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Improved Robustness and Low Area Specific Resistance with Novel Contact Layers for the Solid Oxide Cell Air Electrode

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Stacking of solid oxide cells (SOC) requires that a robust and durable electrical contact between the cell and the interconnect is established. In this work we present a new contact layer solution for the SOC air side, based on the concept of reactive oxidative bonding. The contact layer consists of metallic Mn-Co and Mn-Cu particles that during initiation/operation are oxidized *in-situ* to form well-conductive spinel oxides. The long-term (3000 h) stability of the new contact layers is evaluated by measuring the area specific resistance (ASR) during aging in air at 750 °C, and during thermal cycling. Both Mn-Co and Mn-Cu layers are found to be well compatible with the applied CeCo coated 441 steel, and do not significantly contribute to the resistance across the stack element, which is dominated by the coated steel.

Introduction

Stacking of solid oxide cells (SOC) requires that a robust and durable electrical contact between the cell and the interconnect is established. To achieve this, contact layers are applied during the cell fabrication process or the stack assembly. The contact layer material should have a high electrical conductivity, a suitable thermal expansion coefficient (TEC), be mechanically robust and chemically compatible with the adjacent electrode and interconnect materials. Most planar SOC stacks today employ perovskite oxides as the contact material on the air/oxygen side (1). The perovskite oxides are attractive due to their high electrical conductivity and suitable TEC, however, “hard” sintering of these materials requires high temperatures, (>1100 °C), which may have an adverse effect on other SOC stack components, such as the steel interconnects and the seals (2). As a result of poor sintering at lower temperature, the interface between the air electrode and the interconnect is among the weakest in the stack and the one most prone to loss of contact (3).

In this work we present a new contact layer solution for the SOC air side, based on the concept of reactive oxidative bonding. The contact layer is applied in the form of metal particles that during SOC stack operation (700-800 °C) are oxidized *in-situ* to form well-conducting spinel oxides. The metallic precursors investigated in this work are Mn-Co and Mn-Cu, mixed in the stoichiometric ratio to form MnCo_2O_4 and $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$, respectively. Both oxides have an appreciable electrical conductivity (70 and 225 S/cm at 750 °C, respectively) and a TEC (14.4 and 12.2 K⁻¹ between 25 °C and 800 °C, respectively) matching other typically used SOC materials (4, 5). Due to the high reactivity of the metallic precursors, a strong bond is created to both the coated

interconnect and the air electrode. According to results presented elsewhere (6), the fracture energy of the interconnect-air electrode interface with this contact layer solution is almost a factor of 10 higher than with conventional perovskite oxide based contact materials.

Here, we evaluate the electrical conductivity and long-term stability of the new contact layers by measuring the area specific resistance (ASR) of a stack element comprising a steel interconnect, the contact layer and an air electrode. The ferritic stainless steel AISI 441 is chosen as the interconnect material due to its lower cost compared to more specialized steel grades developed specifically for interconnect application, such as Crofer 22 APU. Previous studies have indicated the potential of 441, but also several challenges, such as formation of insulating silica scales and a poor oxide scale adhesion (7, 8). However, coating the 441 steel with a thin layer of CeCo seems like a promising solution to these challenges (9).

The ASR is recorded during isothermal aging at 750 °C, as well as during thermal cycling. The thermal cycling was introduced to check the mechanical robustness (interface adherence) of the stack elements after the growth of an oxide scale and aging of a fully oxidized interface between the coupling components and the interconnect.

Experimental

A detailed description of the set-up for the ASR measurement can be found in (10). The ferritic stainless steel AISI 441 in 0.3 mm thickness served as the interconnect material. One side of the steel was coated with CeCo (Sandvik Materials) while the other side was left uncoated. The steel was cut into 20x40 mm² coupons and a Pt wire was spot welded along one of the shorter edges of the uncoated side, to act as a voltage probe.

A contact layer (CL) paste for screen printing was prepared using Mn(32 wt.%)-Co(68 wt.%) and Mn(53 wt.%)-Cu(47 wt.%) metallic powders (American Elements), in the stoichiometric amounts to upon oxidation form MnCo₂O₄ and Cu_{1.3}Mn_{1.7}O₄, respectively. The pastes were screen printed onto a 20x20 mm² area of the interconnect with a green thickness of 0.2 mm. The paste was dried at 90 °C for 1 h to evaporate the solvent before assembly.

Bisque-sintered La_{0.85}Sr_{0.1}Mn_{1.1}O₃ (LSM) plates (20x20x1 mm³) spray coated with a 50-60 µm layer of LSM and Co₃O₄ slurry mixture was used as current collection plates. The LSM plates were stacked between the interconnect coupons as illustrated in Figure 1. Gold foil connected to gold wires was placed on the top and bottom of the stack to supply the current. A load of 7 kg was put on top of the stack. The stack was heated in stagnant air following a representative SOC stack heat-up profile used when employing glass-ceramic sealants, see reference (11). This involved heating to 600 °C at 100 °C/h, holding for 1 h, heating to 700 °C at 100 °C/h, heating to 800 °C at 50 °C/h, holding for 1 h and finally cooling to 750 °C at 120 °C/h. At 750 °C, a measurement current of 2 A was employed, corresponding to 0.5 A/cm² considering the nominal contact area between the steel interconnect and the LSM plate.

