Benchmarking Protective Coatings for SOFC ferritic steel interconnects – The SCORED 2:0 Project

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Abstract

Solid Oxide Fuel Cells are considered as one prime technology for residential CHP and power generation applications. Employment in these sectors requires long operational lifetime beyond 10 years. This corresponds to anything between 20,000 and 100,000 hours of operation. In order to ‘survive’ this extended period of time with the challenging conditions set by SOFC operating parameters (high temperatures, high water content, dual atmospheres across the interconnects etc.) the steel interconnects employed by most current developers require a protective coating to prevent excessive oxidation and release of chromium. A number of different coatings and coating processes have been suggested in the past, ranging from wet powder spraying of MnCo oxides to PVD coating of thin commercial steel sheets with Co and Ce.

The SCORED 2:0 is attempting to benchmark coating materials and the processes they are applied with. The project follows three goals:
1. analyse which is the best process to apply specific materials that have been discussed for SOFC interconnect protective coatings,
2. search for new materials and processes to apply protective coatings, and
3. benchmark the processes and materials against the commercial state of the art.

The expected outcome is a systematic analysis of the interplay between materials, steel substrate, and the physico-chemical processes used to apply the layers. This contribution offers the overview and summary to the more specialised papers submitted in parallel.
Introduction

The economic viability and market place entry of SOFC power systems is directly dependent on their longevity and production costs. Adequate operational life spans can only be achieved, if the performance degradation of the SOFC stacks and Balance of Plant components over time can be considerably reduced. At the same time, manufacturing costs have to be lowered dramatically for the specifically necessary components securing the long service life.

As of now, chromium deactivation of the cathode is considered one of the major contributions to the degradation of SOFC stacks. Since chromium steels, on the other hand, are an essential material in reducing stack costs, methods have to be found to make best use of their advantages whilst avoiding chromium transport to the cathode. In addition, the build-up of oxide scales will influence the electrical resistance and contact resistance of the interconnects thus requiring coatings for the stabilisation of the contacts on both cathode and anode side of the SOFC cell. Balance of Plant components upstream of the cathode contribute likewise to the chromium immission on the cathode, a fact that is often overseen and requires protective coatings for any components situated in the air flow pathway towards the cathode.

Within the project Real-SOFC [1] first steps were made towards developing suitable combinations of steels and coatings. It has become apparent that any steel will require a coating in order to sufficiently reduce chromium evaporation and oxide layer build-up, and also sustain a low surface resistivity. More recently, a variety of new coating techniques have been reported that require further evaluation under SOFC relevant operating conditions.

ScoReD 2:0 aims to further elaborate on the production of coated steel components showing markedly improved properties with regard to chromium release, electrical resistivity and scale growth. The focus of ScoReD 2:0 lies on choosing optimised combinations of protective layer materials with different steel qualities (including low-cost options) and analysing the influence, practicality and cost of different methods of coating, also in understanding which factors influence the efficacy of such coatings.

1. Project Approach

Steel interconnect materials are widely believed to offer the optimum route to high-performance, low-cost SOFC stacks. In order to withstand the demanding operating conditions of SOFC (high temperature of 600-900°C, high humidity on the fuel side at high fuel utilisation rates, carbonaceous fuel gases in methane operation, highly corrosive atmosphere on the air side etc.), all interconnect steels used today are of a high chromium content above 17%. Steel offers the advantage of being easily worked to the required interconnect geometries and being moderately cheap to produce. High chromium steels show a degree of chromium evaporation especially when water is present forming chromium hydroxides [2].

Furthermore, it has been shown that Cr evaporation can take place also from Balance of Plant (BoP) components exposed to high temperatures. Especially those components upstream of the SOFC cathode (piping, manifolds, heat exchangers) should therefore be either similarly coated to inhibit Cr volatilisation (in which case the complex geometry of BoP components can be a problem to achieve uniform coating that is suitably protective
and applied with cost-effective processes), or the volatile Cr species should be trapped before they enter the SOFC stack.

