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Application of silver in microtubular solid oxide fuel cells

Artur J. Majewski[1] · Aman Dhir[1,2]

Abstract

In this paper, the behaviour of silver as cathode conductive material, interconnect wire, and sealing for anode lead connection for microtubular solid oxide fuel cells (μSOFC) is reported. The changes in silver morphology are examined by scanning electron microscopy on cells that had been operated under reformed methane. It is found that using silver in an solid oxide fuel cell (SOFC) stack can improve the cell performance. However, it is also concluded that silver may be responsible for cell degradation. This report brings together and explains all the known problems with application of silver for SOFCs. The results show that silver is unstable in interconnect and in cathode environments. It is found that the process of cell passivation/activation promotes silver migration. The difference in thermal expansion of silver and sealant results in damage to the glass. It is concluded that when silver is exposed to a dual atmosphere condition, high levels of porosity formation is seen in the dense silver interconnect. The relevance of application of silver in SOFC stacks is discussed.

Keywords Silver · SOFC · Microtubular SOFC · SOFC stacks

Introduction

Several configurations of solid oxide fuel cells (SOFC) are commercially available; however, the selection of suitable materials and development techniques is still the subject of current research. Within an SOFC cell, the cathode is a significant contributor to the cell overpotential caused by the slow oxygen reduction reaction [1], which occurs at the electrolyte–cathode–air boundary phase (triple-phase boundary). When the temperature of SOFC is low, the oxygen dissociative adsorption slows further because of the decrease in catalytic activity of the cathode oxygen reduction. Key requirements for cathode materials are that they have to be highly conductive for electrons and oxygen ions, and they should maintain thermal stability in SOFC operating temperature. The conductivity of modern cathode materials such as lanthanum strontium manganite (LSM) or lanthanum strontium cobalt ferrite (LSCF) decreases at lower operating temperature. High ohmic losses in the cathode result in reduced cell performance. This can be overcome by the addition of a metal-based current collection layer that enhances the electronic conductivity. The high-conductive layer ensures adhesion and connectivity between the cathode and the interconnect. This consequently reduces the contact resistance of the cathode/interconnect interface.

In planar cells, a silver mesh can be applied to reduce the contact resistance between the interconnect and the cathode [2]. The presence of silver will also act as a catalyst for oxygen reduction [3]. Silver has been proven as a cathode material showing good results at intermediate temperatures in SOFC [1, 4–6]. In these tests, the limiting feature was the length of the oxygen diffusion paths. Moreover, silver does not form a nonconductive oxide layer when exposed to air at elevated temperatures. The high resistance to oxidation at elevated temperatures is thus beneficial for SOFC application. Silver also has one of the highest electrical conductivities of metals (6.30×10^7 S m^{-1} at 20 °C), thus the addition of silver improves electron percolation. Silver is often used as a conductive material for the cathode in microtubular solid oxide fuel cells (μSOFC) [7–10]. This has been implemented for planar [11] or honeycomb [12] cell designs, too. Silver in a μSOFC can also function as a sealant [13, 14]. Infiltration of silver into the porous cathode is an alternative

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method to improve current collection [1, 9]. Infiltration of silver or an alternative highly conductive material such as lanthanum strontium cobalt (LSC) can significantly improve current density of the standard LSM cathode [6, 10, 15]. Adding silver into the cathode system has shown to reduce the overpotential related to oxygen reduction [16]. Porous silver can also function as a cathode for low-temperature SOFC [17] Inert properties and stability in the oxidising atmosphere can make silver a good candidate as a cathode interconnect material for intermediate-temperature SOFC.

However, silver tends to agglomerate during annealing in air or in ambient oxygen [18]. Porous silver tends to become dense at elevated temperatures. For the mixed Ag/cathode systems of yttrium or erbium stabilized bismuth oxide, 1 h of sintering was shown to be enough to result in porosity reduction, separation of compounds, and increase in Ag phase [1]. Silver is also known to be prone to migration at elevated temperature. Compson et al. [19] suggested to use silver as an interconnect for SOFC only at temperatures below 650 °C. Above this temperature, loss of silver caused by sublimation, evaporation, and diffusion transport may affect cell performance.

Using silver as a current collector can reduce cell performance since the low-temperature melting point of silver requires changes in cell preparation technique [12]. Moreover, silver can evaporate even at low (300–350 °C) temperatures [20]. Evaporation of silver increases with temperature and is similar in the air and in the reducing environment [21]. Silver does not have high gas penetrability. However, silver has high oxygen solubility. The solubility allows application of silver as an anode for direct carbon SOFC [22]. Silver tends to migrate when submitted to an electric field at high temperature with of oxygen [23–25]. Silver ions Ag^+ can move under the influence of the electrical field [23]. The presence of Cr can increase the Ag migration into the cathode. Formation of compounds such as $AgCrO_2$ with higher evaporation rate than pure Ag increases Ag migration [15]. Migration of silver and formation of conductive filaments can cause short-circuit failures [23]. Singh et al. [26] observed that exposure to the dual oxidation–reduction environment can damage the silver microstructure. They observed the formation of pores and cracks on the fuel side of the solid silver barrier. They suggested that dissociation and dissolution of H and O into silver and formation of steam cause development of pores in solid silver barriers. Using silver in SOFC cells and stacks has many benefits and for that reason many researchers are trying to improve SOFC performance using silver compounds. However, the incorporation of silver will affect the cell durability. The aim of this work is to discuss the plausibility of Ag as an SOFC material and to highlight the problems that may occur for application of silver in SOFC. In this work, silver is utilised in the µSOFC systems, as an interconnect, as a cathode or

as an additional cathode conductive layer and for the sealing of an anode/lead connection. The aim of this work is to examine the degradation mechanisms of a µSOFC cell.

Experimental

The current interruption method was applied for internal resistance measurements. Electrochemical impedance spectra were performed using Solartron cell test system 1400A/1470E (Potentiostat/Galvanostat). The cell response was measured over a frequency range of 1 MHz to 0.1 Hz with AC voltage amplitude 10 mV at the open circuit voltage (OCV) condition. Electrochemical performance measurements were made using the Solartron in galvanostatic mode.

Long-term cell tests were conducted under potentiostatic mode at a set voltage of 0.7 V. Every 24 h the test was interrupted by I–V test and impedance scan.

Analysis of cell morphology: post-cell test the cells were fractured, cell surface and cell cross-section were characterised using a Hitachi TM3030Plus scanning electron microscope (SEM).

The cell temperature was maintained at the temperature of 650 or 700 °C in a tubular furnace (Vecstar HZ/split-tube) and monitored by thermocouples flanking the test chamber.

