Electroplating of Protective Coatings on Interconnects Used for Solid Oxide Fuel Cell Stacks - DTU Orbit (16/12/2018)

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Solid oxide fuel cell (SOFC) technology can with a high efficiency produce environmentally clean electricity by converting the chemical energy in a fuel to electrical energy. SOFC systems have a high operation temperature, approx. 600-850 °C. Advantages compared to other types of fuel cells, are they can utilize a wide range of fuels, e.g. hydrogen, natural gas and methanol, do not contain noble metals and have a high efficiency.

A major obstacle to the commercialization of SOFC technology is the high degradation rates and costs of the systems. A significant source of degradation is high temperature corrosion of the so called interconnects, which consists of high chromium ferritic steel. In an SOFC stack, interconnects connects the individual fuel cells electrically and mechanically. An interconnect is exposed to a dual atmosphere, with air on the side facing the SOFC cathode and fuel on the side facing its anode. Two high temperature corrosion issues, which both affect the air side of the interconnect, are especially significant, both of: Formation of thick oxide scales on its surface and evaporation of chromium species from the oxide. The oxide scales increases the electrical resistance and the gaseous chromium species can poison the cathode.

Interconnect coatings are a potential solution to reduce the high temperature corrosion issues. An effective coating must consist of a material with the right properties but equally important is the process used for its deposition. It must enable coatings to be deposited with good adhesion, low porosity, uniform thickness, good coverage and importantly at a low cost.

The focus in this project was on electroplated coatings for metallic interconnects. The aim was to reduce the oxidation rate the interconnect when exposed in a cathode side (air) environment. New coatings were developed and their performance and corrosion behaviour was investigated.

Processes were developed for electroplating of coatings consisting of cobalt, the alloys cobalt/tungsten (Co/W) and cobalt/molybdenum (Co/Mo) as well as the composites cobalt/cerium oxide (Co/CeO₂) and cobalt/lanthanum strontium manganite (Co/LSM).

The purpose of the CeO₂ and LSM particles was to reduce the oxidation rate of the steel substrates, using the so called reactive element effect. In addition, the purpose of the LSM particles was to improve the electrical conductivity of the coating, compared to a coating only of cobalt. The purpose of the cobalt was to act as a dense diffusion barrier for chromium in order to prevent chromium evaporation. The coatings were deposited on the steels Crofer 22 APU and Crofer 22 H.

The coatings were tested in a simulated cathode environment (air at 800, 820 or 850 °C). Coatings consisting only of cobalt were also tested in an SOFC stack which was successfully operated time for 3000 h.

The coating only consisting of cobalt oxidized to a Co3O4 spinel after air exposure in the simulated cathode environment. The iron and manganese concentration of the coatings increased as a function of exposure time due to diffusion from the steel. A layer of Cr2O3 formed underneath the oxidized coating. The oxide layers on the composite coated samples were also dual layered, consisting of an outer layer of a cobalt rich oxide and an inner layer of Cr2O3. The particles were distributed in the outer cobalt rich oxide layer.

The alloy coatings did not reduce the oxidation rates of the steels exposed in a simulated cathode environment. The Co/Mo coating was detrimental for the oxidation properties as it resulted in formation of a thick iron oxide scale on the steel. The Co/W coating provided very similar performance to a coating consisting only of cobalt, thus the more complex Co/W alloy electroplating process could not be justified.

The oxide layers on the cathode side of a cobalt coated interconnect exposed in an actual SOFC stack had in most regions a similar composition to that observed in the simulated environment. However, severe corrosion with extensive formation of iron oxides was present in regions where the stack temperature was highest. Extensive diffusion of nickel from the Ni/YSZ anode into the steel was observed. Chromium nitrides had also formed in the interconnect.

The area specific resistance (ASR) of a Ni/YSZ anode in contact and a preoxidized sample of Crofer 22 APU was measured in a simulated anode atmosphere. The ASR was very low (0.2 mΩcm²). It exhibited a temperature dependence typical for a metal. The microstructure of the Crofer 22 APU in the region affected by nickel diffusion was characterized with electron backscatter diffraction and other electron microscopy techniques. The ASR of a Ni/YSZ anode with a CoO2 nickel diffusion barrier layer in contact with Crofer 22 APU was also measured and it was two orders of magnitude higher than without a CeO₂ barrier layer.

Nickel diffusion from the Ni/YSZ anode into the interconnect results in an austenitized diffusion zone at the operating temperature that partially or completely transforms to ferrite during cooling. Other coatings are necessary on the interconnect at the anode side if the microstructure and composition of the interconnect should be maintained. The necessity of such coatings depends on the magnitude of the issue caused by nickel diffusion, which currently is not quantified.

The most promising coating types were after a literature review as well as exposure tests shown to be composite coatings, consisting of cobalt and a reactive element oxide.

The Co/LSM and Co/CeO₂ composite coatings reduced the oxidation rates of Crofer 22 APU and Crofer 22 H greatly, compared to coatings consisting only of cobalt by exposure in air between 800-850 °C. In addition, the Co/LSM coated sample had a very low ASR of approx. 3 mΩcm² after 550 h exposure in air at 800 °C.

The composite coatings may reduce both the contact resistance and oxidation rate of an interconnects. The coatings can be economically deposited on substrates with a geometry relevant for SOFC interconnects.

Hence, are the developed coatings suitable on cathode side of the interconnect and could potentially reduce the degradation rate of an SOFC system and extend its lifetime.