The most common SOFC cathode materials (LSM and LSCF) are generally susceptible to chromium ‘poisoning’ as described in [3]. A gradual loss of performance is observed, generally referred to as ‘continuous degradation’ and is a major hindrance to long-term reliability. In order to render SOFC devices economically viable for stationary power generation applications they would have to show a loss of performance below 0.1 % of voltage per 1000 hours of operation. Although Cr poisoning is not the only phenomenon contributing to continuous SOFC degradation it is commonly believed to be one of the major effects [4, 5].

Systematic experiments have been previously carried out to further clarify the effect of Cr and correlate Cr release with damage done to the cells ([6, 7, 8] and others). Opinion as to the actual damage mechanism(s) varies and several possibilities remain. Nevertheless, it can be concluded that Cr release has to be reliably minimised over a prolonged period of time.

Work at Research Centre Jülich (FZJ) together with VDM and in other steel developing companies such as Sandvik and Plansee has led to steels with an inherently low chromium release and good oxidising and conductivity properties (cf. for instance [9] and results from Real-SOFC on Plansee steels). Although the Cr release can be considerably reduced, uncoated steel will still not meet the requirements for long-term operation of SOFC stacks. The density and stability of protective coating materials will therefore play a significant role in reducing the cathode Cr poisoning problem.

Widespread commercialisation of SOFC power systems is, among other factors, also impeded by the high costs, many of which are related to the metallic interconnects and manufacturing processes of protective coatings. Considering that the issues of weight gain by oxide layer growth (due to the inevitable continuing oxidation in various gas atmospheres) and good surface and bulk conductivity have to also be provided, it follows that the steels have to be coated with a durable layer that will both supply protection and contacting properties, as well as be applied by economically viable processes.

Therefore, a strong interest continues in developing low-cost coating methods that can provide:
• fully dense layers for the most critical components subject to Cr evaporation to avoid any release of Cr species, and
• effective protective coatings for complex geometry steel components upstream of the SOFC cathode, subjected to high temperatures (in particular piping, manifolds and air-side heat exchangers).

Unfortunately the use of wet powder spraying (WPS) techniques leads to layers which become increasingly porous over time probably explaining the progressive degradation observed after several thousand hours of operation. Another parameter not yet fully under control with all coating methods is the application of very thin and at the same time even coatings that allow well-defined contacting of the SOFC cells in a stack and ensure long-term stability of these contacts.

Commercial ferritic stainless steels (series 400) may offer an attractive combination of functional and thermal compatibility properties with the other cell components for the
realisation of low-cost metallic interconnects or BoP components in intermediate temperature SOFC systems (IT-SOFC) at 500 to 650°C operating temperature. Unfortunately, their use has proved to induce a number of corrosion-related problems in terms of increased contact resistance (interconnect) and Cr evaporation (interconnect, BoP) under prolonged exposure due to a much slowed down growth of the Cr oxide passivation layer.

Oxide-based conductive/protective surface layers have been successfully applied on ferritic stainless steel substrates providing a reliable and high-performance behaviour of these materials for IT-SOFC interconnect use, at least in short-term experiments. Overlay deposition of thin layers of complex oxide systems with spinel or perovskite structure have been variously reported in literature by using a wide range of different coating techniques (PVD, sputtering, sol-gel, electrodeposition, etc.). However, the upgrading of most of such coating techniques to a commercial production scale is not straightforward for various reasons including the high cost, arising from use of expensive equipment, complex multi-step processes, batch processes involving vacuum chambers, and labour-intensive procedures.

In order to achieve a single-stage coating process and minimise process costs and materials expenditure, several approaches are being pursued within the SCoReD 2:0 project, essentially divided into optimisation of coating materials and suspensions on one hand, and development of improved coating methods and processes on the other side.

2. Coating Materials and Processes

To facilitate the application of very thin and at the same time very regular coatings, the coating material for especially wet powder spray techniques needs to be tailored and optimised (in particular in terms of microstructure and suspension properties).

The SCoReD 2:0 project is looking into combinations of
- coating materials, and
- coating processes
and the mutual influence they have on each other in determining the coating properties with respect to
- Cr evaporation / release,
- contact resistance, and
- bulk resistance
thus covering the main parameters determining the long-term stability of such layers.