The ASR was calculated according to Ohm's law, by measuring the voltage drop between the Pt-wire connected to the interconnect and a Pt-wire placed between two LSM plates. As illustrated in Fig. 1, the cross-plane resistance (ASR) is measured across five different configurations: a) LSM, b) 441/LSM, c) 441/CeCo/LSM, d) 441/CL/LSM, and e) 441/CeCo/CL/LSM. At least two interfaces of the same type were evaluated. After 3000 h of aging at 750 °C, the stack was thermally cycled 50 times between 750 °C and 200 °C (120 °C/h heating and cooling rate), with a dwell of 5 h at 750 °C between each thermal cycle.

Microstructural characterization after the ASR measurement was performed using a scanning electron microscope (SEM, Hitachi TM3000).

Figure 1. Illustration of set-up used for measuring the area specific resistance. CL = Contact Layer (Mn-Co or Mn-Cu).

Results and Discussion

Isothermal aging at 750 °C

The ASR recorded across the different interfaces during isothermal aging at 750 °C in air is shown in Figure 2. During the 3000 h period the samples were exposed to two unplanned thermal cycles (at ca. 400 h and 2100 h). For clarity, only one curve representative for each interface is plotted in Figure 2. The maximum difference between two ASR measurements of the same interface was $\pm 3 \text{ m}\Omega\text{cm}^2$ for all but the 441/LSM interfaces, for which the scatter was greater ($\pm 16 \text{ m}\Omega\text{cm}^2$). A summary of the average ASR values measured after 3000 h is given in Table I. A degradation rate (increase in ASR with time) was calculated by a linear fit of the ASR recorded the last 500 h of

isothermal aging. The results are presented in Table I. Note that the ASR is calculated on the basis of the nominal contact area (4 cm^2), and that there likely is some difference in the actual contact area among the different samples, e.g. due to slight misalignment between the components and other unintended differences in the established area of contact. For this reason, the change in ASR with time provides a more important measure for comparison than the absolute values of the ASR.

For all but the 441/LSM interfaces the ASR decreased during the initial 1000-2000 h of aging due to improvement of the area of contact and improved conductance of the green and only mildly sintered layers. This is primarily due to creep and sintering of the LSM contacting plates, which are pre-sintered under mild conditions and coated with a LSM/ Co_2O_3 layer. As a consequence, the ASR measured across a single LSM plate continues to decrease over the entire duration of the measurement (12).

The ASR of the 441/LSM interface increased rapidly from the start of the measurement and reached $70 \pm 16 \text{ m}\Omega\text{cm}^2$ after 3000 h of aging, which is above the acceptable limit for the interconnect ASR ($50 \text{ m}\Omega\text{cm}^2$) suggested in some papers (13). The high ASR can be attributed to the relatively faster growth of poorly conductive oxide scales (Cr_2O_3 and SiO_2) on the uncoated 441 steel (7). Compared to the uncoated steel, the ASR after 3000 h of aging is reduced by a factor of 2.6 with the CeCo coating. Previous ASR measurements have shown that a $<1 \text{ }\mu\text{m}$ thick CeCo coating does not contribute significantly to the cross plane resistance, instead, the ASR is dominated by the thermally grown oxide scale on the steel (14). Thus, the low and stable ASR for the 441/CeCo/LSM interface indicates a reduced growth rate and/or improved electrical conductivity of the oxide scale.

Comparing the ASR measured for an interface *with* the contact layer (e.g. 441/CeCo/Mn-Co/LSM) with the equivalent interface *without* the contact layer (e.g. 441/CeCo/LSM), it is clear that the contact layer does not contribute significantly to the cross-plane resistance. This is reasonable considering the much higher electrical conductivity (at $750 \text{ }^\circ\text{C}$) of MnCo_2O_4 (70 S/cm) and $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$ (225 S/cm) compared to Cr_2O_3 ($0.1\text{-}0.01 \text{ S/cm}$ (15, 16)) and SiO_2 ($10^{-10}\text{-}10^{-8} \text{ S/cm}$ (17)), which are the primary constituents of the oxide scale formed on the 441 steel. The contact layers may nevertheless indirectly have influence on the ASR through reactions with the coating, oxide scale and/or LSM plates. According to the degradation rates presented in Table I, the Mn-Cu contact layer results in a small improvement compared to the CeCo coating alone, while the Mn-Co contact layer slightly increases the degradation rate relative to the 441/CeCo/LSM interface.

