



## **Influence of Mn-Co Spinel Coating on Oxidation Behavior of Ferritic SS Alloys for SOFC Interconnect Applications**

**Venkatachalam, Vinothini; Molin, Sebastian; Kiebach, Wolff-Ragnar; Chen, Ming; Hendriksen, Peter Vang**

*Published in:*

Proceedings of the Materials Science and Technology 2014 Conference

*Publication date:*

2014

[Link back to DTU Orbit](#)

*Citation (APA):*

Venkatachalam, V., Molin, S., Kiebach, W-R., Chen, M., & Hendriksen, P. V. (2014). Influence of Mn-Co Spinel Coating on Oxidation Behavior of Ferritic SS Alloys for SOFC Interconnect Applications. In Proceedings of the Materials Science and Technology 2014 Conference (pp. 1213-1220). ASM International.

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

# INFLUENCE OF MN-CO SPINEL COATING ON OXIDATION BEHAVIOR OF FERRITIC SS ALLOYS FOR SOFC INTERCONNECT APPLICATIONS

V. Venkatachalam, S. Molin, W. R. Kiebach, M. Chen, P.V. Hendriksen

Department of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, 4000 Roskilde, Denmark

Chromia forming ferritic stainless steels (SS) are being considered for intermediate temperature solid oxide fuel cell interconnect applications. However, protective coatings are in general needed to avoid chromium volatilization and poisoning of cathodes from chromium species. Mn-Co spinel is one of the promising candidates to prevent chromium outward diffusion, improve oxidation resistance and ensure high electrical conductivity over the lifetime of interconnects. In the present study, uniform and well adherent Mn-Co spinel coatings were produced on Crofer 22APU using electrophoretic deposition (EPD). The oxidation behavior of both the coated and bare alloy was evaluated at 800°C in air for 1000 h. The oxidation kinetics were investigated using weight gain and scale thickness measurements. The weight gain per unit surface area of the bare alloy exhibited parabolic oxidation behavior. The influence of Mn-Co spinel coating on chromia scale formation and corrosion rate of different ferritic stainless steels is also elucidated.

**Keywords:** SOFC, interconnects, EPD, MnCo spinel, Oxidation

## Introduction:

The need for alternative energy sources has been a research focus globally due to the need to mitigate harmful emissions. Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs) (i.e., SOFCs operated in reverse) are solid-state devices that can be used to (a) convert chemical to electrical energy and vice versa<sup>1</sup>. These capabilities make them attractive for energy conversion, energy storage, chemical separation, and chemical synthesis applications. SOFC's are modular, scalable and energy efficient. They are not subjected to carnot cycles limitation and also have low NO<sub>x</sub> emission compared to the previously used power generation technologies<sup>2</sup>.

The material requirements for SOFC interconnects are very challenging because of its exposure to reactive gases, glass bonds or compressive seals, inhomogeneous temperature distribution, and thermal cycling<sup>3</sup>. Also it consumes the major volume and a significant part of the cost of the SOFCs. A major problem with SOFC has been the high operating temperature required for ceramic electrolyte material and the electrodes to achieve sufficient power density<sup>4</sup>. Development of better electrolytes and electrodes has enabled a reduction in operating temperature of SOFC's down to 600-800°C, which opens the opportunity for metallic interconnect materials.

Cr containing ferritic steels are the preferred class of materials for metallic interconnects material because of their electrically conducting chromia oxide scale, good mechanical properties,

appropriate thermal expansion behavior, low cost and excellent manufacturability<sup>5</sup>. However, increase in electrical resistance over time and the evolution of volatile Cr species from the chromia scale under humid conditions currently limit the long term performance and lifetime of the SOFC stack<sup>6</sup>. These effects can be alleviated by applying a protective coating. Many works have been dedicated to finding a suitable protective material. Mn-Co spinel oxide are among the most promising protective coating materials for metallic interconnects<sup>[7,8,9]</sup>. Different coating techniques have been applied such as dip coating<sup>10</sup>, physical vapour deposition<sup>11</sup>, electrolytic deposition<sup>12</sup> and screen printing.

Electrophoretic deposition (EPD) is a low-cost colloidal fabrication process that is widely used for the fabrication of ceramic coatings<sup>[13,14,15]</sup>. EPD has several advantages (over other deposition techniques) such as simplicity, ability to deposit coating on complex shaped substrates, high deposition rate, and easy scalability for mass production<sup>16</sup>. EPD also offers an easy control of coating thickness and morphology through adjustment of the deposition time and applied potential<sup>17</sup>.