Five different processes are being analysed over a succession of ‘generations’, meaning a continuous or sometimes disruptive evolution of the different coatings. These are
- MnCo powders used as a reference and standard in ‘Generation 1’ (G1),
- LaFe surface treatment,
- MnCo powders doped with Fe (MCF),
- further doped MCF powders, and
- different surface treatments, for instance forming a perovskite surface layer instead of a coating.

The application methods used are
- wet powder spraying (WPS) as the standard reference method,
- WPS using an ink jet printing method,
- dip coating,
- thermal spraying (atmospheric plasma spraying, APS),
- electron beam physical vapour deposition (EB-PVD), and
- atomic layer deposition (ALD).

These methods offer a variety of qualities of coatings with respect to
- density – which is expected to play a decisive role on Cr release reduction and reduced
  bulk (and possibly contact) resistance,
- thickness – which obviously will impact total resistance, and
- possibly also choice of materials – since the methods of EB-PVD and ALD do not allow
  arbitrary compositions of elements to be processed in a single pass.

And, finally, the composition of powders and their particle size distribution (in the
processes using powders) will have an influence on densification during heat treatment
and under operation.

Optimisation of powders with respect to their size and towards improving densification can
be achieved by High Energy Ball Milling (HEBM) and jet milling. HEBM consists of
subjecting powder mixtures of selected compositions to a repeated action of energy
transfer from milling tools to milled powder. The energy transfer takes place through the
ball-to-wall impacts that transform the kinetic energy of the balls in activation energy of
different processes. By operating close to room temperature conditions, different chemical
and physical transformations occur in the trapped powder. Materials having unique
properties (e.g., nanocrystalline materials), which are not otherwise obtainable, can be
produced in this way. Extended solid solutions, metastable amorphous phases as well as
nanocrystalline compounds are the common results of the treatment.

For the purpose of optimising the coating material, selected compositions have been
subjected to HEBM within SCoReD2:0 and the phase evolution with milling time was
followed by X-ray diffraction techniques. At selected different milling times, samples of the
material (necessarily possessing different physical-chemical characteristics) were treated
through an innovative micro-fluidising technique in order to break down particle
aggregation (that frequently occurs in a BM process).

Wet powder spraying is currently still the preferred and most used technology to apply
coatings. It is simple, well understood, cost effective, and fast. Nevertheless, it has some
drawbacks in the way of loss of ink material by considerable overspray, relatively low
viscosity of inks resulting in uneven layers formed on shaped surfaces (e.g., flow channels
in interconnects), and requirement of several passes by spray brush to apply sufficiently
thick layers. One way of overcoming these disadvantages is to use inkjet printing instead
of airbrush painting. This allows for precise application of ink (no masking required). On
the other hand, the development and optimisation of inks for the jet cartridges is more
involved. SCORED 2:0 will be looking at applying ink jet printing to three dimensional
surfaces.

Conversion coatings appear to be very promising to passivate stainless steels at low
manufacturing costs. Well-established industrial practices exist for conversion treatments
applied to low corrosion-resistant substrates (i.e., Al, Mg alloys, carbon and low-alloyed
steels) and have been for instance successfully applied in Molten Carbonate Fuel Cell
(MCFC) development. Surface conversion is usually identified by industry as an
inexpensive treatment requiring minimal surface preparation or consolidation post
treatments with little or no increase in volume due to the avoidance of an additional layer
being applied. Large capital investments can also be avoided as these passivation
treatments are prevalently realised through simple one-pot, one-step processes.
Conversion coating treatments are rarely, if ever, applied to stainless steels. However, the project is using a novel conversion treatment specifically developed for stainless steel protection in high temperature environments. The passivation treatment produces a thin layer of compositionally-graded perovskite oxide layer using a proprietary molten salt technology and one-pot, one-step procedures, essentially dip coating. An advantage of this process is that, operating at relatively high temperatures (600/700°C), complete conversion of the metal surface can be obtained with production of pinhole-free and compact coating structures. Secondly, the process can be applied to cover complex geometries such as flow field channels of the interconnects, piping and manifolds, and possibly entire stainless steel components.

