

Project number: 263262 **Project acronym:** STEELCOAT

Project title: Development of Green Anticorrosion Coatings for Steel Protection based on Environmentally Friendly Nanoparticles and Conducting Polymers

Work package:	Lead beneficiary:	Participating organisation:
WP5: Enhanced fundamental understanding of corrosion protection systems	Trento	KTH

Tasks covered:

5.1 Molecular and microscopic understanding of the active corrosion protection mechanism	
5.2 Characterization of corrosion protection properties of the coating applied on the metal substrate using advanced electrochemical techniques	✓

Deliverable number and name	Delivery date (month)	Dissemination level	
D5.2 Understanding the role of ceria and nanoclays	18	PU	✓

Author: Michele Fedel

Date of submission: 17th of October, 2012

Table of Content

1. BACKGROUND	3
2. AIM AND OBJECTIVE	4
3. CORROSION INHIBITION MECHANISMS OF CERIUM OXIDES	5
3.1. LEACHING OF CE IONS FROM THE OXIDES	5
3.2. EFFECT OF THE CeO_2 AS COMPLEXING AGENT	6
3.3. OXIDATION/REDUCTION CAPABILITY OF $\text{CeO}_2/\text{Ce}_2\text{O}_3$	7
3.4. EXAMPLES FROM LITERATURE.....	9
4. EXPERIMENTAL RESULTS AND DISCUSSION	10
5. CONCLUSION	15
6. SUGGESTIONS FOR FURTHER WORK	16
7. REFERENCES	16

1. Background

In the field of corrosion protection, cerium based compounds are attracting more and more attention due to their potential as corrosion inhibitors. In this context, the use of lanthanide oxides and, in particular, cerium oxides, as a pigments inside the paints for corrosion protection have been studied by a few authors [1,2]. To better understand the role of cerium oxides as corrosion inhibitors it is necessary to get some insight into the equilibrium of cerium species in aqueous environment. In fact, the presence of water at the metal/polymer interface is expected during the service life of a coated metal. Considering that steel corrodes due to the presence of water and oxygen (which sustain the cathodic process: $2\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^- \rightarrow 4\text{OH}^-$) it is necessary to point out the behaviour of Ce compounds in water.

The stability of cerium species in aqueous environment has been object of a few studies [3,4]. A good foundation to clarify the formation/dissolution of cerium compounds in water is given by the Pourbaix diagram (Figure 1), also known as potential - pH (E-pH) diagram. Generally speaking, Pourbaix diagrams are a theoretical tool used to identify or predict the conditions for the stability of different compounds in water. Two main variables, pH (chemical) and potential (electrochemical) play an important role on the formation of cerium compounds.

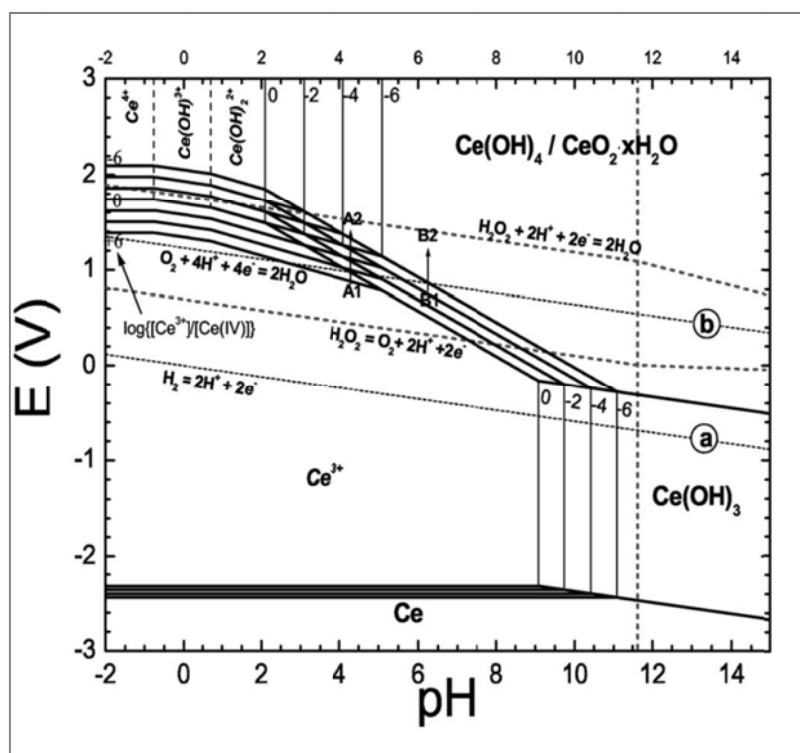
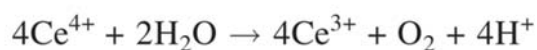
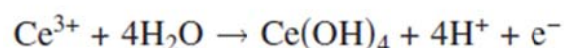
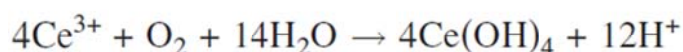
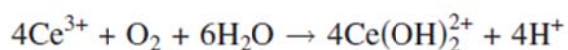


Figure 1 Pourbaix diagram for Ce-H₂O system

Considering Figure 1, it is possible to appreciate that both Ce³⁺ and Ce⁴⁺ exist as stable species depending on pH and potential. It can be seen that, in the low pH range, Ce³⁺ species are stable (see the following reactions)

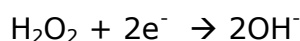
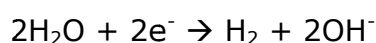


At higher pH, O_2 tends to oxidize Ce^{3+} to Ce^{4+} , mostly as $\text{Ce}(\text{OH})_2^{2+}$, $\text{Ce}(\text{OH})_4$, and $\text{CeO}_2 \cdot x\text{H}_2\text{O}$. For the O_2 - Ce^{3+} - Ce^{4+} system, at relatively high pH values (>5), $\text{Ce}(\text{OH})_4$ is the overwhelming species.

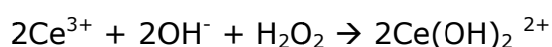
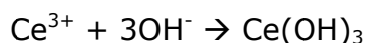


The Pourbaix diagram in Figure 1 also shows other features: a) the pH required for precipitation to cerium oxide Ce^{4+} ions is in the range of 4.5; b) the possibility of the Ce^{3+} to CeO_2 reaction occurs over a broad range of pH and potential; c) the stability region of CeO_2 is large.

