

Zinc Corrosion in a Crevice

C. Taxén* and D. Persson
Swerea-Kimab

*Corresponding author: Dr. Kristinas Våg, 48, SE 102 16 Stockholm, SWEDEN. claes.taxen@swerea.se

Abstract: Comsol Multiphysics is applied to a corrosion problem in an aqueous solution. Corrosion of metals in confined zones is a big industrial problem. The electrochemistry of such localized corrosion processes is complicated by the impact of the corrosion processes on the composition of the local solution. In the present problem, local interaction with the atmosphere causes uptake of O_2 and CO_2 and evaporation of water from the initially dilute NaCl-solution. This model describes the local aqueous equilibria and the transport processes coupled to corrosion reactions at zinc metal. The decrease in the aqueous volume caused by evaporation is implemented by solving the corrosion problem in a moving mesh.

Keywords: Zinc, Corrosion, Electrochemistry

1. Introduction

The present model aims at simulating the processes in an industrial test cycle for galvanized steel. Such tests are performed by the automotive industry and by producers of galvanized steel. [1,2] Test panels with confined zones are subjected to alternating wet and dry cycles. One such cycle can consist of a wetting stage where the test panel is dipped into a dilute solution of sodium chloride. The test panel with the now filled confined zone is exposed to an atmosphere with controlled humidity (~30% relative humidity). Evaporation of water causes the salts in the confined zone to become more concentrated and interaction with gases from the atmosphere maintains a supply of oxygen that drives the corrosion. Depending on the rate of evaporation the test panels with the confined zones are more or less dry after 24 hours in the atmosphere. The cycle is repeated by dipping into the dilute solution of sodium chloride and a new evaporation period. In our laboratory experiments, the confined zone is refilled by injecting the solution through a syringe and not by dipping. The purpose of the test cycle is to evaluate the corrosion resistance of commercial products in service as material in cars. Of particular interest is the extent and location of the corrosion attack on zinc and how well the

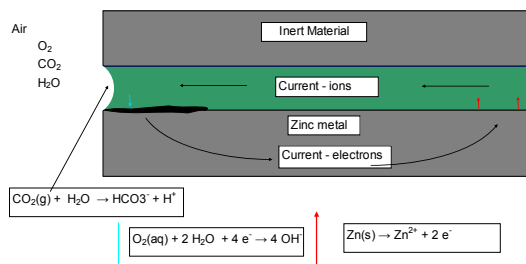


Figure 1. Illustration of the experimental geometry and some of the chemical reactions.

underlying steel is protected galvanically when the initial zinc layer is partially consumed.

1.1 The experimental geometry

Figure 1 illustrates the experimental geometry and the reactions at the water/air interface and at the water/metal interface. The shape of the water/air interface is curved under the influence of capillary forces.

1.2 The model geometry

Figure 2 shows the model geometry. A crevice 0.3 mm high and 20 mm long was studied. The crevice was filled with an initially neutral solution of 1% (~0.17 M) solution of NaCl. Initial calculations were made using an aqueous volume with rectangular shape. However, it soon became apparent that oxygen transport from the air-liquid boundary, to the left in figure 2, to the metal-liquid boundary strongly limited to corrosion rate. Moreover, it was observed that the air-liquid boundary in reality was curved, presumably due to capillary forces. It was realized that such a curved boundary provides a much shorter diffusion path for oxygen. The model geometry was thus modified so that the main features of the curved air-liquid boundary are recreated. In order to keep things simple and to allow systematic variations of the contact angle, a constant slope of the boundary was used.

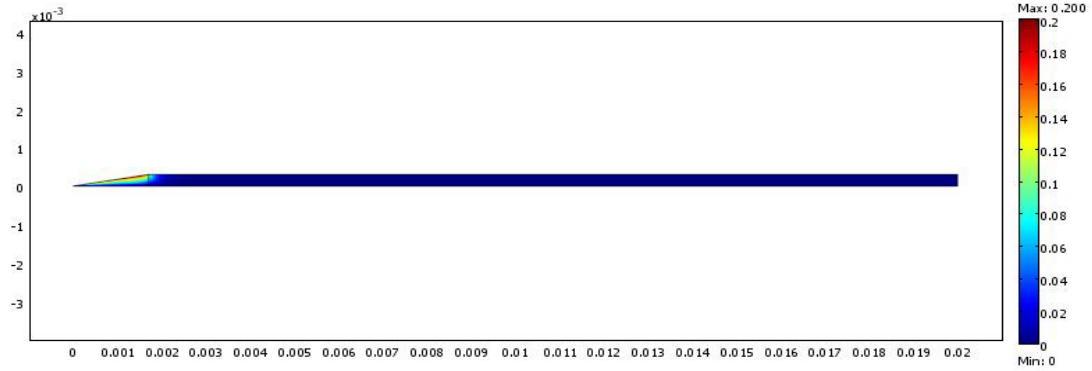
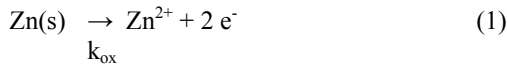