Cell fabrication

The cell tests were conducted using commercial tubular, anode-supported µSOFCs, of size 15.2 cm in length and 6.6 mm in external diameter, of composition Ni-YSZ/YSZ/SDC/LSCF (yttria-stabilized zirconia (YSZ), samaria-doped ceria (SDC)). Silver was applied to improve cell's performance. Silver wires (99.9% pure silver, Scientific Wire Company) 2 × 0.71 mm were used to collect current, with additional six silver wires 2 × 0.20 mm to fasten the current collector to the cathode. Silver paste (ESL 9907, Electroscience UK) was used to connect the current collecting wire to the exposed anode. The paste was dried at 105 °C for 1 h. After attaching the silver wire, an additional layer of silver paste was applied to cover the wire and to improve sealing. This was sintered at 750 °C for 2 h. In addition, the silver was covered by a commercial glass sealant, which was sintered at 850 °C for 8 h. The cathode was coated with silver ink (producer, SPI 5001) to reduce the lateral resistivity and to improve the electrical connection between the cathode and the interconnect. The cathode area was 16.6 cm² consisting of two separate parts (Fig. 1a–b). The silver ink was applied by ink brushing the cathode, then drying at 105 °C for 1 h.

The cell exhaust was cemented (using high-temperature cement) to a manifold, and the gas feed was connected
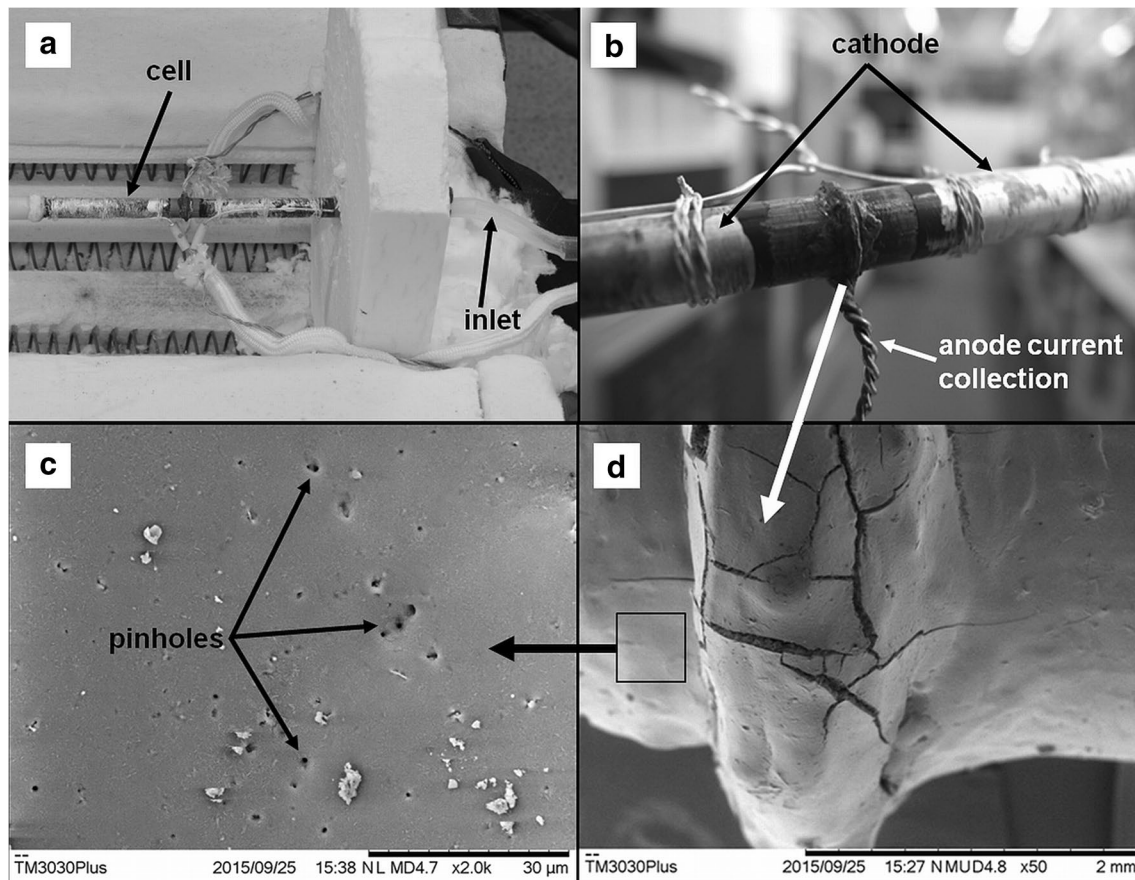
Fig. 1 **a** A tested cell in the furnace; **b** the anode current connection (sealed by glass); **c** the surface of glass sealant; **d** glass sealant at the anode wire connection, visible cracks

using a silicone tube so the cell was free to move in the axial direction. Cells were operated at 650 and 700 °C using either hydrogen or methane/air mixture. Inside the cell/tube, at the inlet, a partial oxidation catalyst (CPOX) (0.1 g) was inserted in the shape of a honeycomb structure. Hydrogen was introduced into the cell at 145 ml min^{-1}, and after 1 h of OCV, a polarisation curve was recorded (galvanostatic mode) with 0.5 V as a lower safe limit. Then the voltage was set to 0.7 V (potentiostatic mode) and a short 1 h constant voltage test was performed. Afterwards, the fuel was changed to a mixture of CH_4:air (dry air) with molar ratio CH_4:air of 1:2.4 and a long-term durability test was conducted at 0.7 V (CH_4 48 ml min^{-1}). These conditions were chosen to simulate the realistic conditions of a μSOFC auxiliary power unit (APU) [27]. The fuel gas connection was outside the hot zone, which eliminated problems with sealing. All tests were conducted under ambient air-condition on the cathode side. Details about the cell test system were described in previous papers [28, 29].

Results and discussion

Benefits from using silver

Usually, tubular cells have large cell voltage and ohmic losses since electrons have to be transported through the cathode along the cell. The addition of silver can reduce this problem. Thus, the surface of the cathode was covered with silver ink (SPI 5001) for these test cells. The primary role of the silver layer was to deliver and distribute the flux of electrons over the whole cathode area. This also helped to reduce the area-specific resistance (ASR) of the connection between the cathode and the interconnect (LSCF-Ag wire). An additional benefit of adding silver was to support oxygen reduction reaction. The silver ink formed a porous layer of 10–30 μm. The high porosity of the silver layer allowed free gas diffusion.

For cells tested without Ag coating on the cathode surface, cathode lead wires (0.71 mmAg) were coated with LSCF to improve contact interconnect/cathode. For cells with the Ag cathode coating layer, the wires were coated with Ag ink.