Due to the particular pH dependence of cerium compounds, cerium salts (in particular cerium nitrates) has been proven to be effective corrosion inhibitors [5-10]. In fact, because of the local pH increase at the cathodic sites due to the generation of OH^- ions ($2\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^- \rightarrow 4\text{OH}^-$), insoluble cerium compounds such as $\text{Ce}(\text{OH})_4$ and $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ are formed. These compounds precipitate on the surface of the metal, reducing the cathodic reaction rate and thus the overall corrosion rate. The reactions that would raise the pH are:



In presence of Ce^{3+} cations the following reactions occur at alkaline pH, leading to the formation of insoluble Ce compounds.



As stated above, the general protection mechanism provided by cerium ions is governed by a local pH increase causing the precipitation of cerium hydroxides, oxides or mixture of both on the metal surface, specifically at the cathodic sites and this is believed to diminish the cathodic current. A decrease of the cathodic reaction rate causes a decrease of the overall corrosion extent.

2. Aim and Objective

Considering different applications, cerium oxides (mainly Ce_2O_3 and CeO_2) have an important functional designation for the manufacture of catalytic converters. In fact ceria is widely used as a reducible oxide support material in the field of

emission control catalysis for the purification of exhaust gases for different combustion systems. However, little literature is present about Ce oxides as corrosion inhibitors and the corrosion protection mechanisms provided by Ce oxides.

In this report the mainstreaming hypothesis on the corrosion inhibition potential of cerium oxides are reported. Moreover, the literature data are used to interpret the experimental results obtained on the cerium oxide particles provided by the different SteelCoat partners. The electrochemical behaviour of a mild steel electrode (substrate to protect) immersed in water solutions containing different cerium oxide nanoparticles was investigated. The aim is to get some insight into the fundamental mechanisms through which cerium oxides are able to provide the metallic substrate with improved corrosion resistance.

3. Corrosion inhibition mechanisms of cerium oxides

Based on the present literature survey, it is possible to identify three possible mechanisms responsible for the performance of cerium oxides as corrosion inhibitors:

- ✓ Leaching of Ce ions from the oxides
- ✓ Effect of the CeO₂ as complexing agent
- ✓ Oxidation/reduction capability of CeO₂/Ce₂O₃

3.1. Leaching of Ce ions from the oxides

This hypothesis considers that a release of cerium cations from the cerium oxide particles occurs due to the increased solubility of the oxides when the particle size is of the order of nanometers. In fact, the Ostwald-Freundlich equation reports the relationship between the relative solubility of spherical particles of identical materials, as reported in literature in the form [11]:

$$\frac{RT\rho}{M} \ln \frac{S_1}{S_2} = 2\gamma_{sl} \left(\frac{1}{r_1} - \frac{1}{r_2} \right)$$

Where R is the gas constant, T is the absolute temperature, M is the molecular weight of the solid in the solution, γ_{sl} is the interfacial tension between the solid and liquid, ρ is the density of the solid, S_1 and S_2 are the solubility of particles of size (radius) r_1 and r_2 , respectively [12]. Accordingly, as stated by the Ostwald-Freundlich equation a decrease of the particle size will increase the equilibrium solubility.

Thus, a decrease of the cerium oxide particle size should lead to an increased tendency of the cerium to enter into the solution as ions. Ce⁴⁺ may react with the OH⁻ groups in the solution leading to the formation of Ce(OH)₄ which precipitates on the metal surface, leading to an inhibition of the oxygen reduction reaction. The proposed mechanism is schematically reported in the following Figure 2 (a,b). Figure 2a schematically depicts the release of Ce cations from the CeO₂

particles while a corrosion process is occurring on the steel surface. Figure 2b schematically depicts the formation of $\text{Ce}(\text{OH})_4$ which precipitates on the metal surface leading to decrease of the corrosion rate.

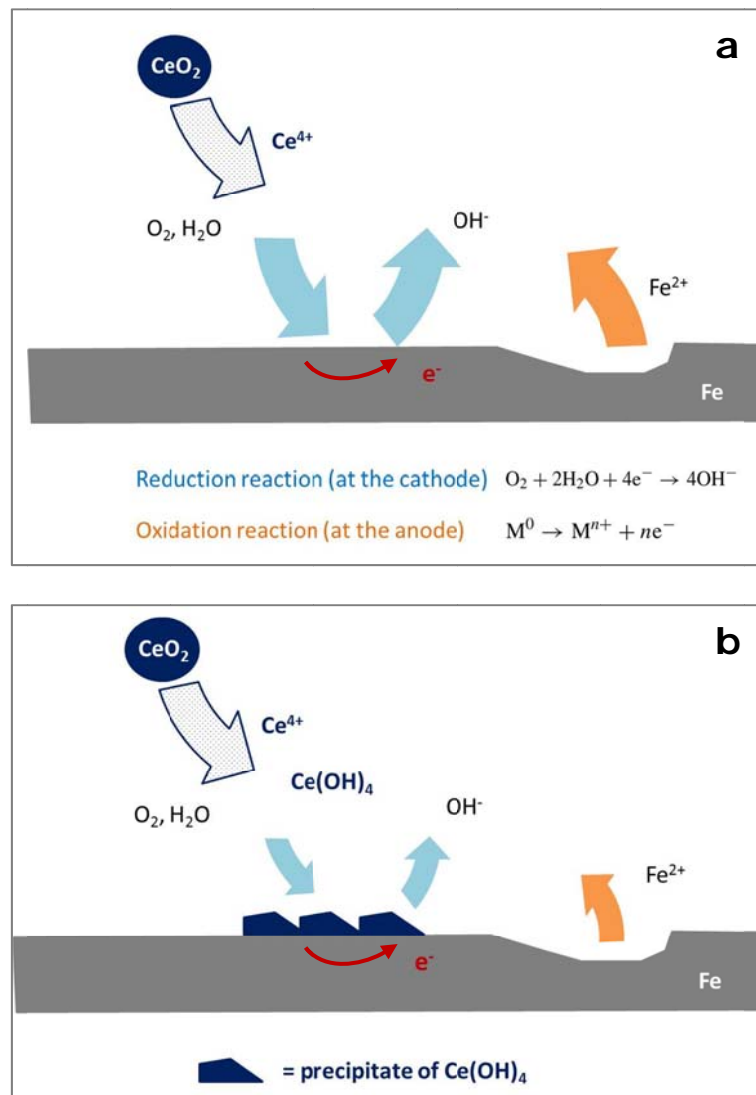
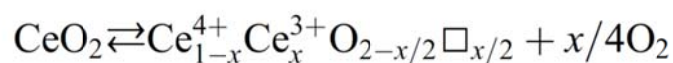


