Abstract

Efficient and durable electrochemical energy conversion solid oxide cell systems can be achieved only by a proper integration technology with a suitable joining and coating materials choice and processing. A crucial aspect in solid oxide electrolysis cell (SOEC) devices is given by the design of stable and reliable glass sealants and ceramic coatings, which must be used to join and coat dissimilar materials.

In SOEC planar configuration, the repeating units are combined together with the help of metallic interconnect. Sealants are also necessary in order to avoid the mixing and leakage of gases at both electrodes of cell. Glass-ceramic based sealants are the best choice thanks to the possibility of tuning their properties by adjusting their composition. For SOEC interconnects, the high Cr steels are most commonly used due to their remarkable properties in terms of high electrical conductivity and low cost. However, the Cr diffusion and evaporation from the interconnect cause poisoning of the other cell components.

This PhD research has been focused on two topics; i.e. synthesis of novel glass-ceramic based sealants and deposition of protective coatings on steel interconnect to avoid Cr diffusion. In this context different novel glass-ceramic sealants were designed and characterized to work in the real SOEC conditions and at the working temperature of 850 °C. The glass-ceramic sealants have been divided in to three series, depending either on the type of used modifiers or their respective concentration. The first and second series have SrO as main modifier, while the third series contains BaO. The crystallization and sintering behavior of glasses were analyzed by differential thermal analysis (DTA) and heating stage microscopy (HSM). The coefficient of thermal expansions (CTE) of as-casted glasses and respective glass-ceramics were measured by dilatometer. The compatibility of different glass-ceramics with the bare Crofer22APU interconnect and 3YSZ electrolyte was analyzed by scanning electron microscope (SEM) after joining and thermal ageing (1000 hours, 850 °C). XRD analyses were carried out to investigate the crystalline phases in the as-joined and thermally aged glass-ceramics (1000 hours, 850 °C). The mechanical characterization of the glass-ceramics sandwiched between two Crofer22APU plates, was carried out at room temperature and 850°C. The electrical resistivity of the Crofer22APU/glass-ceramic/Crofer22APU joined samples was measured for 1000-3000 hours at

850 °C under the applied voltage of 1.7 V. In addition to static air, the electrical resistivity was also measured in dual atmosphere (simultaneously applied reducing and oxidizing) to simulate the working conditions of an SOEC. The SEM-EDS post mortem analyses were carried out to investigate the compatibility and any possible chemical interaction between glass-ceramics and the Crofer22APU. In order to deposit the glass at industrial scale, a new glass paste was formulated and deposited on the real dimensioned (16 cm x 18cm) Crofer22APU interconnects by a stencil printing technique.

$Mn_{1.5}Co_{1.5}O_4$ (MCO) spinel coating was deposited on the bare Crofer22APU substrate by electrophoretic deposition (EPD). The EDP process was also scaled up to coat the real dimensioned Crofer22APU plates. The morphology, uniformity and thickness of the as-deposited coatings on the flat and corrugated Crofer22APU substrates were analyzed by SEM. The area specific resistance (ASR) of MCO coated Crofer22APU was measured for 8600 hours at 850 °C, followed by the SEM-EDS post mortem analyses. CuO was also co-deposited with MCO by EPD process in order to investigate the properties of Cu-doped MCO. The morphology of the CuO doped MCO coating was studied by SEM and XRD after different sintering treatments. The effect of different concentrations of CuO doping on the densification, ASR and corrosion rate of MCO was also investigated for 2000 hours. Besides conventional sintering, flash sintering technique was also carried out to understand its effects on the densification of coatings.

This study shows that a suitable SrO/SiO_2 and BaO/SiO_2 ratio is very important to obtain the desired high CTE crystalline phases in SrO and BaO glass-ceramics respectively. Besides SrO/SiO_2 and BaO/SiO_2, a right balance of all constituents of a glass system, is also requited in order to avoid the formation of detrimental phases, such as Ba or Sr chromates. With a proper SrO/SiO_2 and BaO/SiO_2, the high CTE crystalline phases were formed in the 2^{nd} and 3^{rd} series glasses respectively. The newly designed glass-ceramic sealants showed excellent properties in terms of their sintering ability and thermo-mechanical compatibility. The coefficient of thermal expansions (CTEs) of the as-joined and thermally aged glass-ceramics were closely matching with CTEs of other cell components. The long term testing showed that the Crofer22APU/glass-ceramic/Crofer22APU joined samples based on all glass systems, showed electrical resistivity higher than 10^4 Ω.cm, thus suitable for the SOEC applications to ensure electrical insulation. No evidence was found about the corrosion or chemical interaction between the glass-ceramic sealants and Crofer22APU interconnects after the long term electrical resistivity test in dual atmosphere at 850 °C. Owing to these properties, these glass systems were found to be quite promising to be used as sealants in the SOEC conditions. The newly formulated glass paste also showed good rheological properties that make it suitable to deposit by stencil printing. However, some further modifications in the recipe of glass paste would be required for further optimization.

The EPD deposited $Mn_{1.5}Co_{1.5}O_4$ (MCO) spinel coating are quite uniform on the flat and corrugated Crofer22APU surfaces. The MCO coating has a thickness of ~ 10-15 μm after sintering. After suitable sintering treatment, MCO spinel showed low ASR (15-25 mΩ.cm^2) up to 5000 hours at 850 °C. The Cu doping was found to improve the sintering of the MCO spinel, however no significant effect of Cu doping on the ASR of MCO was noticeable. Moreover, the flash sintering was found to be a suitable technique to improve the densification of the coatings without formation of Cr oxide scale. No crack or delamination at the Crofer22APU/coating interface was observed as a result of the rapid heating/cooling carried out during the flash sintering.

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