The additional coating by silver improved power density. The power density for the cell increased from 0.05 to 0.3 W cm^{-2} at 0.6 V, after the cathode was coated with silver ink. This was also reflected in the impedance characteristic where covering by silver reduced cell impedance (Fig. 2a). OCV was not affected. The power loss for the cell with the LSCF cathode can be attributed to the internal resistance of the cathode/interconnect contact area and to the deteriorated electronic current distribution. Results presented in Fig. 2 show that the application of a good electronic conductor such as Ag or Pt not only improves the contact between the cathode and the interconnector, but also improves electron distribution. Consequently, this leads to a perceived and more homogeneous polarisation of the cathode. Without the Ag layer, the cathode was not used to its full performance capability, the cause of this—in-plane electronic resistance. Without Ag or Pt, not only is the high-frequency intercept higher, but also the electrode impedance is larger. The silver coating significantly reduced the internal resistant loss. The ohmic resistance decreased from 0.23 to 0.03 Ω. The cell polarisation resistance still consisted of at least two arcs. Interestingly, the characteristic frequency of arcs changed only slightly from 20 to 50 Hz for the high-frequency arc and stayed around 0.2–0.3 Hz for the low-frequency arc. The contact resistance between the cathode and interconnect was reduced after silver was added. The anode side of the cell and the electrolyte remained unchanged. Altering the composition at one electrode does not affect the impedance of the second electrode at OCV. A significant change to the cathode impedance may overlap the anode impedance. The LSCF cathode system had a significant contribution to the cell

overpotential. By improving the cathode, the cell performance was enhanced mostly by decrease in ohmic resistance and the overall cell polarisation.

To confirm and compare how the various cathode coatings affect the cell performance, a selection of cells was coated with Pt ink, Ag ink and LSCF ink (to improve connection between already sintered LSCF cathode and Ag wires). These cells were tested at 700 °C. Increasing the cell-operating temperature from 650 to 700 °C reduced the cell overpotential, for the cell covered with Ag (Fig. 2a–b). The possible reason for this was the increased conductivity of the cathode and the electrolyte and higher catalytical activity of the cathode. Slightly larger impedance for Ag was obtained for the cell covered by Pt ink (Fig. 2b). In contrast, for the LSCF coating, the resistance of the cell increased at all frequencies. The cell ohmic resistance for Ag (0.03 Ω) was slightly lower than for Pt (0.04 Ω) and much lower than for LSCF (0.28 Ω). In addition, the size of both impedance arcs was slightly smaller for Ag than for Pt and much smaller than for LSCF. The cell performance depends on the used current collector. The low-frequency semicircle for Pt and Ag was slightly larger than the high-frequency. The characteristic frequency for high and low-frequency arcs was independent of the type of cathode coating.

The EIS spectra confirmed the positive aspect of introduction silver to the cathode structure. The data and results presented clearly show that SOFC with the Ag-coated cathode, operating in the temperature region of 650–700 °C, showed improved performance compared to similar cells without silver in the cathode system.
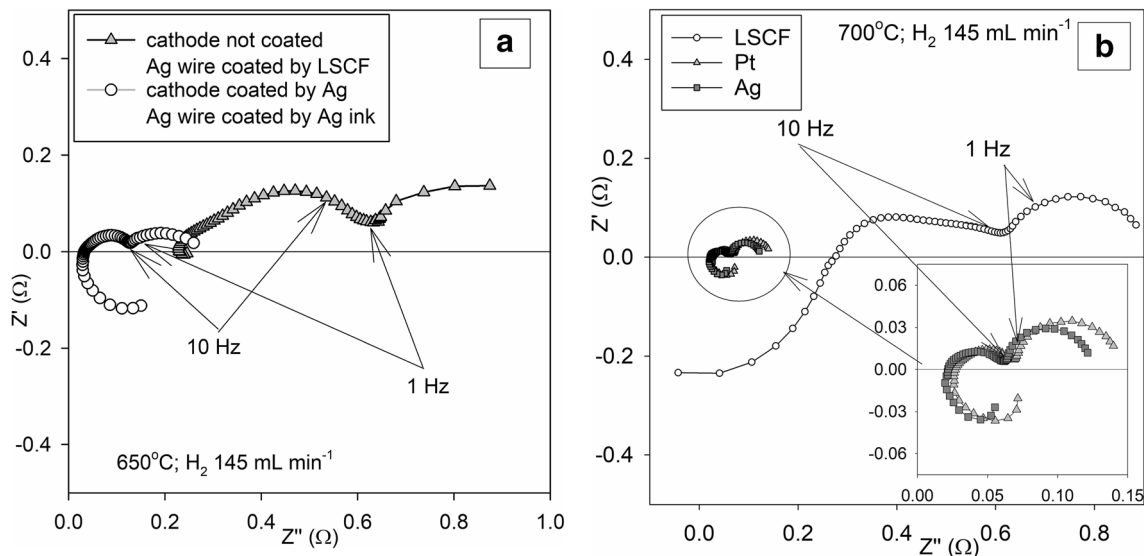

Fig. 2 Electrochemical impedance spectroscopy: **a** cells with LSCF and LSCF + Ag cathode. 650 °C, H$_2$ 145 ml min^{-1}; **b** cells with the cathode coated with Ag, Pt and LSCF 700 °C, H$_2$ 145 ml min^{-1}

Anode Ag sealing interconnect

The whole area of the exposed anode was covered by silver paste to improve the electrical connection and to part-seal the anode. The silver was densified by sintering. However, as the thermal expansion coefficient of silver is higher than that of the ceramic cell, it is expected that the connection between the cell and the interconnect further improves through the silver expansion during heating. Silver is ductile and should easily deform under thermal stress avoiding delamination and keep the cell hermeticity. However, using only silver paste as a sealant resulted in poor sealing. Fuel leakage was seen, indicated by high temperatures detected by the thermocouples around the anode current connection. The cells with only silver as a sealant could operate for around 24–50 h. To investigate the reason for the weak sealing, the cell was tested at 700 °C with H_2 (3% H_2O) for 8 h under OCV. The H_2 leak test conducted after silver sintering indicated gas tightness of the silver/anode joint at room temperature.

During this test, the temperature at the anode current connection increased approximately 100 °C above the operating temperature and the connection became red-hot even at a furnace temperature of 700 °C. After this test, the surface of silver exposed to the fuel side indicated degradation, and the dense silver developed into a porous structure. The layer of silver delaminated from the anode surface creating a gap (Fig. 3a) indicated the increase in cell impedance. Further to this, SEM scans showed that the degradation of solid silver started from the fuel side of the silver by developing porosity (Fig. 3b).