Figure 2. The model geometry. The initial aqueous volume is colour coded after the concentration of oxygen after one hour exposure.

2. Processes

2.1 Electrochemical processes

There are two electrochemical processes that take place in the system: oxidation of zinc metal and reduction of oxygen. Zinc metal is oxidised by reaction (1):



The rate is expressed using a Tafel equation but with an upper limiting passive current density.

$$k_{ox,k} = k_{0,Zn} \cdot 10^{\frac{(-E_{0,Zn} - V)}{b_{a,Zn}}} \quad (2)$$

V in equation (2) refers to the potentials in the solution and therefore has the opposite sign from the conventional expression where the potential refers to the difference between metal and solution.

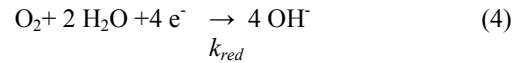
Equation (1) is applied to surfaces free from solid corrosion products. Where solid corrosion products are present at the surface, these may have a limiting influence on the anodic process. The general equation for the rate of the zinc oxidation is:

$$k_{ox} = k_{ox,k} \cdot (1 - \Theta) + \Theta \cdot \min(k_{ox,k}, k_{pass}) \quad (3)$$

Θ is the fraction of the surface that is covered by solid corrosion products. k_{pass} corresponds the rate of oxidation for a surface that is completely covered. The rate of oxidation at a completely covered surface cannot be higher than the rate of oxidation at a surface free from corrosion products. Therefore the rate of the anodic

process at a surface covered by corrosion products is in equation (3) evaluated as the minimum of the two rates.

Molecular oxygen is reduced electrochemically at the corroding zinc metal.



The rate is expressed as a Tafel slope and a first order dependence on oxygen concentration.

$$k_{red} = k_{0,red} \cdot 10^{\frac{-(-V - E_{0,O_2})}{b_{c,O_2}}} \quad (5)$$

Integrated over the whole surface, the anodic dissolution of zinc matches the cathodic reduction of oxygen.

$$\int 2 \cdot k_{ox} dA = \int 4 \cdot k_{red} \cdot [O_2] dA \quad (6)$$

$[O_2]$ in equation (6) is the concentration of oxygen in the solution at the metal surface.

2.2 Gas – liquid reactions

Molecular oxygen is absorbed from the air



The rate is expressed as:

$$r_{O_2up} = k_{O_2up} \cdot ([O_2]_{eq} - [O_2]) \quad (8)$$

$[O_2]_{eq}$ is the oxygen concentration in equilibrium with air and $[O_2]$ in equation (8) is the actual oxygen concentration at the air-liquid interface.

Carbon dioxide is absorbed from the air

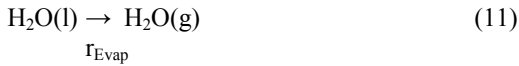


The rate is expressed as:

$$r_{\text{CO}_2\text{up}} = k_{\text{CO}_2\text{up}} \cdot ([\text{CO}_2]_{\text{eq}} - [\text{CO}_2]) \quad (10)$$

$[\text{CO}_2]_{\text{eq}}$ is the aqueous carbon dioxide concentration in equilibrium with air and $[\text{CO}_2]$ in equation (10) is the actual carbon dioxide - carbonic acid concentration at the air-liquid interface.

Water evaporates from the gas-liquid interface.