In the present study, Mn-Co spinel coatings were electrophoretically deposited on two low cost ferritic stainless steels 430 and 441 along with standard Crofer 22APU. The main aim is to evaluate the possibility for use of commercially available cheap ferritic stainless steel (FSS) with protective coating as SOFC interconnects.

### Experimental Procedure:

Square pieces (20mm x 20mm) were cut from 0.3 mm thick Crofer 22APU, AISI 430 and AISI 441 stainless steel. Prior to application of the coating the pieces were ultrasonically cleaned using ethanol and dried.

Mn-Co spinel powder for the coatings was supplied from FuelcellMaterials with an average particle size of 0.5 $\mu$ m. For the EPD application process, the Mn-Co spinel powders were ball milled for 48 hours in ethanol-isopropanol medium (1:1 ratio) to provide 1wt% suspension. The zeta potential of the Mn-Co spinel powder in ethanol medium was measured using Colloidal Dynamic Zeta Probe.

EPD was performed in a Teflon box with a volume of 150 ml. The steel pieces to be coated were fixed in parallel between the two counter electrodes at an equidistance of 15 mm. The counter electrodes were connected to the positive output of the power sources. The spinel coating was applied on different alloys at different voltages (40, 60 and 100 V) for various durations from 0.5 to 6 min. The current density during the deposition was recorded. After deposition, the Mn-Co spinel layers were dried at room temperature. The coated samples were thermally treated at 800°C for 2 hours in H<sub>2</sub>/H<sub>2</sub>O (97% H<sub>2</sub>-3% H<sub>2</sub>O) and then re-oxidized at 800°C for 2 hours in air atmosphere. All heat treatment was carried out at a constant heating and cooling rate of 2°C/min.

The solid fraction of the deposit films was calculated by,

$$\rho = \left[ \frac{\frac{W_d}{\rho_s}}{\frac{W_d}{\rho_s} + \left( \frac{W_w - W_d}{\rho_e} \right)} \right] \quad \text{Equation 1}$$

Where  $W_d$  and  $W_s$  were the weight of wet and dried coating weight respectively,  $\rho_s$  and  $\rho_e$  are the theoretical density of the spinel powder (6.099 g/cc) and ethanol (0.790 g/cc) respectively.

The initial and final weight of the coupons after EPD coatings was measured. The surface morphology of the coatings were analysed using a scanning electron microscope. The theoretically predicted layer thickness was calculated using equation 1 and the actual layer thickness was measured through cross sectional analysis. The coupons were mounted in the epoxy resin, ground through different grades of SiC paper, polished to 0.25  $\mu\text{m}$  finish using diamond pastes, and then carbon coated.

The oxidation kinetics of the uncoated and coated coupons was studied by measuring the weight gain of the samples as a function of oxidation time. The samples were subjected to cyclic oxidation (in a furnace) at 800°C in air for 1000 hours and the samples were weighed periodically with a time interval of 250 hours. The phase, microstructure and layer adhesion were analyzed using XRD and SEM.

### Results and Discussion:

The factors influencing the deposited weight of an EPD process are often found to be well described by Hamaker's Law<sup>18</sup>:

$$w = \mu CEAt \quad \text{Equation 2}$$

where,  $\mu$  is the electrophoretic mobility, C is the concentration of the suspension, E is the electric field strength, A is the electrode surface area and t is the duration of deposition.