Singh et al. [26] suggested that pores and voids in silver are developed because of water vapour formation. Adsorption and dissolution of H and O gaseous molecules in silver interconnect is followed by diffusion and reaction of dissolved species and water vapour formation. The hydrogen and oxygen concentration in silver increases up to a critical pressure and bubbles are generated. The increase in the size of the pores in the silver layer can finally result in fuel leakage. According to Jackson et al. [30], 24 h of exposure to the dual atmosphere is enough to form pores across a 1-mm thick silver membrane. The high temperature of fuel combustion and possible anode oxidation at the middle of the anode can result in crack formation and damage to the cell.

The fact that porosity always began to form from the fuel side of the silver layer suggests faster solubility of oxygen than hydrogen. Also the ratio of O:H 1:2 in water promotes nucleation closer to the hydrogen source. The diffusivity and highest concentration in silver under dual atmosphere at 800 °C is, respectively [30]: H_2 2.9×10^{-4} $cm^2 s^{-1}$; 6.1×10^{-7} mol cm^{-3}, O_2 1.1×10^{-5} cm^2 s^{-1}; 1.1×10^{-5} mol cm^{-3}.

The rapid degradation of silver mechanical integrity and hermeticity after exposure to dual atmosphere affects the cell performance. Formation of pores in the silver also has an influence on the stability of the silver seal. Such degradation of the structure leads to fuel leakage. For this system of tubular cells with the anode connection at the middle of the cell, the silver seal would be exposed to the dual atmosphere. Therefore, if silver is applied as a sealant/current collector for a μSOFC, it has to be isolated to avoid exposure to the dual atmosphere. The additional sealing of the silver by glass was needed to extend the cell operation. This was achieved by coating the silver anode connection by a 10 μm layer of glass sealant. This extended the life of the μSOFC up to more than 800 h.

However, due to the difference in thermal expansion coefficient of silver and glass, there is a risk of damage to
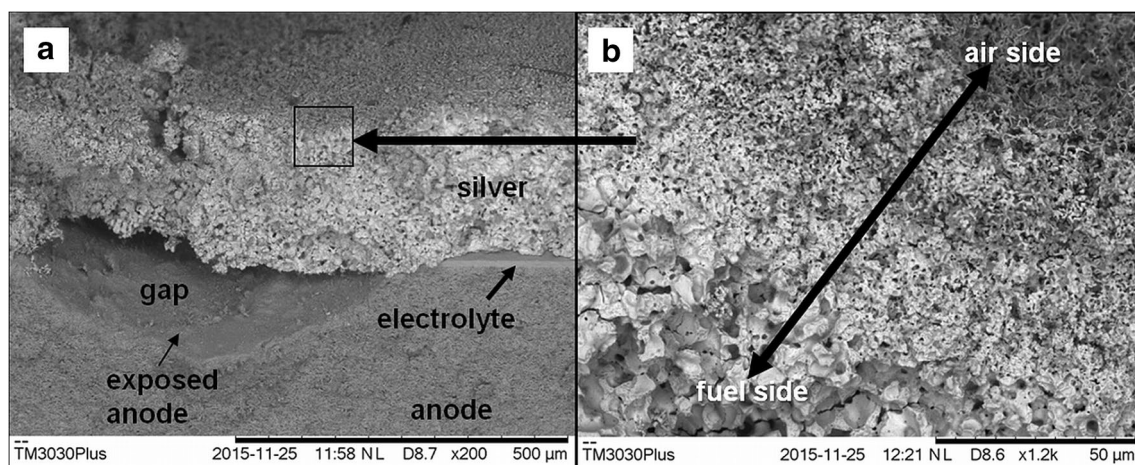

Fig. 3 SEM scans: **a** the cross-section of the anode current connection (Ag-YSZ-Ni/YSZ, 8 h at 700 °C); a visible gap formed between the anode and the silver sealant; **b** the cross-section of silver sealant near the air side

the glass coating. The components that have much lower thermal expansion coefficient than silver are YSZ 10.5, Ni/YSZ 12.5, SDC 12.8 and cathode 14.6, compared to silver 18.9×10^{-6} K^{-1}. The glass sealant's thermal expansion coefficient was selected to match the expansion of the cell components and was around 12×10^{-6} K^{-1}. With this mismatch in thermal expansion, significant internal stress is created. After the glass sintering (at 850 °C for 8 h), there was no visible damage to the glass surface. However, the long-term cell operation at elevated temperature or thermo-cycling resulted in the crack formation in the glass structure (Fig. 1d). These studies suggest that the high silver coefficient of thermal expansion can create problems for application of silver as an anode interconnect (and sealant) for the µSOFCs even with a glass coating. For this specific application, the rapid start and cooling required by APU could favour crack formation within the glass sealant.

The glass surface showed visible pinhole formation, approximately 1 µm in diameter. Several effects, including the application/deposition technique, can cause this effect. In this case, it has been attributed to the irregular surface of silver to which it was applied. Due to the complex shape of wire/anode connection, it was difficult to obtain a smooth silver surface. Pinholes usually indicate localised microbubbles or dewetting that degassed during sintering. Contaminants like dust particles can cause a formation of localised microbubbles. This could come from insulation material. The glass coating thickness is in a micron range, and it is possible for the debris to be larger in diameter than the coating thickness. The electrostatic attraction is enough to hold small particulates on the surface. Some particulates could also have a high moisture level. In addition, if there are existing cracks on the glass surface, the

heat generated by fuel combustion could be enough to melt the glass and produce pinholes. For future work, the glass coating technique has to be improved.

In this study, the long-term stability of the Ag-based anode current collection was examined. For the cells tested for more than 850 h, not only the degradation of the silver sealing layer (Ag paste) was observed, but additionally, a significant disintegration of the silver current collecting wire fastened to the anode. The cell with the CPOX catalyst was fed with the mixture of CH$_4$ and air in the molar ratio 1:2.4. Approximately, 70% of the fuel was converted on the catalyst before it reached the anode [28]. The power of the cell was around 0.14 W cm^{-2} at 0.7 V. Low operation temperature (650 °C) decreased the rate of oxygen reduction and conductivity of the YSZ electrolyte. Post-mortem analysis showed part of the wire close to the anode surface was damaged. The silver anode current collecting wire and all the silver interconnect had become highly porous. The solid silver appeared in a sponge-like structure (Fig. 4a–b).