Figure 2. Protection mechanism through Ce ion release from the oxides

3.2. Effect of the CeO_2 as complexing agent

Due to its fluorite structure, the oxygen atoms in a ceria crystal are all in a plane with one another, allowing for rapid diffusion as a function of the number of oxygen vacancies [13]. As the number of vacancies increases, the ease at which oxygen can move around in the crystal increases, allowing the ceria to reduce and oxidize molecules. It has been shown that the electrochemical/catalytic activity of ceria is directly related to the number of oxygen vacancies in the crystal, and to the Ce^{3+} to Ce^{4+} ratio in the crystal.

Oxygen evolution equilibrium of CeO_2 is represented in the following reaction



\square : oxygen defect

The ideal $r(M^{n+}) / r(O^{2-})$ ionic size ratio of MO_8 eight coordination oxide is 0.732. In the case of CeO_2 , $r(Ce^{4+})/r(O^{2-})$ is 0.703, indicating that Ce^{4+} is not large enough to stabilize the fluorite structure. In order to take a more stable eight coordination of the fluorite structure, some Ce^{4+} have a tendency to be reduced to Ce^{3+} , which has a larger ionic size than Ce^{4+} in order to release oxygen molecules accompanied by the formation of oxygen vacancies [14,15].

As evidenced by Peng Gao *et al.*[16] cerium oxide tends to create anion deficiencies: the oxygen vacancies can move through the lattice relatively easily because of the character of the fluorite structure and the electronic configuration ([Xe]4f5d6s) of Ce atoms.

The oxides with this structure can readily incorporate dopant (such as ions) by forming charge-compensating defects on the oxygen sublattice [17]. Such a structure is prone to incorporate ions, thus acting as a complexing agent leading to the formation of a stable layer of compounds on the metal surface. The proposed mechanism is reported in the following Figure 3 (a,b), which schematically depicts the complexing effect of CeO_2 in presence of a corrosion process occurring on the steel surface.

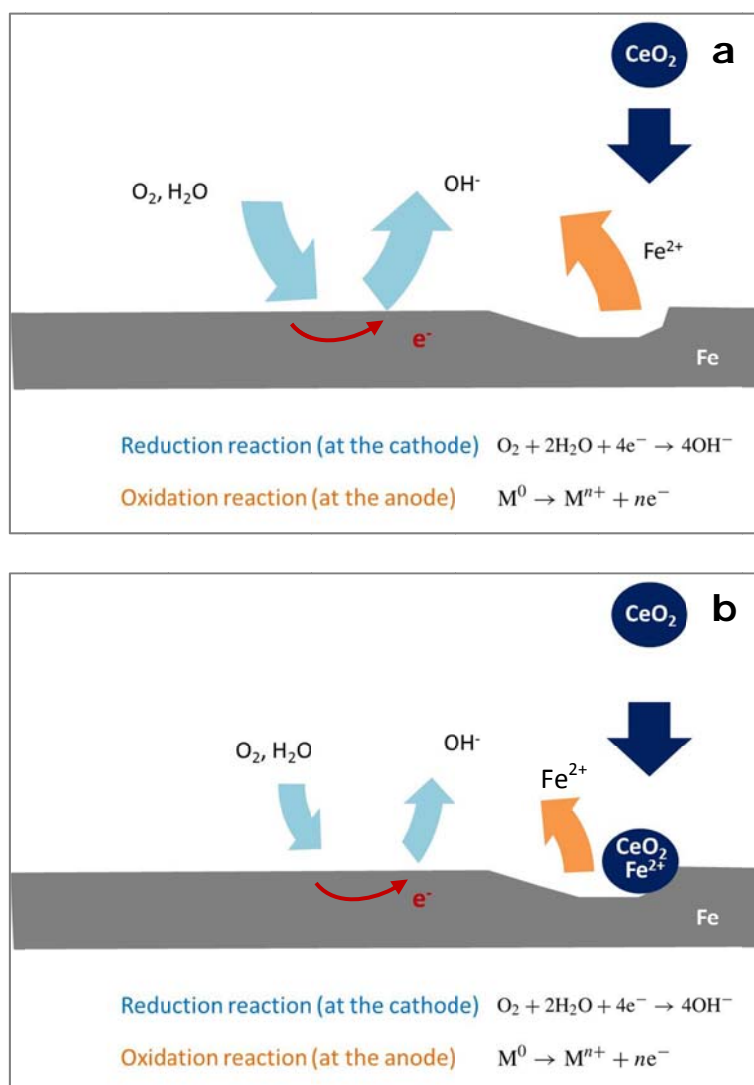
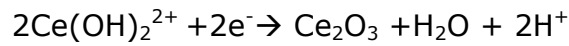
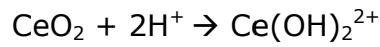