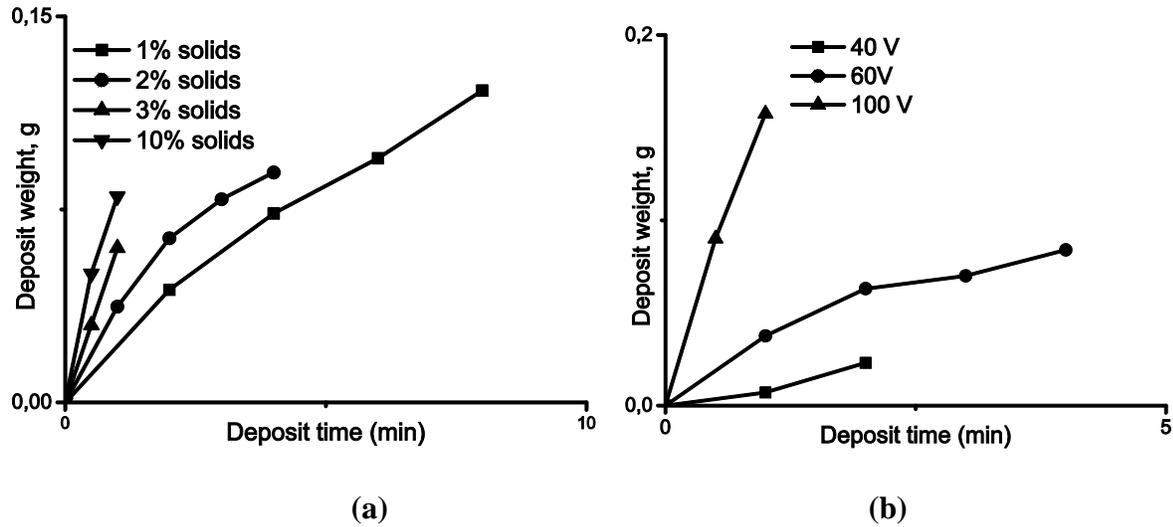
From Equation 2, for a chosen solvent the electrophoretic mobility of the powder remains same. The suspension concentration and applied electric field has direct impact on the amount of powder deposited. Hence, the concentration of the suspension and the applied electric potential is varied for various duration and calculated the deposit weight per unit area in  $\text{g/m}^2$  using the following equation,

$$w = \frac{2}{3} \left( \frac{C \epsilon_0 \epsilon_r \zeta E t}{\eta L} \right) \quad \text{Equation 3}$$

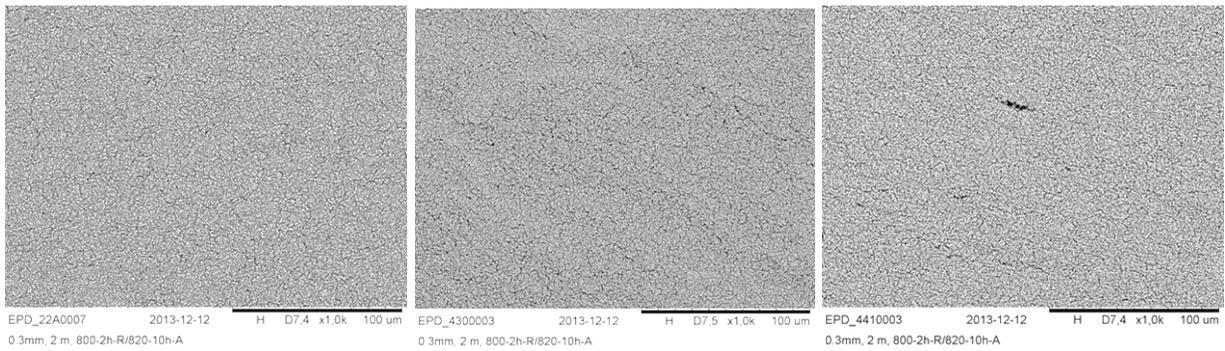
where, C is the concentration of the suspension in g/L,  $\epsilon_0$  is the permittivity of the free space;  $8.854 \times 10^{-12}$  F/m,  $\epsilon_r$  is the permittivity of the suspension medium,  $\zeta$  is the Zeta potential of the powder particles in the suspension medium in millivolts, E is the electric potential used for deposition in Volts, t is the duration of deposition in seconds,  $\eta$  is the viscosity of the solvent medium in mPa/sec and L is the distance between the electrodes in meter.

Figure 1 shows the amount of spinel powder deposited calculated using equation 3 against deposition time for various concentration of solid content in the suspension. It indicates that the deposition rate increases with increasing solid loading of the suspension and the potential used for deposition as expected. Although the rate of deposition is higher initially, the longer duration provides time for particle to deposit and rearrange to achieve good packing density. During the EPD process, under the applied potential, the particles move with the velocity of  $v = \mu E$ . With increasing applied voltage, the electro osmotic flow of the particles increases resulting in higher

deposit rate. It has been previously demonstrated that the particle deposit and rearrange with increasing applied voltage resulting in better packing<sup>19</sup>.



**Figure 1: Variation of deposit weight with (a) time and (b) electric potential for deposition, for various solid content of the suspension.**



**Figure 2: Surface images of the Mn-Co spinel EPD coated on different FSS (a) Crofer 22A (b) 430 (c) 441**

Based on the above deposition results, for further studies the coating was deposited using 1 wt% solids in ethanol: isopropanol medium at 60V for 2 min, resulting in ~20μm thick coatings.