Pores formed across all surface areas of Ag wire. The silver wire at the anode connection became brittle. Surprisingly, the cell performance was stable for more than 850 h of operation under such gas leakage conditions. Formation of silver crystals damaged the glass sealing and increased the exposure of the wire to air. These results did not confirm Compson's conclusion [19] that for silver interconnects 650 °C is a safe operating temperature. After 850 h of operation at 650 °C, all the interconnect wire and sealing paste was significantly deformed and damaged. It can be concluded that silver paste should not be used as a sealant for the anode connection for long-term cell operation.
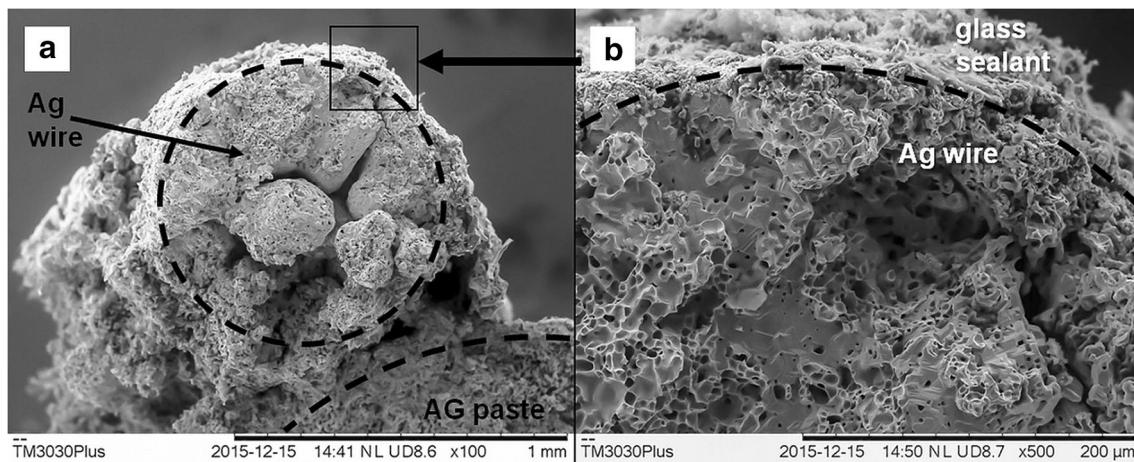

Fig. 4 SEM scans: **a** the cross-section of the anode current collection wire; **b** the cross-section of silver wire; after 850 h at 650 °C~0.2 A cm^{-2} with CH$_4$ reformate as a fuel

Ag wires

Samples of Ag wire (taken 1 cm away from the cell) from the anode and the cathode side were analysed to check the stability of silver as an interconnect wire. These samples of wires after long-term cell testing were compared with unused wires to detect any visible microstructural changes that had occurred during cell operation. An erosion of the silver wire surface is visible on the SEM scans (Fig. 5a–d). The initially smooth surface of tested wires developed faceting and striation structures after being exposed to air at 650–700 °C. Faceting is related to surface energy minimisation. According to Lu and Zhu [21], striation and faceting of the silver surface occur only in an oxygen atmosphere. Faceting made of large structures developed on the surface of Ag wire at the cathode side after 850 h at 650 °C (Fig. 5a–b).

At higher operating temperature (450 h at 700 °C) the structures formed were more intensive; all surfaces of the wire had changed; however, the structures were smaller (Fig. 5d). Wires at the anode side behaved differently. Some faceting was visible, but significant wire area became porous

(Fig. 5c). This part of the wire was only 10 mm from the anode connection (presented in Fig. 4), and after damage to the glass the coating was exposed to the dual atmosphere. The damage to the silver wire microstructure was observed even 10 mm from the point of wire exposure to the dual air–fuel atmosphere after long operational time. After several hours of operation, silver wires became brittle. This affected the mechanical strength and integrity. Even low physical stress could break the wire. This is important if a stack with silver wires is considered for an APU unit in vehicles where the system must resist vibrational stresses and strains. A cell with such brittle wires would be prone to damage caused by vibration. The risk of breaking the wire connection is significant. All these problems with silver will lead to degradation of the cell structural stability and in long-term operation to the degradation of the cell/stack performance. Zhong et al. [12] using Ag mesh for cathode current collector did not observe this type of degradation. However, they used Pt paste to improve the strength of the connection, and the test time was short. Silver commercially available has the purity of 99.95%. Silver is rarely used by
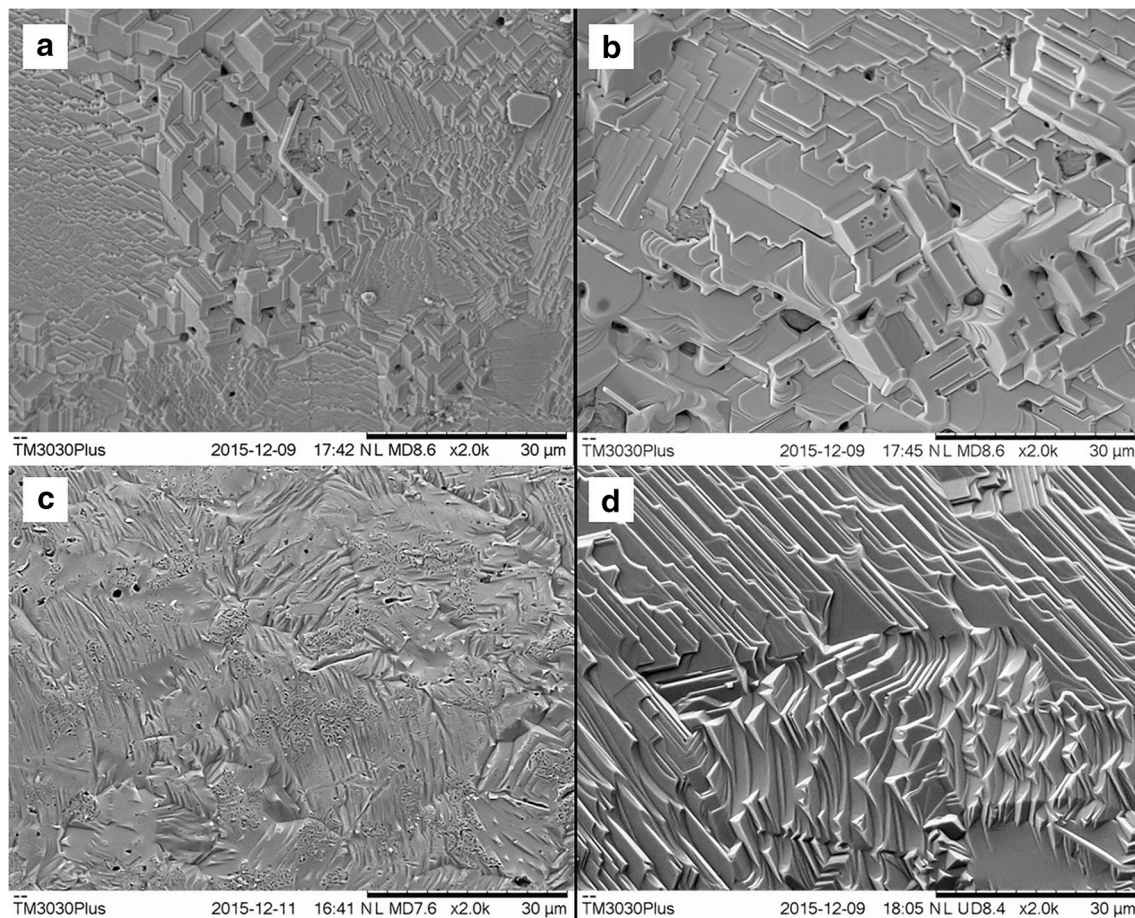