The rate could be expressed as:

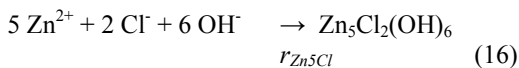
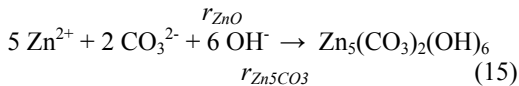
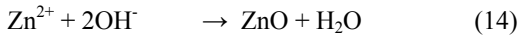
$$\Gamma_{\text{Evap}} = k_{\text{Evap}} (\text{aW} - \text{RH}) \quad (12)$$

Where aW is the activity of the liquid water and RH is the relative humidity in the air at the gas-liquid interface. However, the activity of water differs little from unity in the solutions studied and the relative humidity is usually controlled to a constant value in our experiments. The rate of the evaporation is therefore set to a constant value.

$$\Gamma_{\text{Evap}} = \text{Const.} \quad (13)$$

2.3 Surface reactions

In addition to the electrochemical oxidation of zinc and the reduction of oxygen, the precipitation of solid corrosion products is considered to take place as a scale formation on the corroding zinc metal. Three solid corrosion products are considered.



The rates of precipitation are described as first order reactions with respect to zinc. The degree of (super-) saturation is first calculated. The saturation a is calculated from the local concentrations and activity coefficients. Super saturation and precipitation occurs if the activity of e.g. ZnO is greater than unity ($a_{\text{ZnO}} > 1$).

$$r_{\text{ZnO}} = k_{\text{prec}} \cdot (a_{\text{ZnO}}) \cdot \{(a_{\text{ZnO}} > 1) \cdot (1 - \Theta_{\text{ZnO}}) + \Theta_{\text{ZnO}}\} \quad (17)$$

$$r_{\text{Zn}_5\text{CO}_3} = k_{\text{prec}} \cdot (a_{\text{Zn}_5\text{CO}_3}^{1/5} - 1) \cdot \{(a_{\text{Zn}_5\text{CO}_3} > 1) \cdot (1 - \Theta_{\text{Zn}_5\text{CO}_3}) + \Theta_{\text{Zn}_5\text{CO}_3}\} \quad (18)$$

$$r_{\text{Zn}_5\text{Cl}} = k_{\text{prec}} \cdot (a_{\text{Zn}_5\text{Cl}}^{1/5} - 1) \cdot \{(a_{\text{Zn}_5\text{Cl}} > 1) \cdot (1 - \Theta_{\text{Zn}_5\text{Cl}}) + \Theta_{\text{Zn}_5\text{Cl}}\} \quad (19)$$

The equations work for precipitation as well as for dissolution. Of course there can be no dissolution of a salt or oxide if this substance is not present locally. The presence of a solid is in equations represented by the coverages, Θ . The relation between the amount of the corrosion products and the coverage conferred by these solid is given by equations (20) and (23). The total coverage by corrosion products is first calculated by an expression that asymptotically approaches unity.

$$\Theta_{\text{Tot}} = 1 - e^{-\frac{(m\text{ZnO} + m\text{Zn}_5\text{CO}_3 + m\text{Zn}_5\text{Cl})}{\text{NM} \cdot m_0}} \quad (20)$$

$m\text{ZnO}$, $m\text{Zn}_5\text{CO}_3$ and $m\text{Zn}_5\text{Cl}$ are here the amounts of corrosion products that has accumulated locally in moles Zn/m². m_0 is the amount of zinc in one monolayer and NM is a number of monolayers. The amount of corrosion products that corresponds to the product $\text{NM} \cdot m_0$ can be regarded as a characteristic amount that conveys a coverage of 63%.

$$\Theta_{\text{Tot}} = 1 - e^{-1} \approx 0.63 \quad (21)$$

Double the amount leads to a further coverage and passivation to about 86%.

$$\Theta_{\text{Tot}} = 1 - e^{-2} \approx 0.86 \quad (22)$$

The individual coverage for e.g. ZnO is calculated as

$$\Theta_{ZnO} = \frac{mZnO}{mZn + mZn5CO3 + mZn5Cl} \cdot \Theta_{tot} \quad (23)$$

2.4 Equilibrium reactions in solution

Reactions between aqueous species are generally fast and local equilibrium is assumed. This means that at any single site in the solution volume the ion product of protons and hydroxide ions, corrected for activity coefficients is equal to the ion product of water, K_w .

$$[H^+] \cdot \gamma_H \cdot [OH^-] \cdot \gamma_{OH} = K_w \quad (24)$$

Local equilibrium is assumed between the zinc containing species Zn^{2+} , $ZnOH^+$, $Zn(OH)_2(aq)$, $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $ZnCl^+$ and between the carbonate containing species $CO_2(aq)$, HCO_3^- and CO_3^{2-} .