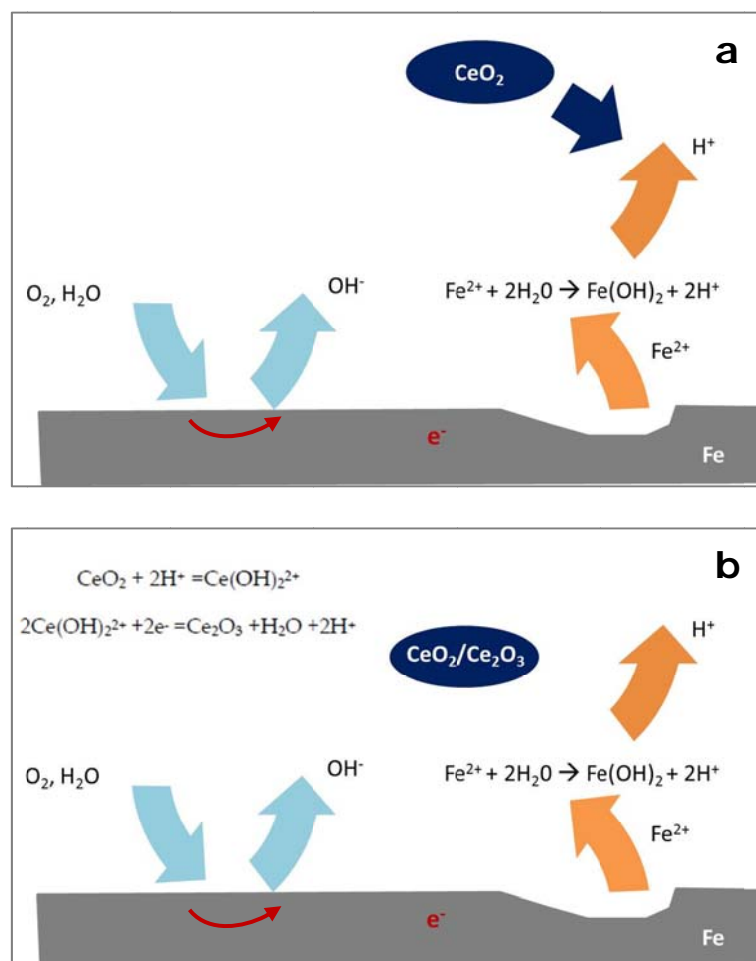
Figure 3. Protection mechanism of CeO_2 as complexing agent

3.3. Oxidation/reduction capability of CeO_2/Ce_2O_3

The last proposed mechanism relies on the activity of the Ce^{3+} and Ce^{4+} redox couple, shifting between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions [17]. Even in presence of CeO_2 a $\text{CeO}_2/\text{Ce}_2\text{O}_3$ mixed oxide can easily be generated. In fact in presence of H^+ ions (which are commonly present in correspondence of the anodic sites due to metal hydrolysis) the following reactions take place:



When reduction of Ce^{4+} to Ce^{3+} takes place and a $\text{CeO}_2/\text{Ce}_2\text{O}_3$ couple is formed. The above mentioned reactions occur as a result of the extraordinary oxidation-reduction capability of the $\text{CeO}_2/\text{Ce}_2\text{O}_3$ couple. Due to these reactions during the corrosion process, the CeO_2 particles will be changing, enriching themselves in Ce_2O_3 . Owing to its reduction capability ($\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$) the $\text{CeO}_2/\text{Ce}_2\text{O}_3$ mixed oxide in contact with a steel substrate can trigger the passivation of the metallic material. The cathodic reduction of CeO_2 , which occurs at the corrosion potentials, established for the systems $\text{CeO}_2/\text{Ce}_2\text{O}_3/\text{steel}$ is the main reason for the formation and preservation of the passive state of the steel substrate. The proposed mechanism is reported in the following Figure 4 (a-c), which schematically show the formation of a $\text{CeO}_2/\text{Ce}_2\text{O}_3$ couple in correspondence of a corrosion process occurring on the steel surface. Figure 4c depicts the passivation of the steel substrate due to the formation of a $\text{CeO}_2/\text{Ce}_2\text{O}_3/\text{steel}$ system.



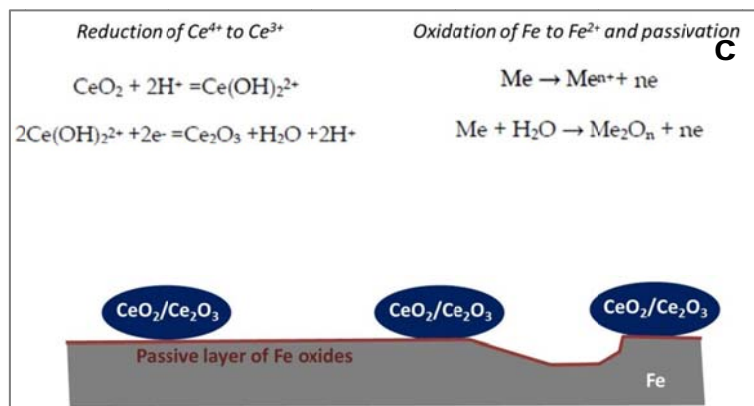


Figure 4. Protection mechanism based on the oxidation/reduction capability of CeO₂/Ce₂O₃

3.4. Examples from literature

In the previous section three different hypothesis of the mechanism of corrosion protection of cerium oxides were proposed. Up to now, the present literature did not clarify the correct mechanism through which Ce oxides provide a metal substrate with improved corrosion resistance. However literature reports examples of effective application of cerium oxides as corrosion inhibitors for metallic substrates. The idea of an oxide nanoparticles which can absorb inhibitor ions and, when in contact with moisture, slowly release them, was proposed by Zheludkevich et al. [18]. In their study, zirconia nanoparticles were firstly synthesized followed by cerium nitrate addition, for Ce³⁺ absorption. EIS analysis demonstrated that the films prepared with cerium doped zirconia nanoparticles conferred higher corrosion than the un-doped after 250h of immersion on neutral media, and this fact is attributed to the formation of an oxide layer between the metal and the film. Moreover, the oxide layer resistance versus time of immersion for films with cerium doped zirconia nanoparticles showed a slight decrease on the downward direction, as an indicative of a slower releasing of cerium ions. Films without the cerium treatment showed a rapid decrease of the protection properties.

The evaluation of inhibition properties of cerium oxide nanoparticles submitted to a cerium nitrate treatment was studied by M.F. Montemor et al. [19]. CeO₂ nanoparticles and CeO₂ + Ce ions were added as filler on silane films on galvanized steel. Scanning vibrating electrode technique (SVET) was used to investigate scratched samples of CeO₂ filled films which exhibited low current densities until the 72th hour in correspondence of the defect. After that, delamination of the films and an increase on the current densities were observed. The presence of cerium ions on the CeO₂ + Ce filled films, however, promoted a better adhesion and inhibition, owing to insignificant delamination and slight anodic activity longer than 72 hours. Moreover, d.c. polarization curves were performed and both filled films, CeO₂ and CeO₂ + Ce, shifted the corrosion potential to the noble direction.