Figure 2 shows the surface images of the coating on various steels. The surface of the coatings was found to be smooth and uniform.

#### Oxidation:

Figure 3 shows the weight gain per square centimeter of the Mn-Co spinel coated ferritic alloys, heat treated at 800°C up to 1000 hours in air. The oxidation follows parabolic growth, as described by Wagner's theory of high temperature oxidation.

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t + C \quad \text{Equation 4}$$

Where,  $\Delta m$  is the weight change during the heat treatment,  $A$  is the surface area of the sample in  $\text{cm}^2$ ,  $k_p$  is the corrosion rate  $\text{g}^2/\text{cm}^4\text{sec}$  and  $t$  is the duration of exposure in seconds.

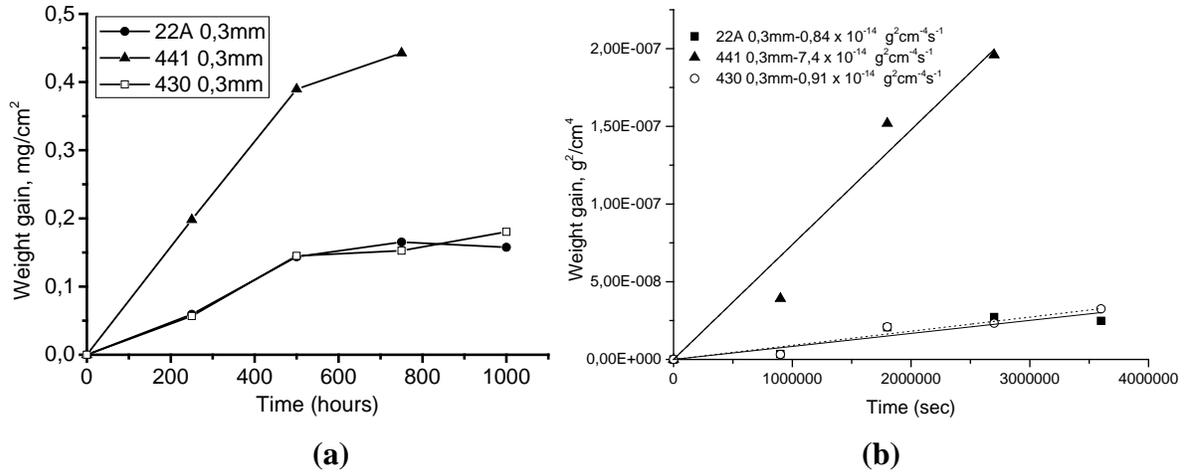
Hence, by plotting  $\left(\frac{\Delta m}{A}\right)^2$  vs time it forms a linear curve and the slope of the curve gives the corrosion rate of the alloys, Figure 3.

The oxidation rate following a parabolic type behavior indicates that the rate limiting step will be diffusion of anions or cations i.e. some process where the net weight gain decreases in proportional to the scale thickness. For the here presented chromia forming alloys, the studies indicates that the rate limiting step is chromium outward diffusion.

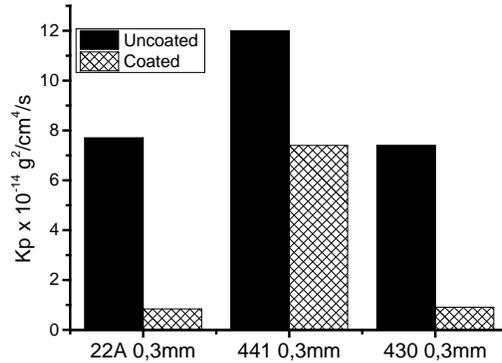
Comparing the corrosion rate of uncoated and Mn-Co spinel coated alloys from Figure 4, its evident that the Mn-Co spinel coatings greatly reduces the corrosion rate of all the alloys. In particular there is a significant reduction in corrosion rate of Crofer 22APU ( $0.84 \times 10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ ) and 430 FSS alloys ( $0.91 \times 10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ ) compared to 441 FSS alloys ( $7.4 \times 10^{-14} \text{ g}^2\text{cm}^{-4}\text{s}^{-1}$ ).