The activity coefficients, γ , for charged species were estimated from the local ionic strength using Davies' approximation:

$$\lg \gamma = -.509 \cdot z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 \cdot I \right) \quad (25)$$

z is the charge of the species and I is the ionic strength.

$$I = \frac{1}{2} \sum z_i^2 \cdot c_i \quad (26)$$

3. Comsol formulation of the problem

With the infinitely fast aqueous equilibria assumed, the laws of conservation of mass does not apply to a single species but rather to specific groups of species. These groups of species are here termed total concentrations, e.g. cHT and cCO2T for the total concentration of H^+ and the total concentration of carbonates, respectively.

The formalism for time dependent transport equations is

$$\frac{\partial c}{\partial t} + \nabla \Gamma = F \quad (27)$$

In two dimensions the differential operator ∇ is equal to $(\frac{\partial}{\partial x}, \frac{\partial}{\partial y})$ and Γ is equal to the

components of the flux in the x and y direction, respectively, (j_x, j_y) . F in equation (27) represents the sources and since the formulations used here obey the laws of conservation, the sources are set to zero. Thus, it is the components of the flux

and the boundary conditions that have to be entered into the transport equations.

Our implementation of the model uses one mode for each total concentration, cHT, cCO2T, cZnT, cClT, cNa, cO2. For the last two modes, there is only one species i.e., Na^+ and O_2 , respectively. In addition one mode is required for each free ion concentration i. e. cH, cHCO3, cZn, cCl. A constraint to the solution is that the local charge should be zero:

$$\sum z_i \cdot c_i = 0 \quad (28)$$

4. Input data

Thermodynamic data for the complex aqueous species were compiled from various sources [3,4]. Diffusion coefficients were calculated from limiting ionic conductivities [5]. For complex species where diffusion coefficients could not be found in the literature, the value for the free species was used. Kinetic data for oxygen reduction on zinc was recalculated from ref. [6]. Kinetic data for zinc oxidation in chloride solutions was recalculated from ref. [7].

5. Procedure

Calculations start with only total aqueous concentrations supplied as initial values. Component concentrations are needed only as rough estimates to start the first iterations. In order to simplify the start up procedure of the solution of this relatively large set of non-linear equations, the initial state includes a solution with a low concentration of oxygen. To start with a low concentration of oxygen is an advantage because oxygen reduction at a large area of corroding zinc metal is a relatively fast process and leads to strong transients in the calculations. These transients in oxygen concentrations immediately transfer to transients in the proton equilibria, since oxygen reduction produces hydroxide ions, and the transients in the zinc concentrations since zinc ions are produced with a rate that balances the rate of the oxygen reduction.

The standard procedure adopted for the model simulations is to allow the corrosion processes, the gas-liquid processes and the liquid-solid reactions to proceed for one hour without evaporation. This corresponds to the atmospheric exposure in at approximately 100%

relative humidity. After one hour evaporation starts and the aqueous volume is decreased at a fixed rate. Evaporation is allowed to proceed until only the small triangular part of the initial solution volume remains. At this point the liquid is so concentrated that approximations that are reasonable for dilute solutions are no longer valid. This applies both to the model for estimating activity coefficients from local ionic strength and to the relation between ionic mobility and diffusion coefficient.

Calculations during the evaporation phase were performed in stages with several steps to create geometry from deformed mesh and to change the mesh resolution. With the approach selected, information about the parts of the zinc surface that has dried out is continuously lost from the solution. In order to collect information about the local depth of the corrosion attack and about the amounts of corrosion products deposited, previous solutions have to be examined together with the present solution.

6. Results

Figures 3 and 4 shows the anodic and the cathodic current densities, respectively, at various location in the crevice. The lower left, blue, line represents the state after one hour exposure without evaporation. The other lines represent the state after two through ten hours in steps of one hour.

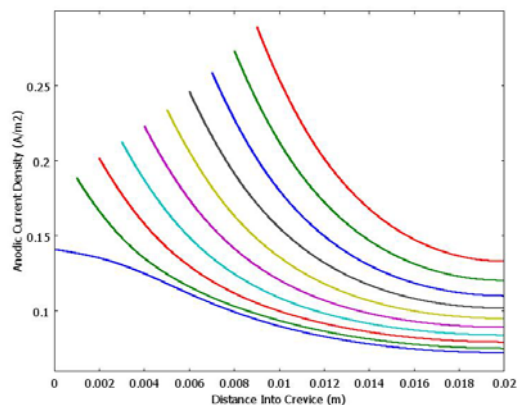


Figure 3. The anodic current density at various locations in the crevice. The lower curve shows results after one hour exposure. The other curves show results for two through ten hours exposure with evaporation.