The study evidenced that CeO₂ nanoparticles promote the stabilization of the passive film. In addition, the presence of cerium ions, enhances this mechanism and justify the better performance showed by the CeO₂ + Ce filled films.

A different study containing CeO₂ and SiO₂ nanoparticles added as an additive in a urethane primer, top coated with a polyester/epoxy blend over galvanized steel

was done by Fedel et al. [20]. After 500h of exposure, superior salt spray chamber performance was observed for systems containing the SiO₂/CeO₂ and SiO₂ pigments, in which a good protection with a little delamination was observed. However, EIS evidenced a possible synergistic effect when CeO₂ was added together with SiO₂. Two hypotheses were suggested to explain the role of cerium; (a) (OH⁻) ions produced at the cathode reacted with cerium ions released by cerium oxide particles, the product of this reaction precipitated on the cathodic sites and reduced the cathodic current; (b) cerium oxides promotes the formation of complexes compounds with greater corrosion stability.

The hypothesis (a) comes to an agreement with reports given by [21]. The hypothesis (b) is better detailed by Aramaki [22], who described the formation of a passive film, composed of Zn(OH)₂, ZnSi₂O₅ and some cerium, silicates (Ce³⁺ - SiO₅²⁻) salts or complexes, on zinc surface protected with sodium silicate (Na₂Si₂O₅) and cerium-(III) nitrate Ce(NO₃)₃. Studying the corrosion protection of galvanized steel, the author evidenced that after oxidation of Zn into Zn⁺² at the anodic region, Zn²⁺ ions reacts with hydroxyl ions produced at the cathodic process and Si₂O₅⁻, forming a passive film on the surface. In addition, Si₂O₅⁻ ions reacts with Ce⁺³ and forms a Ce₂(Si₂O₅) compound.

4. Experimental Results and Discussion

The ceria nanoparticles supplied by the partners of the SteelCoat project were analysed in order to evaluate their potential as corrosion inhibitors for mild steel. Among the different materials studied, in this report only a few experimental results are reported. In particular the samples that show a relatively clear inhibition effect are reported and discussed in details.

The University of Aarhus- AU, Denmark provided dispersions of nanoparticles in a liquid. Since the aim is to get some insight into the fundamental mechanisms of corrosion protection, the effectiveness of the nanoparticles as corrosion inhibitors was evaluated by means of potentiodynamic measurements carried out on mild steel using the dispersions of nanoparticles as electrolyte. For comparison, the potentiodynamic measurements were performed also on mild steel substrates immersed in 0,3wt% Na₂SO₄ solution. The pH of the solution was modified according to the pH of the different dispersion of particles. Since the pH has an influence on the stability of Ce³⁺ and Ce⁺⁴ and their compounds, this aspect has to be considered for the interpretation and discussion of the experimental results.

Table 1 shows the samples tested. For these samples it was possible to gain relatively clear and repeatable results allowing us to discuss possible corrosion protection mechanisms of the cerium oxides.

Investigated samples	
Label	Properties
AU-C-W1	Cerium oxides particles in water
AU-C-W2	Cerium oxides particles in water
AU-C-W5	Cerium oxides particles in water with surfactant
AU-C-W6	Cerium oxides particles in water

Table 1.

The mild steel samples were immersed in the different dispersion of Ceria nanoparticles (without any further dilution) and the anodic and cathodic branches of the potentiodynamic curves were collected immediately. The results were compared to the behaviour of mild steel in a solution containing 0,3wt% Na₂SO₄ at different pH. The Na₂SO₄ based electrolyte is not aggressive for mild steel and its conductivity is comparable to the nano-ceria dispersions. Therefore the Na₂SO₄ solution was used as control. The curves were collected at room temperature, the scan rate was set to 0,166 mV/s and the termination potential was -1,0 V vs open circuit potential for the cathodic polarization and +1,0 V vs open circuit potential for the anodic polarization. A three electrodes arrangement was used: Ag/AgCl reference electrode (+205 mV vs SHE), platinum ring counter electrode and mild steel as the working electrode. The measurements were repeated twice to confirm the experimental results. The repeatability of the experimental measurements was considered satisfying. Figure 5 shows the anodic and cathodic polarization curves for the mild steel electrode immersed in the AU-C-W1 cerium oxides particles solution.

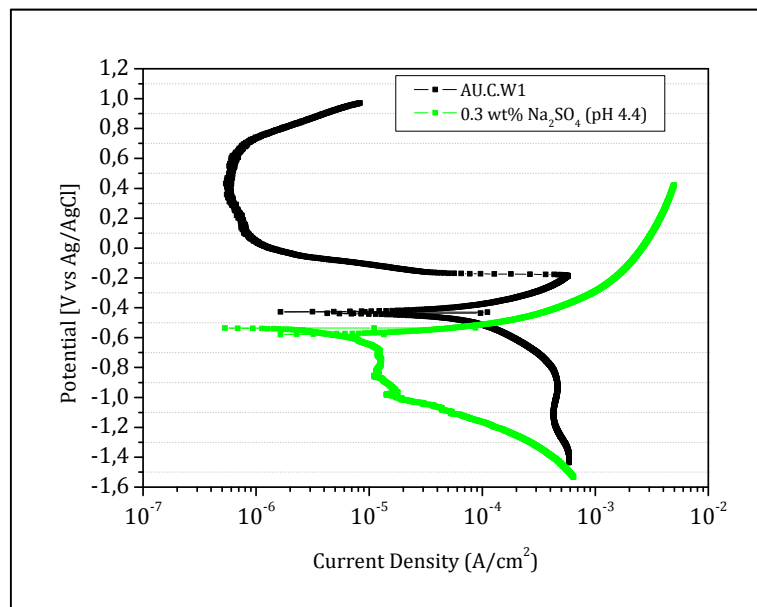


Figure 5. Potentiodynamic curves for the steel electrodes immersed in AU-C-W1 solution and control solution

As reported in Figure 5, the anodic branch of the potentiodynamic scan collected on mild steel immersed in the dispersion AU-C-W1 shows an almost active/passive behavior characterized by a passive region between 0,1 and 0,7 V (vs Ag/AgCl) and a passivation potential at -0,2 V (vs Ag/AgCl). In correspondence of the passive region the passive current density reaches relatively small values around 10⁻⁶ A/cm². AU-C-W1 seems to behave as an anodic inhibitor for steel. A small increase of the open circuit potential is also observed (from -0,5 V to -0,4 V vs Ag/AgCl).

