

## Abstract

The aim of this work was the investigation of corrosion protection of zinc substrates by compact and porous silica sol-gel coatings of different thicknesses. Coatings were deposited on zinc and, for comparison, on glass substrates by dip-coating. For preparing mesoporous layers, cationic or non-ionic surfactant templates were applied.

Thickness and porosity of layers on glass were determined by analyzing the transmittance spectra in terms of thin layer optical models. Surface morphology was studied by scanning electron microscopy and it was found that silica coatings could not flatten out completely the surface of zinc.

Corrosion tests were carried out in 0.2 g/L aqueous solution (pH=5) of  $\text{Na}_2\text{SO}_4$ . The electrochemical data (open-circuit potential, polarization resistance, corrosion potentials and the corrosion current densities) showed that all the coatings provided corrosion protection and it was found that two-layered coatings are more efficient than single ones. Interestingly, the porous coatings provided better protection than compact ones.

## Keywords

Sol-gel coatings · porosity · optical properties · zinc · corrosion

Emőke Volentiru

Mária Nyári

Zoltán Hörvölgyi e-mail: [zhorvolgyi@mail.bme.hu](mailto:zhorvolgyi@mail.bme.hu)

Budapest University of Technology and Economics,  
Department of Physical Chemistry and Materials Science,  
H-1521 Budapest, Budafoki út 6-8, Hungary

Gabriella Szabó

Liana Maria Mureşan e-mail: [limur@chem.ubbcluj.ro](mailto:limur@chem.ubbcluj.ro)

Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering,  
400028 Cluj-Napoca, str. Arany János nr.11, Romania

## 1 Introduction

The need to replace the harmful chromate-based surface treatments of galvanised steel with environmentally friendly methods promoted the development of new treatments based on electropolymerization [1], conversion coatings [2-5] and sol-gel synthesis [6,7,8]. Among these, the sol-gel coatings for corrosion protection of metals are considered a promising alternative due to their easy preparation at low temperatures and to the possibility to incorporate various additives and/or nanoparticles in order to control the physical and chemical properties of the coatings [9,10].

Layers of oxides such as  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , etc. provide effective protection to metal substrates due to their very good chemical and thermal stability. Among them,  $\text{SiO}_2$  layers act very efficiently as corrosion protectors of metals under different temperatures. Moreover, due to the fact that using alkoxysilanes as precursors in the formation of silica sol-gels the reaction is quite gentle, this approach is extensively used in pretreatment of metal surfaces [6]. It should be emphasized that the introduction of dopants, such as small amounts of nanoparticles (e.g.  $\text{CeO}_2$ ,  $\text{ZrO}_2$  [10] etc.) in the  $\text{SiO}_2$  layer could significantly improve the barrier properties of the coatings and, consequently, their corrosion resistance. Moreover, properties of  $\text{SiO}_2$  sol-gel coatings and nanoparticles can be influenced by using different surfactants during the preparation process [11].

Zinc has found widespread use as the basis of a whole range of sacrificial coatings for ferrous substrates. However, the life span of such coatings is limited due to the aggressive nature of some environments, particularly those containing industrial pollutants. Consequently, efforts are made in order to enhance their service life.

In this context, our investigation was focused on the preparation and characterization of different type of porous and compact silica-based protective coatings on zinc and glass substrates by using sol-gel method, in the absence or in the presence of surfactants. The optical and the electrochemical properties of the coatings, as well as the effect of film thickness on its protection ability were also studied.

## 2 Experimental

### 2.1 Synthesis of precursor sols

Three different types of silica precursor sols were prepared by the acid catalyzed, controlled hydrolysis of tetraethyl-orthosilicate (TEOS, for synthesis, >99%, Merck) in ethanolic media (EtOH, a. r., >99.7%, Reanal). Hydrochloric acid (HCl, purum, 37%, Fluka) was used as catalyst and it was added together with water as a 0.1M aqueous solution.

*Precursor sol (1)* was synthesized for depositing compact silica sol-gel (*compact SiO<sub>2</sub>*) coatings. The molar ratios for TEOS: ethanol: water: HCl were 1: 18.6: 5.5:  $1 \times 10^{-3}$ , and the mixture was stirred for 1 h at room temperature [12].

Porous silica (*CTAB/porous SiO<sub>2</sub>* and *Pluronic/porous SiO<sub>2</sub>*) layers were prepared from precursor sols (*precursor sol (2)* and *precursor sol (3)*) containing surfactant templates.