The cross sectional analysis of the Mn-Co spinel coated alloys, oxidized at  $800^\circ\text{C}$  for 1000 hours in air is shown in Figure 5. A dense chromium oxide layer is formed beneath the spinel coatings. The spinel layer was found to be dense near the alloy surface and porous on the outside. The Crofer 22APU still retains a porous structure in the spinel coating with a thin dense chromium oxide layer of about  $4 \mu\text{m}$  thickness beneath the spinel coating. The 441 alloy, having similar composition of Crofer 22APU, shows slightly denser spinel coating and the thickness of the chromia subscale is about  $2\text{-}3 \mu\text{m}$ . Due to the different thermal expansion coefficient of the formed thick chromia subscales through Cr outward diffusion and the Mn-Co spinel layer, the coatings crack along the interface in the 441 steel. Thus, in the case of 441 alloys the chromia subscale cracks, creating further Chromium outward diffusion to protect the surface by forming chromium oxides. Hence thick chromia subscale is formed in 441 alloys. This could be the reason for a higher corrosion rate of 441 alloys even with the spinel coatings.

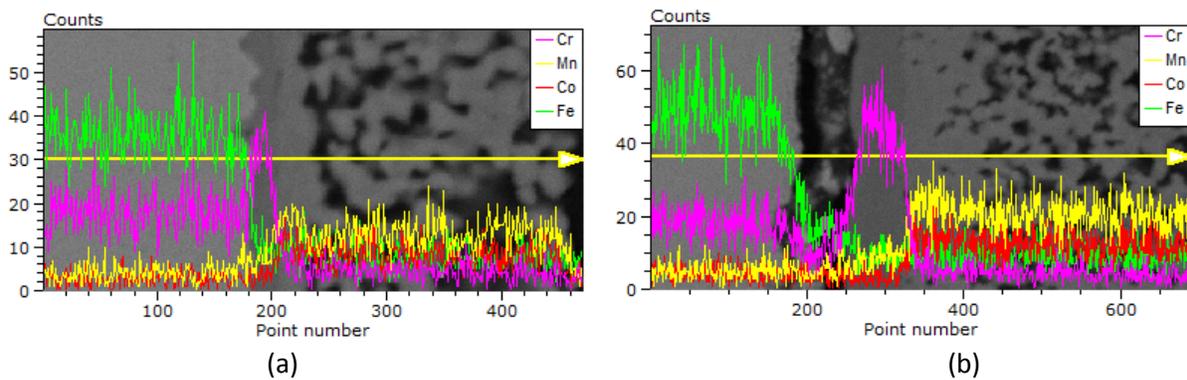
Surprisingly, for the 430 alloys with less chromium than the other two, the Mn-Co spinel coating was found to be intact. Also the thickness of the chromia subscale formed was  $\sim 1\mu\text{m}$  and has denser spinel layers compared to the other two alloys. The difference in behavior of Mn-Co spinel on the alloys could be due to their difference in preferential outward and inward migration of Cr and O ions. More studies on the ion transport in these alloys with coatings have to be carried out for further in depth understanding.

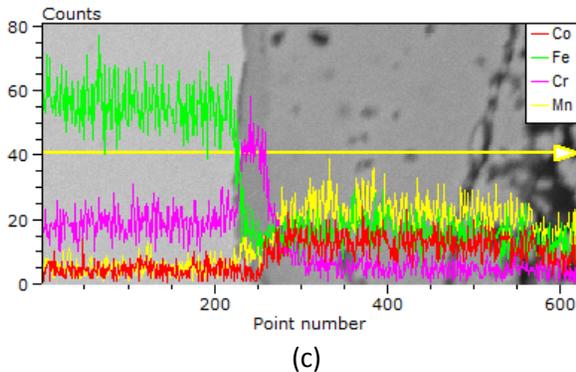


**Figure 3: (a) Weight gain of the Mn.Co spinel EPD coated on different FSS at 800°C for 1000 hours in air, (b) Square of weight per unit surface area Vs time.**



**Figure 4: The corrosion rate (kp) of different FSS - uncoated and Mn.Co spinel EPD coated at 800°C up to 1000 hours in air**





**Figure 5: Cross sectional SEM images with EDX line scan mapping of different FSS Mn.Co spinel EPD coated and oxidized at 800°C for 1000 hours in air. (a) Crofer 22A APU, (b) AISI 441, (c) AISI 430**

### Conclusions:

The EPD process seems to be suitable technique for application of protective layers on SOFC interconnects. From the preliminary results, the 430 alloy coated with Mn-Co spinel is found to have sufficient high temperature corrosion resistance for the use in an SOFC stack. It shows a low corrosion rates, similar to the specially designed alloys for SOFC applications. Long term stability of these coated alloys has still to be verified. Also, the area specific resistance measurements of these alloys with Mn-Co spinel coatings must be evaluated for further exploitations of its use in SOFC applications.