The efficiency of this material as corrosion inhibitor seems very high, since it promotes the decrease of at least three orders of magnitude of anodic current respect to the control sample and the formation of a passive layer of the steel substrate. To better understand the mechanism through which the AU-C-W1 particles are able to promote a passivation of the steel surface and, therefore, a strong reduction of the anodic current, steel samples were put in contact with the

solution containing the cerium particles for different immersion time. Potentiodynamic measurements were performed on the steel samples conditioned in the cerium oxide containing solution in order to investigate the presence of conversion or passive layers. The analyses were carried out in 0,3wt% Na₂SO₄ solution. Figure 6 shows the potentiodynamic curves for the steel electrodes conditioned for different immersion time in the AU-C-W1 cerium oxide containing solution.

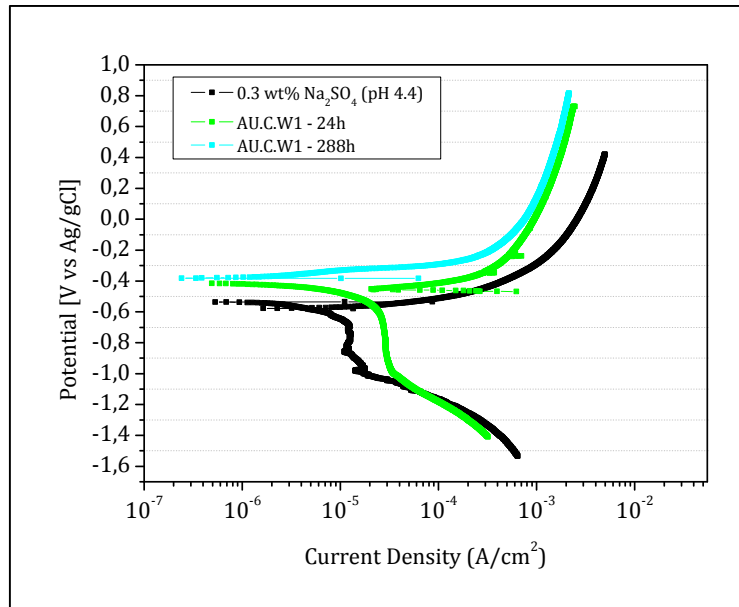


Figure 6. Potentiodynamic curves for the steel electrodes conditioned for different immersion time in the AU-C-W1 cerium oxide containing solution.

As one can appreciate from Figure 6, the immersion in the AU-C-W1 cerium oxide containing solution for 288 h causes an observable reduction of the anodic current. After 24 hours of immersion a remarkable reduction of the cathodic current is also observable. However, it is no longer possible to appreciate the presence of a passivation of the steel substrate. It seems that the continuous presence of the particles is necessary to ensure the formation of a passive layer on the steel surface. Further investigation of the condition of the surface of the steel electrodes is needed, but the present results seem to suggest that some type of ceria nanoparticles are able to promote a passivation of the metal surface according to the mechanism described in section 4.3. In addition, the experimental results highlighted that the continuous presence of the passivating agent (probably CeO₂/Ce₂O₃ couple) is necessary to maintain the passive layer. Figure 7 shows the potentiodynamic curves for a steel electrode in AU-C-W2 cerium oxide nanoparticles dispersion.

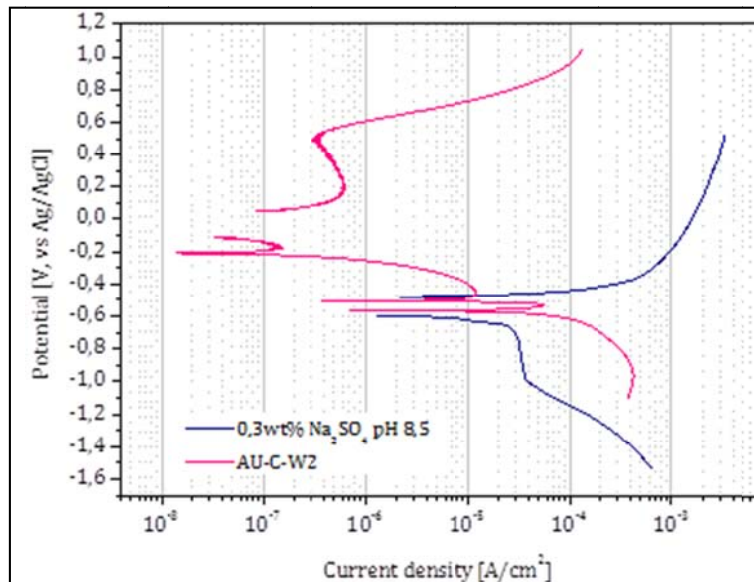


Figure 7. Potentiodynamic curves for the steel electrodes immersed in AU-C-W2 solution and control solution

As far as AU-C-W2 is concerned, in Figure 6 it is possible to appreciate that also in this case a noticeable decrease of the anodic current is ensured by the presence of the nano-ceria particles. However it is not possible to define a clear an active/passive transition and the passivity potential. The presence of AU-C-W2 leads to a decrease of at least three orders of magnitude of anodic current in the potential range from 0.1 to 0.5 V. A sort of passive region is present between 0,2 and 0,5 V (vs Ag/AgCl). In correspondence this region the current density is quite stable and reaches relatively small values (less than 10^{-6} A/cm²). An increase of the open circuit potential is also observable (from -0,5 V to 0,0 V vs Ag/AgCl). Considering the obtained experimental results it seems that also Au-C-W2 cerium oxides behave as a passivating agent for steel as Au-C-W1.

