Influence of electrical load on the stability of glass sealings

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The stability of sealing glasses is one of the critical issues concerning the long-term operation of SOFC. Different reasons are responsible for failures of the glass sealings resulting from thermal cycling, stack deformation or chemical degradation due to interactions with fuel gas, interconnectors or protective coatings. Reactions with interconnector materials (for instance Crofer 22 APU) lead to crystalline product layers, which affect the bonding strength and microstructure of the sealing material. Externally applied voltages can force diffusion processes and interfacial reactions between sealing glasses and metallic interconnector materials. As a consequence glass- to-metal bonds will be weakened and the requirements on seals are not fulfilled anymore. Studies on the development of sealing glasses for SOFC often consider intrinsic properties of the glasses such as the TEC, crystalline phases, viscosity and short time chemical compatibility with metallic and ceramic substrates[1]. Several publications also regard the long term stability of the aforementioned glass properties at high temperatures[2,3]. Only a few studies regard the facts that SOFCs sealing glasses are exposed to a dual atmosphere and, depending on the design, to the electrical voltage [4]. No studies are published about interfacial reactions of SOFC sealing glasses in contact with metallic interconnector materials under the influence of electrical voltage in air or in dual atmosphere.

A reliable method to investigate these complex reactions between glass and interconnector materials by regarding effects of a dual atmosphere and electric load is given by tests of model sealings under conditions comparable to the operating conditions of SOFC. Model sealings can be prepared from glass powders which are processed to pastes or tapes. Such samples can be exposed in a dual atmosphere furnace, which allows various fuel compositions; electric load (up to 30V d.c.) and max. temperatures up to 1000 °C for testing (fig. 1).

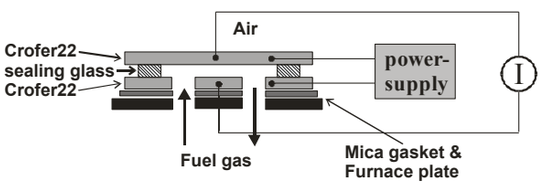


Fig.: Schematic cut of the experimental setup, showing a model sealing with electrical connections placed on the furnace ground plate

During the test the electric resistance of the samples is registered continuously. In figure 2 the area specific resistances of four model sealings treated in a dual atmosphere at 850°C with different electric loads applied across the sealing glass are shown. 30 V is chosen as a maximum voltage because this value corresponds to the open circuit voltage of a SOFC-stack consisting of 30 repeating units. It is seen that maximal resistance reached after short times of testing with applied voltage is increased (after 120 h at 0,7 V and 1,0 V, 80 h at 1,3 V and 30 h at 30 V). Also the decay of the resistances after passing the maximum value increases with higher voltages, indicating different changes in the glass..

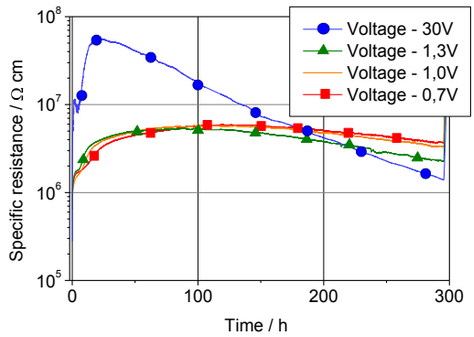
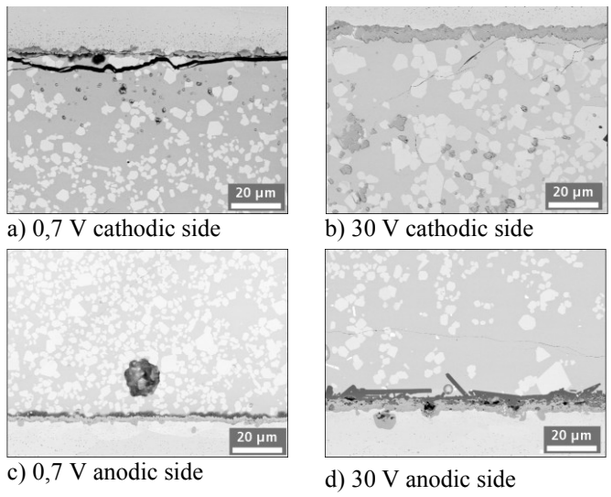


Fig. 2: specific resistances of model sealings exposed to dual atmosphere with different electrical voltages.

The microstructure of the glass-metal interfaces and the sealing glass itself is investigated by SEM. In figure 3 a comparison of cathodically and anodically polarized glass-metal interfaces from samples exposed in dual atmosphere with externally applied voltages of 0,7 V and 30 V are shown.



a) 0,7 V cathodic side b) 30 V cathodic side

c) 0,7 V anodic side d) 30 V anodic side

Fig. 3: Micrographs of cathodically and anodically polarized glass metal interfaces at 0,7 and 30 V.

It has been fond that higher voltages applied to the samples lead to thicker interfacial layers in comparison to samples treated with lower voltages (0,7 V). The EDX-analysis has shown that the compositions of the formed layers differ not significantly. They consist of a Cr-Mn-Zn-oxide scale as a result of the reaction of the Crofer 22 APU with the ZnO-component of the glass. Depending on the polarization and the applied voltage a growth of these crystallites into the bulk glass occurs. At the anode an additional silica crystallites on top of the Cr-Mn-Zn-oxide layer are observed. At higher voltages these crystallites also form a continuous layer.
As a conclusion it can be made, that the reactions between sealing glass and interconnect depend strongly on the externally applied voltage, the direction of polarization and thus on redox sensitive components in the glass.

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