This process promises to have the necessary requirements for high volume and low-cost production. Stainless steels covered by LaFeO₃-based perovskite conductive thin layers have already been proved to be highly corrosion-resistant in simulated MCFC environments at temperatures up to 650°C [10]. Within SCORED 2:0 the use of such conversion coatings is being extended to temperatures higher than 650°C for IT-SOFC applications based upon the primary consideration that perovskite ABO₃ materials are highly compatible with ferritic steel substrates due to very similar thermal expansion behaviour.

For Atomic Layer Deposition (ALD) the coating process is based on chemical precursors, which are reacted directly at the steel surface to be coated in the ALD reactor and combined with flushes of reactant gases. Compounds can be formed by sequential deposition of the element precursors. For ALD coating, the material optimisation includes finding the optimal chemical precursors for the selected coatings, and optimising the deposition process for these. ALD will be utilised in SCORED 2:0 to produce thin (submicron) high quality coatings. It is a surface controlled layer-by-layer coating method based on self-limiting gas-solid reactions that is well suited for producing inorganic high performance coatings. The precursor chemicals are introduced to the surface with alternative pulse-purge sequences. The inert gas purges the excess precursor off the surface before the next precursor is introduced. This way the film growth proceeds by consecutive atomic layers that cover uniformly everything inside the reaction chamber.

Due to the self-limiting growth mechanism the formed film closely follows the topography of the surface to be coated. In addition, due to the growth mechanism, the formed coating layer is conformal, dense and crack and pinhole free. Moreover, the thickness control is simple and accurate (growth per cycle). Due to the layer-by-layer growth process it is also possible to accurately manufacture layered and graded structures. Previously the ALD coating has been tested in ex-situ exposure tests and showed very promising results. Now it will be applied to 'real world' interconnect topographies and tested in the proof-of-concept stack environment.

Magnetron sputtering is a well-established, high quality PVD deposition process, often employed in the production of high quality, industrial scale coatings. The process does not induce any significant increase in surface roughness, but rather faithfully reproduces the texture of the underlying substrate. The Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUBMSIP) approach, developed by Teer Coatings Ltd. transforms the basic magnetron sputtering process, producing high-quality, well-adhered films [11]. The closure of the magnetic fields of two or more magnetrons (with opposite magnetic polarities) minimises the loss of electrons from the plasma to the earthed walls of the surrounding coating chamber. Increased ionisation in the discharge due the resulting increase in
electron-atom ionisation events results in enhanced ion current density (ICD) at a negatively biased substrate [12]. The operation of the magnetron sputtering sources (at low currents) further enhances the ICD during an initial sputter cleaning phase, where the negatively biased substrate is subjected to continuous Ar ion and energetic particle bombardment, resulting in an atomically clean surface, immediately prior to the deposition of the coating. The power to the magnetron sources is increased and the ion-to-atom arrival ratios at the growing coating surface are significantly larger than those seen under similar substrate bias voltage levels in conventional "mirrored field" systems (in which the magnetrons have identical magnetic polarities) or single magnetrons [13].

CFUBMSIP allows high quality film deposition at relatively low operating pressures (e.g. <0.1 Pa) which is beneficial in terms of the characteristics of the deposition plasma and the cleanliness of the deposition atmosphere. The application of Pulsed DC for the substrate bias in the CFUBMSIP in industrial vacuum coating has also been shown to be particularly advantageous [14].

Reactive sputtering from metallic targets is an economic way to deposit compound films, including conductive metal oxides. An automatic feedback mechanism links the flow of the reactive gas to the intensity of a metallic emission line from magnetron sputtering plasma. This enables the system to be controlled in a dynamic mode, ensuring that the compound formation at the magnetron target is restricted, maintaining a high and stable sputtering rate, and a high net deposition rate at the substrate [15]. This approach can also be applied in reactive CFUBMSIP, and for example complex multi-element nitrides can be deposited in this way [16].

The coating structure can be controlled, from a simple uniform, monolithic layer, through deliberately graded compositions, to uniformly distributed nano-composites or macro- or nano-multilayers. Each structure can offer particular advantages, for example magnetron sputtered multilayers are known to improve the corrosion resistance (e.g. [17]) and mechanical properties [18]. The deliberate gradation of coating properties is used to optimise the thermal, wear and corrosion properties of metallic and ceramic surfaces [19] and such graded structures are readily achieved in multi-magnetron coating systems, where the relative powers and electrical characteristics of the magnetrons, the substrate bias conditions, and the deposition atmosphere can all be systematically varied to dynamically modify the structure, composition and habit of the growing coating [20].