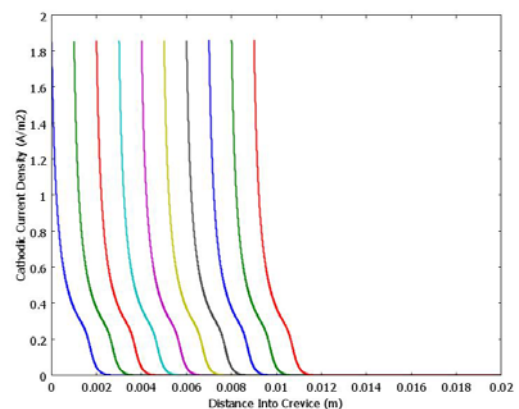


Figure 4. The cathodic current density at various locations in the crevice. The left hand curve shows results after one hour exposure. The curves show results for two through ten hours exposure with evaporation.

The figures show that the cathodic current is much more localized than the anodic current. Figure 5 shows the pH at various locations in the crevice. The lines represent the pH at the surface at one through ten hours exposure. The left, blue curve in figure shows that the pH at the mouth of the crevice exceeds pH 12. At longer exposure durations this pH value decreases slowly as the separation between anodic and the cathodic regions decreases.

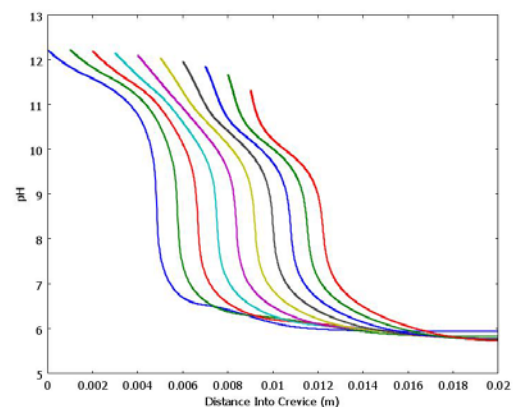


Figure 5. The pH at various locations in the crevice. The left hand curve shows results after one hour exposure. The other curves show results for two through ten hours exposure with evaporation.

Figures 6 and 7 show the concentrations of chloride and sodium, respectively, at various locations in the crevice. The curves illustrate the state at one through ten hours exposure. The left, blue, curve shows an initial depletion of chloride at the mouth of the crevice whereas sodium is enriched. At longer exposure durations where evaporation sets in, both the sodium and chloride ions accumulate at the mouth of the crevice.

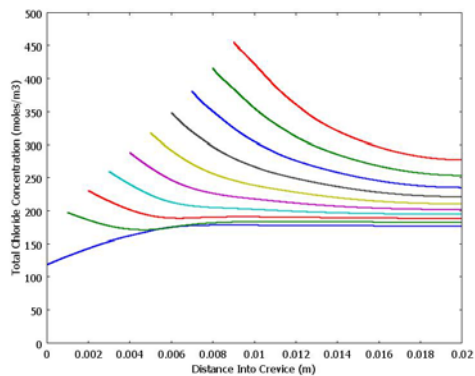


Figure 6. The total chloride concentration at various locations in the crevice. The left hand curve shows results after one hour exposure. The other curves show results for two through ten hours exposure with evaporation.

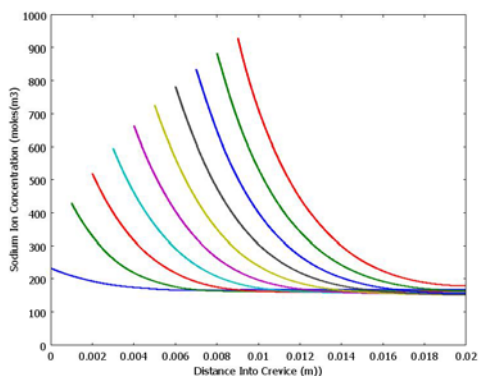


Figure 7. The sodium ion concentration at various locations in the crevice. The left hand curve shows results after one hour exposure. The other curves show results for two through ten hours exposure with evaporation.

Figure 8 shows the amounts of solids deposited at the zinc surface after one hour exposure. Figure 9 shows result after one drying cycle (~17 hours exposure). Figure 10 shows experimentally observed corrosion products after 1 hour exposure.