### Acknowledgements

The financial support from EUDP (Danish Energy Agency) project 64012-0225 “SOFC Accelerated – Development to Accelerate Field Demonstrations” is gratefully acknowledged.

### References:

- 1 M. Haile, Fuel cell materials and components, Acta Mater. 51 (2003) 5981–6000
- 2 S. Linderoth, Solid oxide cells R&D at Risø National Laboratory—and its transfer to technology, J. Electroceramics. 22 (2009) 61–66
- 3 Z. Yang, G. Xia, P. Singh, J.W. Stevenson, “Electrical contacts between cathodes and metallic interconnects in solid oxide fuel cells”, J. Power Sources 155 (2006) 246–252.
- 4 N. Shaigan, W. Qu, D.G. Ivey, W. Chen, “A review of recent progress in coatings, surface modifications and alloy developments for solid oxide fuel cell ferritic stainless steel interconnectsReview”, J. Power Sources 195 (2010) 1529–1542
- 5 S.S. Pyo et al., “Characteristic of  $(La_{0.8}Sr_{0.2})_{0.98}MnO_3$  coating on Crofer22APU used as metallic interconnects for solid oxide fuel cell” Int. J. Hydrogen Energy 36 (2011) 1868–1881.
- 6 Y. Li et al., “Oxidation behavior of metallic interconnects for SOFC in coal syngas”, Int. J. Hydrogen Energy, 34 (2009) 1489–1496

- 
- 7 J. Wu, C.D. Johnson, Y. Jiang, R.S. Gemmen, X. Liu, "Pulse plating of Mn-Co alloys for SOFC interconnect applications", *Electrochim. Acta* 54 (2008) 793-800.
  - 8 C.C. Mardare et al., "Investigation of thermally oxidized Mn-Co thin films for application in SOFC metallic interconnects", *Appl. Surf. Sci.* 255 (2008) 1850-1859
  - 9 Y. Larring and T. Norby, "Spinel and Perovskite Functional Layers Between Plansee Metallic Interconnect (Cr-5 wt % Fe-1 wt %  $Y_2O_3$ ) and Ceramic  $(La_{0.85}Sr_{0.15})_{0.91}MnO_3$  Cathode Materials for Solid Oxide Fuel Cells", *J. Electrochem., Soc.*, 147, 3251 (2000)
  - 10 Y Xu et al., "Cu doped Mn-Co spinel protective coating on ferritic stainless steels for SOFC interconnect applications", *Solid state Ionics*, 192 (2011) 561-564.
  - 11 P Gannon et al., "Advanced PVD protective coatings for SOFC interconnects", *Intl J of Hydrogen Energy*, 33 (2008) 3391-4000
  - 12 M R Bateni et al., " Spinel coatings for UNS 430 stainless steel interconnects", *Surface & Coatings Technology*, 201 (2007) 4677-4684
  - 13 L. Besra, M. Liu," A review on fundamentals and applications of electrophoretic deposition (EPD)", *Prog. Mater. Sci.* 52 (2007) 1-61
  - 14 Z Yang et al., "Electrical contacts between cathodes and metallic interconnects in solid oxide fuel cells", *J of Power Sources*, 155 (2006) 246-252
  - 15 H Zhang et al., "Electrophoretic deposition of  $(Mn,Co)_3O_4$  spinel coating for solid oxide fuel cell interconnects", *J of Power Sources*, 196 (2011) 8041-8047
  - 16 I Corni, M P. Ryan, A R. Boccaccini, "Electrophoretic deposition: From traditional ceramics to nanotechnology", *J of European Ceramic Society*, 28 (2008)1353-1367.
  - 17 W Huang et al., "Evaluation of Electrophoretically Deposited  $CuMn_{1.8}O_4$  Spinel Coatings on Crofer 22 APU for Solid Oxide Fuel Cell Interconnects", *J of Electrochemical society*, 155 (2008) B1161
  - 18 H C Hamaker, "Formation of a Deposit by Electrophoresis", *Trans. Farad. Soc.*, 35 (1940) 279-87
  - 19 C Ji, W Lan, P Xiao, "Fabrication of Yttria-Stabilized Zirconia Coatings Using Electrophoretic Deposition: Packing Mechanism During Deposition", *J of Am. Ceram. Soc.*, 91 (2008) 1102-1109