Fig. 5 SEM scans of the surface of Ag interconnect wire (1 cm from the cell) after test under constant current for 850 h at 650 °C: **a**, **b** cathode lead; **c** anode lead; **d** the surface of Ag cathode wire after 450 h at 700 °C

industry in pure form caused by its softness and suscepti- bility to damage. Also for SOFC application, silver alloys should be considered instead of pure silver. Where higher strength at elevated temperature is required, silver-palladium alloys are more suitable; however, that would increase the cost. Also the application of Ag(Al) alloys can enhance the thermal stability of silver [31]. The addition of aluminium reduces silver agglomeration at elevated temperature and prevents diffusion of silver into the matrix of support mate- rial. Wires with high Ni, Fe or Cr content are less suitable because of formation of a nonconductive oxide layer and reduced conductivity between the cathode and the intercon- nect. The addition of other elements and alloy formation on the silver surface may be the solution for application of silver current collectors in SOFC. Silver wires coated with gold are slightly more expensive than pure silver.

Cathode conductive layer

The risk of vaporisation and sublimation of silver exposed to air increases at higher reaction and operating tempera- tures. The vaporisation rate depends on temperature and atmosphere, and is higher in air than in H_2/H_2O atmosphere. Meulenberg et al. [2] extrapolated that up to 2% of silver can evaporate after 40,000 h at 690 °C in air. The evaporation will increase with the increase in the silver surface area. The cathode silver layer used in presented experiments was porous. Considering high porosity of the silver layer and its thickness 10–30 μm, a significant part of the silver can evaporate after the cell's lifetime. The glass sealant, which is applied to maintain gas tightness, also poses a problem as glass sealants usually require sintering at 850 °C for several hours—leading to evaporation of silver into and through the glass matrix. In our previous report [29], the cathode was coated with silver ink to receive good current collection before glass sintering. This exposed the porous silver to the high temperature of 850 °C for 8 h. The reverse fabrica- tion, with sintering glass before coating the cathode with silver, reduced silver degradation. However, it increases the complexity of the cell mass production. The Ag current col- lection film can be applied after the glass sintering for a single cell, although this process is impractical for the stack manufacture.

It can be concluded that cells with silver require low- temperature sealing materials. Tested cells were operated at the moderate temperature of 650–700 °C to avoid silver exposure to high temperature. The cathode current collection Ag wires were attached to the cathode after the glass sinter- ing process. The cathode Ag coating was brush-painted after the glass sintering. The porous structure of silver coating allowed gas distribution and improved current collection. Observed agglomeration of silver (Fig. 6) reduced all these benefits. Part of the cell power degradation is caused by silver agglomeration. Silver agglomeration and formation of holes and hillocks followed by formation of islands (Fig. 6a) increased electrical resistivity. The formation of solid sil- ver increased after the long-term (850 h) testing. Faceting of agglomerated silver was visible (Fig. 6b). From the cell surface images, it is evident (Fig. 6) that the silver layer has either evaporated or diffused into the LSCF coating layer from the original deposition layer. Change in the surface morphology affected the electrical conductivity of the silver layer. After several hours of operation and formation of iso- lated silver 'islands' on the cathode surface, the role of silver as an electron distribution to the whole cathode area was significantly reduced. The silver after agglomeration did not provide a continuous electronic pathway through the cath- ode. This also affected the function of silver as an electron conductor from the cathode to interconnect and increased ASR of the connection between the cathode and attached Ag
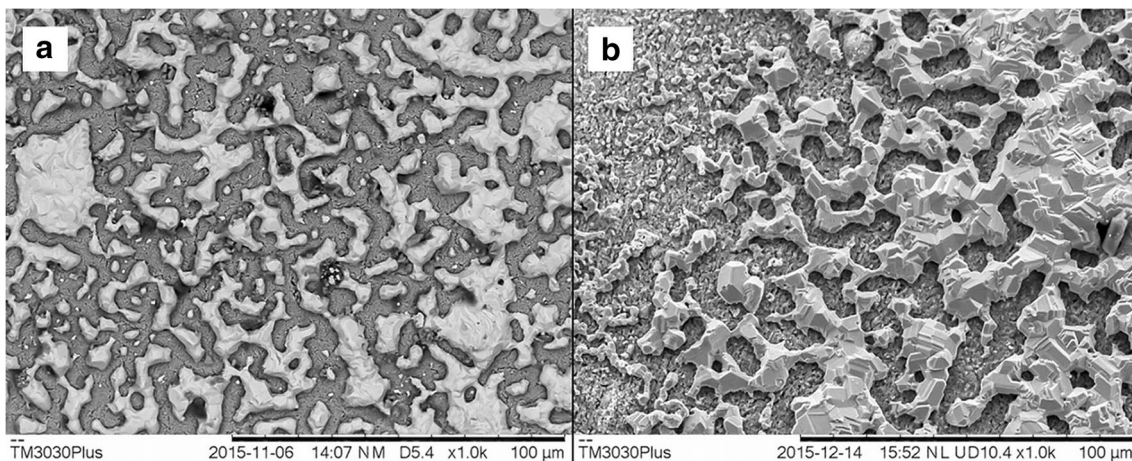

Fig. 6 SEM of the cathode surface covered by Ag: **a** after 100 h at 650 °C; **b** after 850 h at 650 °C

lead wire. Creating a long oxygen diffusion path through the bulk silver limits also the quantity of oxygen transported to the electrolyte. Lower silver porosity reduced oxygen reduction zone. Agglomeration of silver reduces the contribution of silver to the catalytic activity of the cathode. Lower silver porosity reduces the length of the three-phase boundary. On the other hand, during silver agglomeration and formation of a dense silver phase, a significant part of the cathode was exposed allowing free gas diffusion. Camaratta and Wachsman [1] observed a similar reduction in silver porosity for Ag-YSB and Ag-ESB cathode systems. They suggested that agglomeration of silver and reduction of porosity diminished cathodic reaction zone and reduced gas transport. Coating the cathode with silver may deteriorate oxygen reduction reaction. Sasaki et al. [32] observed that dense silver reduced gas transport to the significant part of the cathode.