Figure 8 and Figure 9 show the potentiodynamic curves for the steel electrodes immersed in the AU-C-W5 and AU-C-W6 cerium oxide dispersions. Unlike AU-C-W6 cerium oxide nanopowders, AU-C-W5 cerium oxide nanopowders are stabilized using surfactants. As one can appreciate from Figure 8 and Figure 9, the presence of the surfactants seems to decrease the corrosion inhibition efficiency of the cerium nanopowders, since a strong reduction of both anodic and cathodic currents was observed for the mild steel electrode immersed in the AU-C-W6 cerium oxide dispersion without surfactant. It is worth highlighting that the surfactants are added to the powders to stabilize the dispersion of the nanoparticles and to facilitate the homogeneous dispersion of the particles in a polymeric paste.

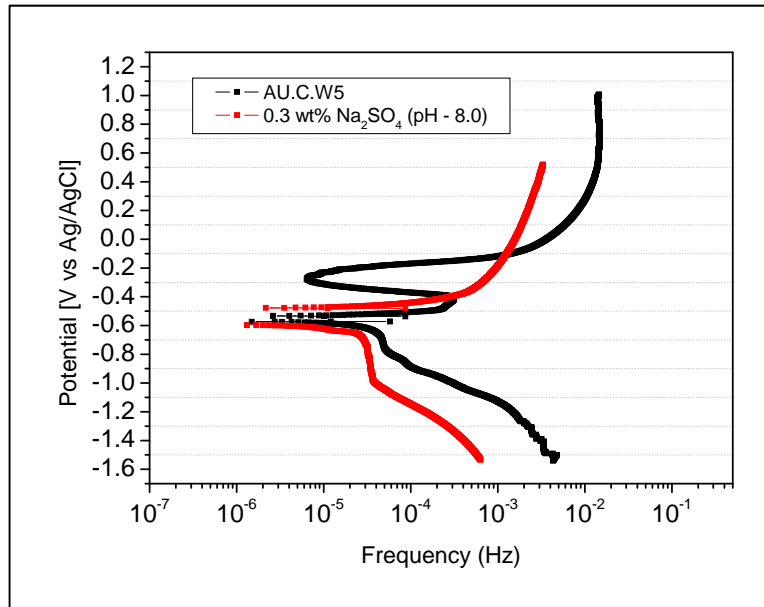


Figure 8. Potentiodynamic curves for the steel electrodes immersed in AU-C-W5 solution and control solution

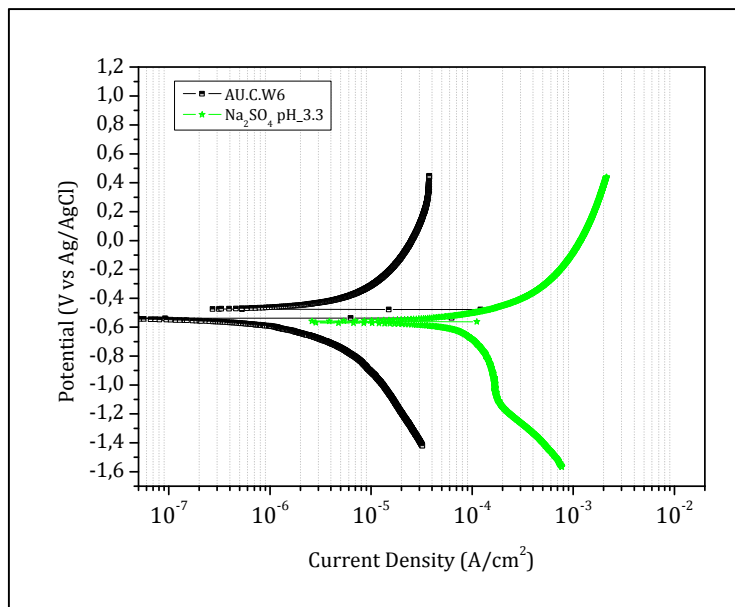


Figure 9. Potentiodynamic curves for the steel electrodes immersed in AU-C-W5 solution and control solution

Considering the behaviour of the steel electrode immersed in the solution containing the AU-C-W6 nanoparticles, as depicted in Figure 9, it is possible to appreciate a decrease of both anodic and cathodic currents. However, in this case a clear passivation of the steel surface is not appreciable. Since both AU-C-W5 and AU-C-W6 are mixtures of CeO₂/Ce₂O₃, it is difficult to explain the different behaviour between the two samples. In both cases an inhibition effect of corrosion of steel is clearly observable, but the mechanisms of protection seem to be different. In this sense it is worth highlighting that due to the ultra-small particle size of AU-C-W5 it is likely that a relatively larger proportion of Ce-III should be present in this sample compared to all other samples.

To better clarify the protection mechanism of AU-C-W5 cerium oxides nanoparticles, as in the previous case mild steel samples were put in contact with

the solution containing the cerium particles for different immersion time. Potentiodynamic measurements were performed on the steel samples conditioned in the cerium oxide containing solution in order to investigate the presence of conversion or passive layers on the mild steel surface. The analyses were carried out in 0,3wt% Na_2SO_4 solution. Figure 10 shows the potentiodynamic curves for the steel electrodes conditioned for 288 h in the AU-C-W5 cerium oxides containing solution.

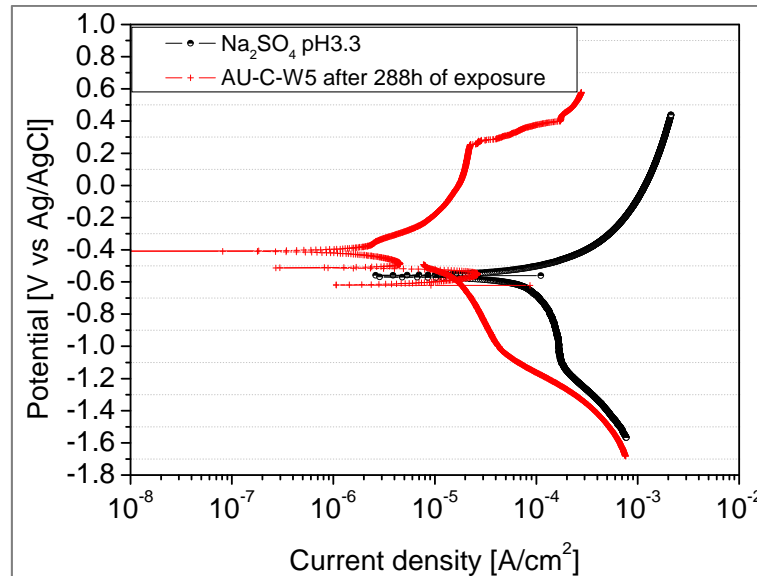


Figure 10. Potentiodynamic curves for the steel electrodes conditioned for 288 hours in the AU-C-W5 cerium oxide containing solution.

