, which leads to

![Figure 5. X-ray diffraction patterns of CuO/GDC films: (1) as-deposited; (2) annealed at a temperature of 1000 °C; (3) annealed at a temperature of 1200 °C.](image)
change in the GDC lattice parameter. CuO exhibits a monoclinic structure with lattice parameters $a = 4.6906 \, \text{Å}$, $b = 3.4167 \, \text{Å}$, $c = 5.1161 \, \text{Å}$, $\beta = 99.3982$. It was observed that interplanar distance of (111) planes of Cu$_2$O increased after annealing. It increased due to the phase transformation Cu$_2$O to CuO. The crystallite sizes are 67 and 22 nm for GDC and CuO phases, respectively. The formation of Cu$_2$O and CuO phases is consistent with the diagram of the state of copper with oxygen [24]. After annealing at 1200 °C, no Cu compounds were detected on the CuO/GDC diffractograms. This is consistent with the chemical analysis of this film.

On the basis of surface characteristics studies, it can be concluded that Cu, similar to Ni in magnetron-sputtered composite films, agglomerates on the surface of the 2 µm thick CuO/GDC film during reducing in H$_2$ by 750 °C. The driving force for Cu migration involves a decrease in the free energy of the Cu/GDC system, due to Cu having a lower surface energy than GDC. A characteristic feature of magnetron sputtering is the formation of a film from atomic flows of a material sputtered from a target. Therefore, CuO or NiO are highly dispersed in the as-deposited magnetron sputtered films. It is known that as the particle size decreases, the melting and evaporation temperatures decrease. This explains the disappearance of Cu from CuO/GDC films annealed at 1200 °C, despite the fact that the melting point of copper oxide is 1326 °C.

Since Cu has a much lower melting point than Ni (1453 °C), at the same temperatures the agglomeration and evaporation processes will be more intense for it. As we have shown above, the use of pre-calcination at 1200 °C, which is successfully used for nickel-containing films, cannot be used for magnetron sputtered copper-based films due to Cu evaporation. Pre-calcination at 1000 °C or below does not give the desired effect, since at this temperature there is no sufficient attachment of CuO to the GDC phase.

One approach for improving thermal stability of Cu-based composites is to use bimetallic electrodes in which Cu provides carbon tolerance and a second metal provides thermal stability.

4. Conclusion
Magnetron sputtering is a good technique for preparation of the Cu-based cermet thin films. However, due to high mobility of Cu at fuel-cell operating temperatures after reduction in hydrogen, the Cu agglomerates on the surface of the film. Preliminary annealing of CuO/GDC films deposited on 10Sc1CeSZ substrates in air at a temperature of 1000 °C allows reducing the Cu mobility, as a result of which, isolated Cu particles in a smaller quantity are formed on the surface of the film. At an annealing temperature of 1200 °C, Cu evaporates from the film and porous GDC layer is formed. Thus, annealing does not solve the problem of Cu agglomeration in magnetron sputtered CuO/GDC SOFC anodes. X-ray phase analysis showed that after deposition, the film consists of cubic fluorite structures GDC and Cu$_2$O; i.e. has a deficit of oxygen atoms. Cubic Cu$_2$O phase transformed to a monoclinic CuO phase after film annealing at 1000 °C.

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