*Precursor sol (2)* and *precursor sol (3)* were prepared by dissolving 1.5 g of cetyltrimethylammonium bromide (CTAB, cationic surfactant, 99+%, Acros Organics) and 2 g of Pluronic PE 10300 triblock copolymer (non-ionic surfactant, BASF, Ludwigshafen Germany) in 22 mL of ethanol respectively.

In both cases ethanol, TEOS and 0.1 M HCl were mixed in another beaker applying the same molar ratios as for the preparation of precursor sol (1) with the total volume of 35 mL. Both mixtures were stirred for 30 min at room temperature and for additional 30 min after mixing the two solutions.

### 2.2 Preparation of coatings

For layer deposition processes zinc wafers and – for comparison – microscope glass slides (76x26x1 mm, Thermo Scientific, Menzel-Gläser) were used as solid substrates.

Prior to film deposition, zinc substrates were polished with emery paper (grade 1200) then treated with 0.1M HCl solution and rinsed with 2-propanol (a. r., >99.7%, Reanal).

Glass slides were erased with 2-propanol impregnated cotton, then rinsed with 2-propanol and distilled water (18.2 MΩ·cm, purified with a Millipore Simplicity 185 filtration system). Both glass and zinc substrates were dried at room temperature before using.

Sol-gel films on glass and zinc substrates were prepared from the precursor sols by the dip-coating method (dip coater, MTA TTK MFA, Hungary). Cleaned and dried substrates were immersed into the precursor sol and pulled out with a constant speed. Withdrawal speeds were 10 cm/min for *compact SiO<sub>2</sub>* and *CTAB/porous SiO<sub>2</sub>* and 8 cm/min for *Pluronic/porous SiO<sub>2</sub>* film deposition. Multilayered coatings were obtained by the consecutive application of the dip-coating method.

The deposited films were annealed in a drying oven (Nabertherm B170) at 450°C (glass substrate) and 410°C (zinc substrate) for 1 h with a heating rate of 20°C/min. In the case of multilayered coatings prepared onto glass slides heat treatment was applied after each layer deposition. In order to spare the

surface of Zn substrate in case of multilayer deposition annealing was carried out only after the final layer formation.

### 2.3 Optical characterization of coatings

Optical properties of mono- and multilayered coatings on glass substrates were measured by UV-Vis spectroscopy. Transmittance spectra of the bare substrates and coatings were taken using a Spe-cord 200-0318 spectrophotometer in the wavelength range of 350-1100 nm with 1 nm resolution and a scanning speed of 5 nm/s.

The obtained transmittance curves were analyzed in terms of thin layer optical models. Transmittance spectra of coatings were fitted with a homogeneous layer model [13] supposing perpendicular angle of incidence and identical homogeneous monolayers on both sides of the transparent substrate. The fitting procedures provided effective refractive index and film thickness values. As the glass substrate had weak absorption, the transmittance spectra were corrected before fitting to eliminate the effect [13,14]. The fitting procedure used a Levenberg – Marquardt algorithm [15]. Porosity of coatings was estimated using the Lorentz-Lorenz formula [16,17,18].

### 2.4 Characterization of coatings by SEM

Surface morphology of the emery paper, of the polished zinc substrate and selected samples (two layered *compact SiO<sub>2</sub>*, four layered *CTAB/porous SiO<sub>2</sub>* and four layered *Pluronic/porous SiO<sub>2</sub>*) prepared onto zinc substrates were investigated by scanning electron microscopy. Overview images were taken using a JEOL JSM 6380LA scanning electron microscope. The samples were sputtered by Pd/Au alloy (JEOL gold coater).

### 2.5 Electrochemical investigations

Electrochemical investigations were carried out in a three - electrode cell containing a working electrode (pure Zn and SiO<sub>2</sub>-coated samples, S = 2 cm<sup>2</sup>), a counter electrode (platinum wire), and a reference electrode (Ag/AgCl/KCl<sub>sat</sub>). All corrosion measurements were performed in 0.2 g/L aqueous solution (pH=5) of Na<sub>2</sub>SO<sub>4</sub> (Riedel–de Haën, Germany). Measurements were carried out with a computer-controlled potentiostat AUTOLAB, PGSTAT302N (Eco Chemie BV, Utrecht, Netherlands) and GPES program was used for data analysis. In each case, before the polarization measurements, the open circuit potential (OCP) was recorded during 1 hour, until it was stabilized. The corrosion potentials and the corrosion current densities were estimated by using Tafel plots.