It can be concluded that initial morphological structure of the porous silver current collector was destroyed as a reason of silver sintering and evaporation. The silver microstructure was unstable at intermediate cell operating temperature. Therefore, for a long-term application, silver is not suitable as a conductive material. Mixing silver with the ceramic phase or infiltration of silver with ceramic precursors could prevent silver densification. The ceramic shell can restrain densification of silver porous structure [9]. Another method is to incorporate silver into a ceramic matrix of the cathode [19]. The decrease in temperature operation of SOFC can increase the stability of silver. Zhu et al. [3] obtained high performance of the cathode with silver nanoparticles at 500 °C. The stability of Ag nanoparticles was increased by the strong metal-support (Ag–SNC) bonding interaction. Mixing silver with SSZ can reduce silver agglomeration on the cathode. Morphology of this cermet is stable at 500 °C [32]. Application of silver ink with thinner can improve the wetting and impregnation of silver into the cathode matrix.

However, from our experience, application of lower viscosity silver ink directly on the LSCF cathode can sometimes result in a cathode flaking.

Several things can cause cathode delamination. The peeling of the cathode was more frequently observed when slightly thicker silver layers were utilised. The thickness of the silver layer is difficult to control during hand brush painting. Therefore, it can be speculated that increased shrinkage of the outer layers of the silver film forced the cathode to curl away. Shrinkage of silver created stress in the cathode film that can lead to cracking, curing and flaking. Cracks in the silver coating were often initiated along the Ag lead wire connection. However, the formation of cracks in the cathode structure near the edge of silver grains formed by silver agglomeration was observed (Fig. 7b). That could increase the risk of silver penetration through the electrolyte and created the risk of cathode delamination. Other factors, which may lead to delamination, are in the SDC layer fabrication during the cell preparation. The SDC layer prevents reaction between cathode and electrolyte compounds. At the interconnect/SCD interface, formation of the separation area was occasionally observed. These cracks were parallel to the electrolyte surface. However, usually the parallel crack does not disturb the cathode stress field, as the stress also acts parallel to the electrolyte surface. However, if the parallel crack was followed by buckles formation, this would generate a large tensile stress and result in cathode spallation. These parallel cracks increased the risk of interrupting the electrical connection between interconnect and cathode. It can be speculated that the calcination of SCD was conducted at very low temperature. The difference in thermal expansion coefficient may create internal stress and cause slow separation of the cathode layer from the electrolyte during the cell operation. The cell delamination could increase the cell internal resistance. Usually, delamination is caused
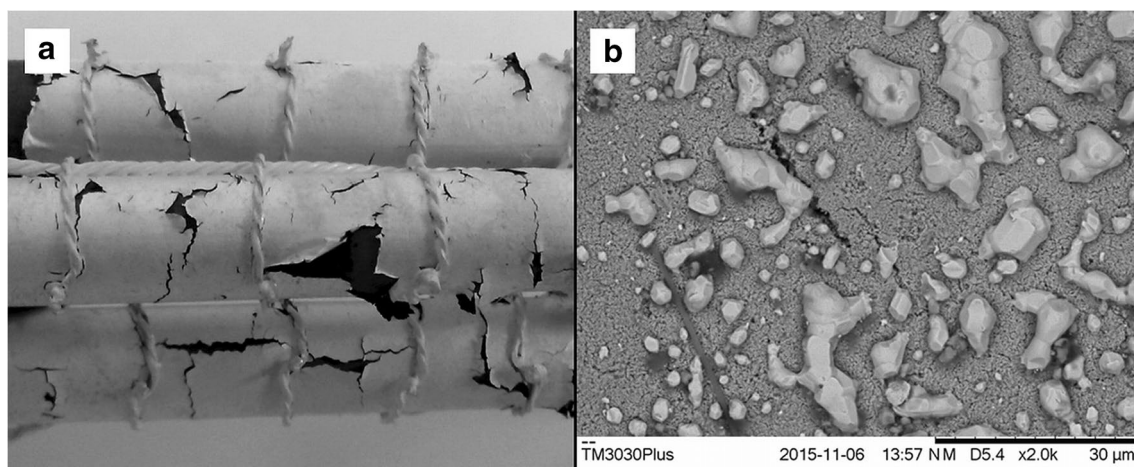

Fig. 7 SEM scans: **a** cells with cathode exfoliation, **b** the surface of the Ag-coated cathode, visible crack formation

by mismatching in thermal expansion coefficient of cell parts. Changes to LSCF surface morphology caused by the chemical and thermal reactions of LSCF may lead to oxide segregation. Decomposition and transformation of cathode materials can also be a result of cathode delamination. Cobalt instability and decomposition of perovskite were reported in the literature [33]. If the cathode was partially delaminated, the cathodic polarisation would be enlarged because of concentration in current conduction. The current collection efficiency was reduced. An electrode delamination results in the interruption of the ionic path, and detachment of the interconnect interrupts the electronic path.

Migration of silver and agglomeration at the electrolyte interface could also result in cathode peeling [34]. Silver tends to agglomerate at elevated temperature, which can lead to cathode delamination. However, no silver was detected in the SDC layer for samples where cathode delamination or cracks in the SDC layer occurred. In addition, no silver was detected on the electrolyte for areas where the cathode exfoliation occurred. Therefore, silver penetration into SDC was not responsible for the cathode delamination.

For some cells, rapid degradation of performance was observed. Post-mortem inspection of these cells confirmed short-circuit formation. The short-circuit effect was observed after few hours of cell operation. Short-circuits were generated always at the cell area near the cell inlet. The exact location of short-circuit was difficult to determine. Looking at the SEM images of the cell cross-section (Fig. 8a), the Ag layer porous structure is visible. Results of EDX elemental mapping of the cross-section of the cell after testing at 700 °C are presented in Fig. 8. For some samples, it was observed that silver accumulated in the SDC layer (Fig. 8b). Our results confirmed De Silva et al. [35] observations that silver may migrate from the cathode to the surface of the electrolyte. The contact of silver with an electrolyte

may temporarily increase the cell performance because of increase in the three-phase boundary, but the silver deposits may short-circuit the cell. Deposition of silver increased the risk of silver penetration into pinholes in the electrolyte and consequently short-circuit formation [36]. The silver migration was noticed only for the part of the cell near the cell inlet. This was the most active part of the cell with highest current density caused by high fuel partial pressure. This confirmed that silver migration was responsible for short-circuit formation. No silver migration was detected for parts of the cell beyond 2 cm from the cell inlet (Fig. 8a). No silver diffusion into or reaction with the YSZ electrolyte was observed. Camaratta and Wachsman [1], after testing ESB and YSB electrolytes with Ag in the cathode, also concluded that no silver diffused into the electrolyte.