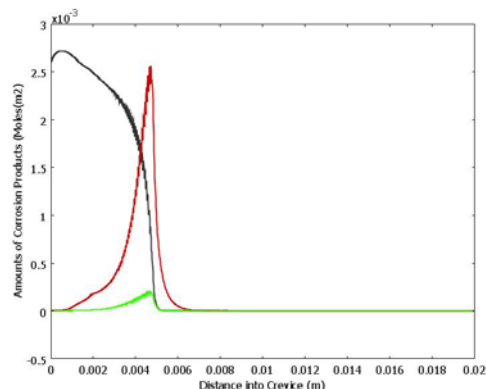


Figure 8. The amounts of solid corrosion products deposited at various locations in the crevice after one hour exposure.

Red Curve: $Zn_5(CO_3)_2(OH)_6$
Green Curve: $Zn_5Cl_2(OH)_8$
Black Curve ZnO

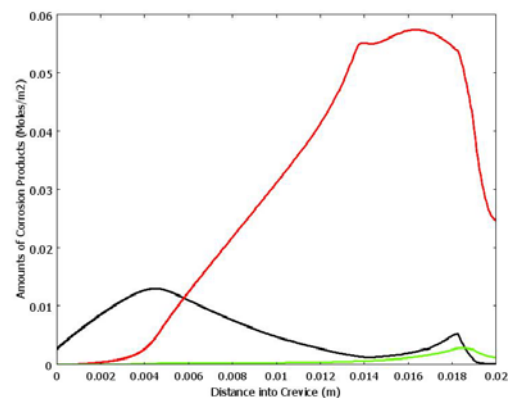


Figure 9. The amounts of solid corrosion products deposited at various locations in the crevice after one drying cycle.

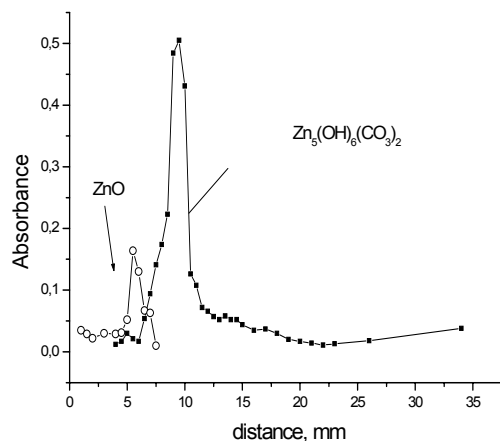


Figure 10. Relative amounts of corrosion products observed by FTIR after 1 hour exposure.

7. Conclusions

The model can relatively well describe the amounts of corrosion products deposited in the crevice. The specific compounds as well as their location in the crevices agrees with observations. The results are very detailed and allow assessment of the importance of the various complex forming reactions. The importance of carbonate from the atmosphere is evident. The limited supply of CO₂ in the confined geometry is a prerequisite for the large pH-gradients that develop. Various interesting phenomena such as the appearance of large diffusion potentials that is caused by the evaporation become evident in the model results.

However, the corrosion processes and the rate seem to be controlled almost completely by the supply of oxygen.

8. References

1. A. Amirudin, D. Thierry, Corrosion Mechanisms of Phosphated Zinc Layers on Steel as Substrates for Automotive Coatings ; A review of Mechanisms, *Progress in Organic Coatings*, **28**, 59 (1996)
2. D. Persson, A. Mikhaylov, D. Thierry, The influence of important parameters on the atmospheric corrosion of materials used in automotive applications. SCI publication 73019:1, Korrosionsinstitutet , Sweden (2002)
3. R. M Smith and A. E. Martell, NIST Standard Reference Database 46, NIST Critically Selected Stability Constants of Metal Complexes Database Ver. 2.0 , U.S. Department of Commerce (1995)
4. C. F. Baes and R. E. Mesmer, The Hydrolysis of Cations, Wiley, New York (1976)
5. Handbook of Chemistry and Physics. 71:st ed. CRC, Boca Raton
6. H. Dafydd, D. A. Worsle and H. N. McMurray, The kinetics and mechanism of cathodic oxygen reduction on zinc and zinc-aluminium alloy galvanized coatings, *Corr.Sci*, **47**, 3006-3018 (2005)
7. L. M. Baugh, Corrosion and polarization characteristics of zinc in neutral-acid media-I Pure zinc in solutions of various sodium salts, *Electrochim. Acta*, **24**, 657-667 (1979)

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