## 3 Results and discussion

### 3.1 Optical properties of mono- and multilayered coatings

For characterization of coating samples, optical model investigations were carried out. Transmittance spectra were taken from uncoated glass substrates and from all types of mono- and multilayered silica coatings prepared on glass substrates.

All the prepared silica sol-gel layers had higher transmittance than their bare substrates for the whole studied wavelength range (Figure 1 a), b) and c)) and the highest transmittance was found for Pluronic templated coatings. Film thickness and effective refractive index values resulted from the fitting procedures were collected in Table 1. The reduced chi-square values of the fitting were in the range of  $10^{-7}$  -  $10^{-8}$ , and the coefficient of determination ( $R^2$ ) value was above 0.995 which indicated a good agreement between measured and calculated spectra.

Porosity values calculated in view of effective refractive index of the layers and refractive index of the bulk silica ( $n_{\text{bulk}} = 1.450$ ) and air ( $n_{\text{air}} = 1$ ) are also listed in Table 1. Thickness value of 2 layered compact silica coating ( $136 \pm 5$  nm) is commensurable with that of 1 layered CTAB/porous silica ( $136 \pm 2$  nm) and Pluronic/porous silica ( $124 \pm 3$  nm) coatings, while layer thickness of 4 layered compact silica ( $251 \pm 2.5$ ) with thickness of 2 layered porous coatings ( $198 \pm 6$  nm and  $219 \pm 2$  nm for CTAB and Pluronic templated silica coatings respectively). As can be seen the Pluronic template is more effective for increasing porosity.

### 3.2 Characterization of surface morphology by scanning electron microscopy (SEM)

SEM images were taken from the emery paper (Figure 2) used for smoothing the surface of Zn substrates, from the surface of the polished Zn substrate (Figure 3) and from the multilayered coatings with commensurable layer thickness values, deposited onto the polished Zn surfaces: 4 layered compact silica coating (Figure 4), 2 layered CTAB/porous silica and 2 layered Pluronic/silica coatings (Figure 5 and Figure 6 respectively). Figure 3 shows that the surface of the polished, bare Zn substrate still has stripe - type unevenness. Similar surface pattern was also observed in the case of coated surfaces (Figure 4, Figure 5 and Figure 6). It means that the investigated sol-gel coatings cannot flatten out completely the metal surface. As can be seen in case of four - layered silica (Figure 4) a special cracking - type pattern superposes onto the original one.

### 3.3 Electrochemical properties of coatings deposited onto Zn surfaces

The polarization tests carried out in a potential range of  $\pm 20$  mV vs. OCP were used to determine the polarization resistance ( $R_p$ ) of zinc and of  $\text{SiO}_2$ -coated zinc samples from the slope of the linear  $E=f(i)$  curve, and the results are presented in Table 2.

It can be observed, that the uncoated Zn has the most negative OCP value and that a positive shift of the OCP is noticed in the case of all  $\text{SiO}_2$  coated samples, suggesting that these samples acquired more noble character and thus, an increased corrosion resistance.

On the other hand, the uncoated Zn samples exhibit the lowest  $R_p$  value, while the highest  $R_p$  value is recorded in the case of the zinc sample coated with 2 porous layers of  $\text{SiO}_2$  prepared in the presence of CTAB. This proves the protection ability