After the conditioning for about 288 h in the aqueous dispersion containing the AU-C-W5 cerium oxides, the steel electrodes show a strong decrease of the anodic current. In addition a decrease of the cathodic current is observable as well. In this case it seems that a conversion or a passive layer has been formed on the steel electrode. In fact the anodic and cathodic current are reduced even if the cerium oxides particles are no longer present in the testing solution. The conversion or passive layer on the steel surface is likely to be responsible for the decreased rate of both anodic and cathodic currents. In fact in presence of a conversion layer of Ce compounds or in presence of a passive film the rates of both anodic and cathodic reactions decreases, thus decreasing the overall extent of corrosion.

5. Conclusion

According to the present literature survey and the experimental results obtained in this project, it seems that a certain type of cerium oxides nanoparticles can act as a passivating agent of the steel surface. However, it is not clear if the $\text{CeO}_2/\text{Ce}_2\text{O}_3$ mixed oxide is present in the passive layer or if it promotes only the formation of a stable iron oxide. Moreover, different types of ceria nanoparticles exhibit different inhibition behaviour, in some cases the presence of the particles is necessary to maintain the passivity of the steel electrodes (for examples in case of AU-C-W1) while in other cases the exposure to the solution containing the $\text{CeO}_2/\text{Ce}_2\text{O}_3$ mixed oxide for a certain time is sufficient to promote the formation of a conversion/passive layer which is stable also in absence of the particles (for examples in case of AU-C-W5).

6. Suggestions for Further Work

To better understand the role of CeO₂/Ce₂O₃ nanoparticles it is necessary to perform surface analysis to characterize in detail the surface condition of the steel electrodes in order to understand the composition of the conversion/passive layer. In addition, to define the operating condition of CeO₂/Ce₂O₃ as a corrosion inhibitor, the effect of the pH, environment and dissolved gas in the solution has to be investigated in depth.

For the coatings containing ceria nanoparticles, both electrochemical and in-situ AFM studies of selected samples are needed to elucidate the role of ceria nanoparticles in the corrosion protection.

7. References

1. M. Schem, T. Schmidt, J. Gerwann, M. Wittmar, M. Veith, G.E. Thompson, I.S. Molchan, T. Hashimoto, P. Skeldon, A.R. Phani, S. Santucci, M.L. Zheludkevich, *Corrosion Science* 51 (2009) 2304.
2. F. Deflorian, M. Fedel, S. Rossi, P. Kamarchik, *Electrochim. Acta* 56 (2011) 7833
3. Pu Yu, Scott A. Hayes, Thomas J. O'Keefe, Matthew J. O'Keefe, and James O. Stoffer, *Journal of The Electrochemical Society*, 153 (2006) C74.
4. Scott A. Hayes, Pu Yu, Thomas J. O'Keefe, Matthew J. O'Keefe, and James O. Stoffer, *Journal of The Electrochemical Society*, 149 (2002) C623.
5. M.L. Zheludkevich, R. Serra, M.F. Montemor, K.A. Yasakau, I.M. Miranda Salvado, M.G.S. Ferreira, *Electrochimica Acta* 51 (2005) 208
6. Y.C. Lu, M.B. Ives *Corrosion Science* 37 (1995) 145
7. C. Motte, N. Maury, M.-G. Olivier, J.-P. Petitjean, J.-F. Willem, *Surface and Coatings Technology* 200 (2005) 2366
8. M.F. Montemor, A.M. Simões, M.G.S. Ferreira, M.J. Carmezim, *Applied Surface Science*, 254 (2008) 1806
9. M.A. Arenas, J. de Damborenea *Surface and Coatings Technology* 200 (2005) 2085
10. A. Conde, M.A. Arenas, A. de Frutos, J. de Damborenea, *Electrochimica Acta* 53 (2008) 7760
11. P. Borm, F.C. Klaessig, T.D. Landry, B. Moudgil, J. Pauluhn, K. Thomas, R. Trottier, S. Wood, *Toxicol. Sci.* 90 (2006) 23
12. W. Wu, G.H. Nancollas, *J. Sol. Chem.* 27 (1998) 521
13. N. J. Lawrence, *Synthesis and Catalytic Activity of Nanostructured Cerium Oxide*, Master thesis, University of Nebraska, 2010. On website: <http://digitalcommons.unl.edu/chemistrydiss/16>
14. Ruixing Li, Shinryo Yabe, Mika Yamashita, Shigeyosi Momose, Sakae Yoshida, Shu Yin, Tsugio Sato, *Solid State Ionics* 151 (2002) 235
15. N.V. Skorodumova, S. I. Simak, B. I. Lundqvist, I. A. Abrikosov, and B. Johansson *Physical Review Letters*, 89 (2002) 166601-2
16. Peng Gao, Zhenchuan Kang, Wangyang Fu, Wenlong Wang, Xuedong Bai, Enge Wang, *Journal of American Chemical Society*. 132 (2010) 4197
17. E. Stoyanova and D. Stoychev, *Corrosion Behavior of Stainless Steels Modified by Cerium Oxides Layers*, in: "Corrosion Resistance" by H. Shih (Ed.), pp. 239-269, InTech (2012)
18. M. Zheludkevich, R. Serra, M. F. Montemor, M. G.S. Ferreira. *Electrochemistry Communications*, 7 (2005). 836
19. Montemor, M.F., M.G.S. Ferreira, *Electrochimica Acta*, 52 (2007) 6976
20. M. Fedel, F. Deflorian, S. Rossi, P. Kamarchik, *Progress in Organic Coatings* 74 (2012) 36
21. A. J. Aldykiewicz, J., A.J. Davenport, H.S. Isaacs, *Journal of Electrochemical Society*, 143 (1996).
22. K. Amasaki, *Corrosion Science*, 44 (2002) 14.