3. Developing the Coating Generations

The project uses four 'Generations' of coatings to be applied throughout the project. These have now been amended by a fifth type of coating. At the first project meetings it was agreed to use MnCoO as the starting point as coating material for several reasons:
- this is a commonly used material in protective coatings for SOFC interconnects, and
- the powder(s) are commercially available in a standardised quality.

The initial idea of using a mixture of Mn to Co in the ratio 1:1 in order to reduce the use of environmentally dubious Cobalt and lower the cost of powders by reducing the Co contribution was quickly proven sub-optimal due to reluctance of the powders to form the desired composition even after 100 hours of milling whereas the 1:2 mixture was already stable after 45 hours. Therefore it was decided to use commercial MnCo$_2$O$_4$ powders (MCO) as the starting point for Generation 1 (G1).
As a variant, experiments were conducted to first using a layer of MnO before applying the MCO. The manganese oxide was thought to improve the adhesion of the protective layer and reduce spallation. The outcome of the tests, though, was not in favour of the double layer coatings.

As the project began its work, partner Teer Coatings Ltd. introduced samples that had been surface modified. These showed some beneficial properties with respect to Cr retention and contact resistance. Therefore it was decided to combine surface modified samples with MCO deposition as Generation 2 (G2) coatings.

It was also decided to use iron doped MCO (MnCoFe, MCF) powders as Generation 3 (G3). MFC had been reported by [21] as supplying improved coating behaviours, both as powder for WPS or APS processes. MCF was applied to a stack that was operated in excess of 25 000 hours with very low degradation values (~0.25%/khrs). The protective layers in this stack were applied by atmospheric plasma spraying [22]. This material and method has been further explored by company Turbocoating in the project MMLCR=SOFC. Experiments with different MFC compositions have been reported in [23].

Generation 4 will consist of copper doped MCF in order to increase the densification of the protective layers applied by wet powder processes, copper being used as a sintering additive, and increase the electronic conductivity for the APS and PVD processed layers. WPS applied layers are known to develop porosity during their service life which might compromise their function. The choice of G4 treatment, materials and processes will also depend on the respective process applied and the same approach may not be valid for all three coating work packages at this point in the project. A main focus of this project is to look into the optimal process to applying the different coating materials.

All Generations >1 are being benchmarked against G1 to quantify and map progress towards the criteria of chromium retention, contact and bulk resistance, weight gain, spalling, and (chemical) interaction between steel substrate and coating. It is understood that the different processes might follow different routes from G2 onwards as to the choice of precursor composition due to the interaction of process with coating materials.

### 4. Results

Instead of a comprehensive review of results, this paper should merely point at the other contributions in this conference that offer detailed insight into the single work tasks performed in SCORED 2:0.

Results from surface modification are reported in [24] to [27].

WPS powder and process development are described in [28] and [29].

First results from diffusion and degradation modelling are compiled in [30].

Comparative results from the third generations of coatings are reported in [31].

### 5. Outlook

At the time of writing the first three stacks have entered proof-of-concept long-term testing. Currently it is still too early to discuss stack results. Process optimisation is continuing,
with respect to adhesion, cost, thickness of layers etc. The accompanying research on the chemical (degradation) modelling, and analysis of economic and environmental impact will take up the developments feeding into the final stack test (and prior to this) in order to be based on the most advanced project results.

The example of Real-SOFC shows that although the project terminated many years ago (in 2008), the final stack test is still ongoing [32]. From the point of view of science this is maybe a lesser achievement, since the stack technology implemented in the respective stack (and its successful follow-ups) is still the conventional technology today, but may be able to receive more recent improvements. Nevertheless, the experiment is very encouraging when talking about the lifetime of SOFC stacks. Long-term testing of SCORED 2:0 stacks may therefore be continued post-project and still deliver substantial insight.

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**References**