The mechanism responsible for migration of silver and condensation across the SDC layer is unclear. It is unlikely that thermal effect alone is responsible for Ag migration to SDC. The temperature distribution along the cell was relatively uniform and silver deposited in the SDC layer was observed only at the cell inlet (the most active part of the cell). Silver migration could be a result of electromigration [6] or it can be associated with the formation of Ag (g) species and vapour transport to the cathode–electrolyte face followed by reduction to metal phase [11]. Ag (g) has higher vapour pressure than Ag_2O (g) at the SOFC operation temperature. Therefore, it is thought Ag (g) formation and penetration in SDC are possible for this mechanism. However, electromigration and evaporation/deposition of silver are too slow to be alone directly responsible for the observed rate of silver migration during the electrode polarisation [37]. Mosialek et al. [16] observed silver migration on the YSZ electrolyte in the potential range -0.2–0.5 V; no migration was observed without polarisation. In addition, no migration was observed without
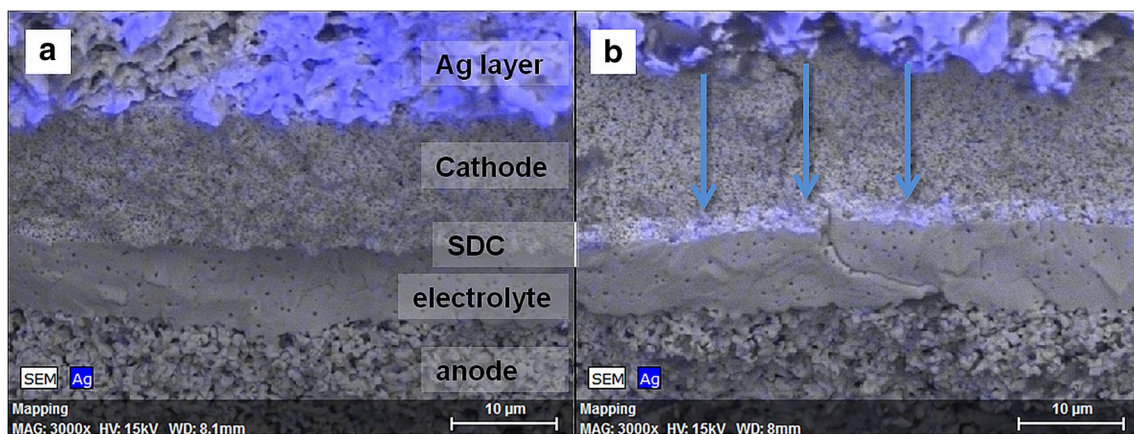

Fig. 8 SEM micrographs of the cell after 48 h operation at 700 °C: **a** the cross-section of the cell 2 cm from the CPOX catalyst; **b** the cross-section of the part of the cell near the CPOX

the electrolyte. They concluded that for the formation of silver dendrites, it is necessary to have a potential difference between the cathode (with Ag) and the oxygen ion conductor. Therefore, silver migration is not correlated directly with current density. Similar results were reported for the GDC electrolyte [37]. The mechanism responsible for silver mass transport is difficult to distinguish. Silver migration is possibly related to electron transfer and oxygen flux. The flow of electrons can promote silver electromigration. This can explain the agglomeration of silver at the edge of electrolyte since electrolyte can conduct only ions. The short 1–2 h OCV break in the cell power generation affected the performance of tested cells. Rapid cell degradation was often seen directly after OCV. Since the OCV state is not conductive for thermal or electromigration of silver [35], the cathode polarisation must promote silver migration. Moving from one state (including OCV) of operation to another could affect cell performance. The process of cell passivation/activation resulted in the difference in temperature distribution along and across the cell and could result in some microcrack formation in the electrolyte. Also, the risk of coke deposition on the anode during OCV was significant because no steam was formed from fuel electrooxidation and only 60–70% of fuel was converted on the CPOX catalyst [28]. Formed coke and temperature gradient may also result in microcracks formation in the electrolyte structure. However, SEM scans did not confirm electrolyte cracks. Simner et al. [11] observed that fresh cell was not affected by holding it under OCV. This confirms our result that short-circuit occurs directly after a short OCV break in the cell operation if the cell was in operation for several hours. Another possible explanation is that during OCV period (no current flow through electrodes), silver deposited in the SDC layer was saturated with oxygen. This oxygen was reduced after the cell returned to the operation mode with the flow of electrons. According to Simner et al. [11], during OCV, it is possible that the formation of oxygen-containing species can block the oxygen charge transport.

Silver metal diffusion through the electrolyte and ion migration can be a nanoscale phenomenon [38], which is impossible to be detected by SEM during post-mortem analyses. This can explain the detection of the short-circuit (at room temperature) without any visible cracks in the electrolyte, despite many SEM/EDX cross-section scans. However, this will require rigorous further investigation to validate the theory proposed.

Therefore, it is concluded that silver is a poor candidate for a contact material interconnect/cathode despite low and stable ASR. Gold is an alternative material for the current collector. In contrast to Pt and Ag, Au does not represent the tendency for migration into the SDC layer [11]. However, the performance of the Au conductive layer may decrease with time of operation.

Conclusion

The application of silver as a cathode conductive material, interconnect wires, and sealing for anode lead connection for a µSOFC was studied. The addition of silver as a cathode conductive layer reduced the cell overpotential and increased the cell performance. However, the results showed that silver was also responsible for the cell degradation. Using silver in SOFC stacks reduces system durability. The silver thermal expansion did not match with the thermal expansion of the other cell materials, and therefore, caused damage to the glass sealant. Silver was also found unstable in the dual atmosphere. The results demonstrated that the microstructure of the silver anode lead connection wire changed after it had been exposed to the dual atmosphere, the solid silver wires and the seal became porous. The formation of striation structures and porosity affected the mechanical strength of the Ag interconnect wires.

The cathode polarisation process after OCV promotes silver migration what can lead to the cell short-circuit.

It can be concluded, that silver is not suitable as interconnect at the intermediate temperature in the long-term SOFC application if there is a risk of exposure to the dual atmosphere. Silver migration was also responsible for short-circuit formation.

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