Applying the Mn-Co or Mn-Cu contact layers directly to the 441 (i.e. no CeCo coating) also results in low and more stable ASR compared to the bare steel. This is not surprising considering that the oxidized form of the contact layers, i.e. MnCo_2O_4 and $\text{Cu}_{1.3}\text{Mn}_{1.7}\text{O}_4$, have been employed as interconnect coatings (18–20). Nevertheless, it is clear that the best performance in terms of ASR is achieved by combining the contact layer with a CeCo coating. The CeCo coating is furthermore beneficial for reducing the release of poisonous Cr(VI)-species from the interconnect (21).

Figure 2. ASR measured in air at 750 °C. Right side plot shows an excerpt of the ASR between 15 and 35 mΩcm².

TABLE I. ASR measured after 3000 h at 750 °C and degradation rates extracted from last 500 h of ASR measurement. Activation energy for ASR determined during cooling from 750 °C to 500 °C. Average and standard deviation of measurement of 2-4 interfaces of the same kind.

Interface	ASR after 3000 h [mΩcm ²]	Degr. rate [mΩcm ² /1000h]	ASR after 50 thermal cycles [mΩcm ²]
LSM (contact component only)	28	-0.7	29
441/LSM	70±16	8.8	80±29
441/CeCo/LSM	25±3	-0.3	24±3
441/Mn-Co/LSM	25±1	0.8	24±1
441/Mn-Cu/LSM	21±1	0.3	20±1
441/CeCo/Mn-Co/LSM	19±2	0	20±1
441/CeCo/Mn-Cu/LSM	18±1	-0.3	17±1

Thermal cycling

Figure 3 shows the ASR during 50 thermal cycles between 750 °C and 200 °C. For clarity, only the ASR recorded at 750 °C is plotted. The ASR measured after the 50th cycle is reported in Table I. In case of the uncoated 441 steel directly contacted to LSM, the degradation rate during thermal cycling is increased to 13.5 mΩcm²/1000 h, compared to the degradation rate during isothermal aging at 750 °C (8.8 mΩcm²/1000 h). The increased ASR during thermal cycling may be caused by a decrease in the effective contact area between the steel and LSM plate, due to partial oxide scale spallation. Oxide scale spallation typically occurs during thermal cycling due to stresses that develop from the TEC mismatch between the steel and the oxide scale and is a known challenge with the 441 steel (22, 23).

For the samples with a CeCo coating and/or Mn-Co/Mn-Co contact layer the degradation rate during the thermal cycles is similar to that measured during the last 500 h of isothermal aging at 750 °C, i.e., the thermal cycles do not accelerate the degradation. This can be attributed to the good TEC match and sufficiently strong bonding between the different layers, which is supported by the high values of interface toughness reported in (6).

Figure 3. ASR measured during thermal cycling between 750 °C and 200 °C. Only data recorded at 750 °C is plotted for clarity.

Post-ASR microstructural analysis

SEM cross sectional images of selected interfaces after the ASR measurement are shown in Figure 3. Both the Mn-Co and the Mn-Cu contact layers, which were deposited as metallic particles, are fully oxidized after the > 3000 h of aging at 750 °C. On the non-coated 441 steel (Fig. 3a) an oxide scale of ca. 3.0-3.5 μm thickness has formed. On the CeCo-coated steel contacted with Mn-Co (Fig. 3b) the thickness of this oxide scale was reduced to ca. 2.0-2.5 μm , while on the CeCo-coated steel contacted with Mn-Cu (Fig. 3c) the thickness of this oxide scale was reduced to ca. 1.0-1.5 μm . These observations correlate with the ASR measurements, where interfaces with the Mn-Cu contact layer were shown to give the lowest ASR. In case of samples with the Mn-Cu contact layer, the interfaces between the oxide scale, coating and contact layer are difficult to distinguish due to interdiffusion of Cr and Cu at the interfaces. This interdiffusion likely contributes to the strong interface adherence achieved with the Mn-Cu contact layer, as presented in (6).

Figure 3. Cross sectional SEM images of the samples after the ASR measurement. a) 441/LSM, b) 441/CeCo/Mn-Co/LSM, c) 441/CeCo/Mn-Cu/CL.

Conclusions

The metallic precursors Mn-Co and Mn-Cu have been evaluated as contact materials for solid oxide cell stacks by measuring the area specific resistance (ASR) during aging at 750 °C. The precursors are oxidized to well-conductive spinels during aging. The ASR was found to be dominated by the oxide scale thermally grown on the 441 steel and was significantly reduced by the application of a CeCo coating. The lowest ASR was measured for CeCo coated 441 with a Mn-Cu contact layer. Both Mn-Co and Mn-Cu were found to be well compatible with the CeCo coated 441 steel, and did not significantly contribute to the resistance across the stack element. These materials are thus promising for the application as SOC air side contact layers.

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