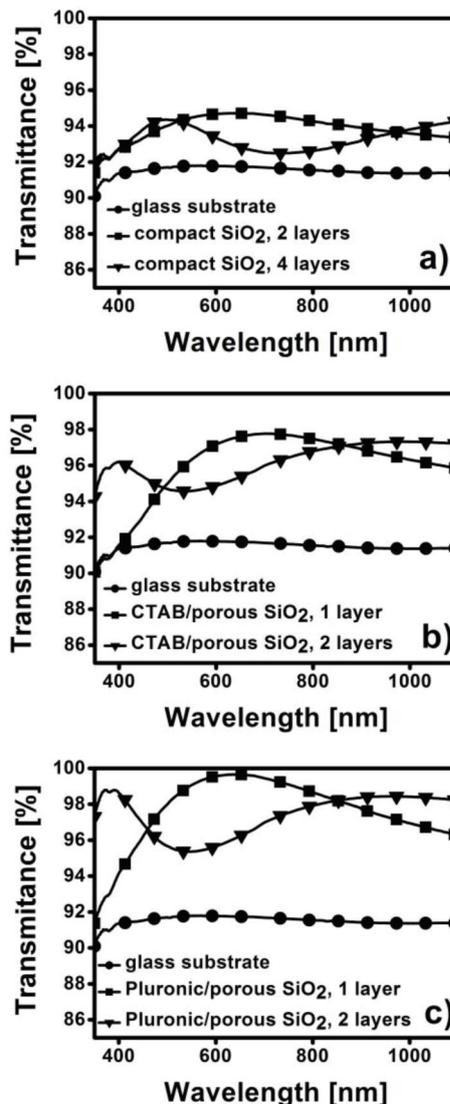


Fig. 1. Measured transmittance spectra of different samples a) compact silica coatings: (2 layers: squares, 4 layers: triangles; b) porous  $\text{SiO}_2$  sol-gel coatings templated with CTAB (1 layer: squares, 2 layers: triangles; c) porous  $\text{SiO}_2$  sol-gel coatings templated with Pluronic PE 10300 (1 layer: squares, 2 layers: triangles). Transmittance of bare glass substrates (circles) are also depicted in every case.

Tab. 1. Fitted layer thickness and refractive index values for mono- and multilayered coatings on glass substrates

Sample	Layer thickness [nm]	Effective refractive index	Porosity [%]
compact $\text{SiO}_2$ , 2 layers	$136 \pm 5$	$1.452 \pm 0.007$	-
compact $\text{SiO}_2$ , 4 layers	$251 \pm 2.5$	$1.439 \pm 0.001$	2
CTAB/porous $\text{SiO}_2$ , 1 layer	$136 \pm 2$	$1.364 \pm 0.010$	17
CTAB/porous $\text{SiO}_2$ , 2 layers	$198 \pm 6$	$1.371 \pm 0.001$	16
Pluronic/porous $\text{SiO}_2$ , 1 layer	$124 \pm 3$	$1.280 \pm 0.004$	35
Pluronic/porous $\text{SiO}_2$ , 2 layers	$220 \pm 3$	$1.320 \pm 0.003$	26

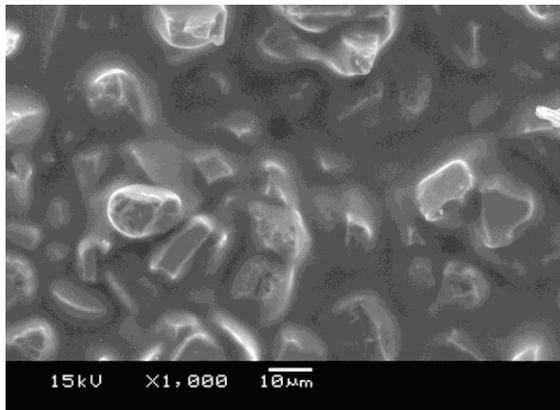


Fig. 2. SEM image of the emery paper

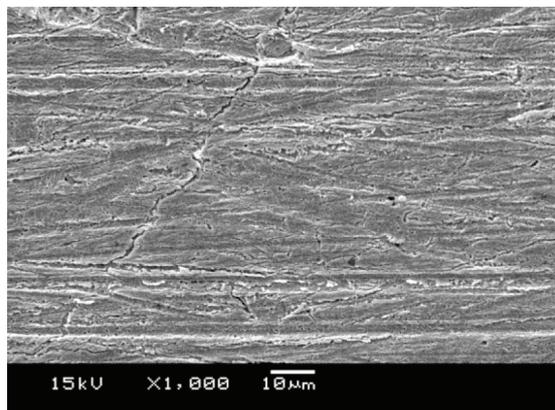


Fig. 3. SEM image of the polished Zn substrate

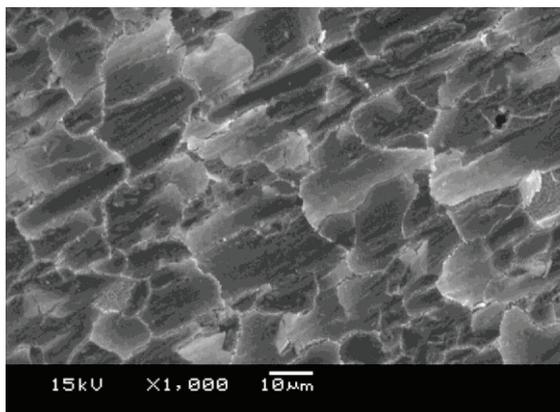


Fig. 4. SEM image of the compact SiO<sub>2</sub> coating, 4 layers

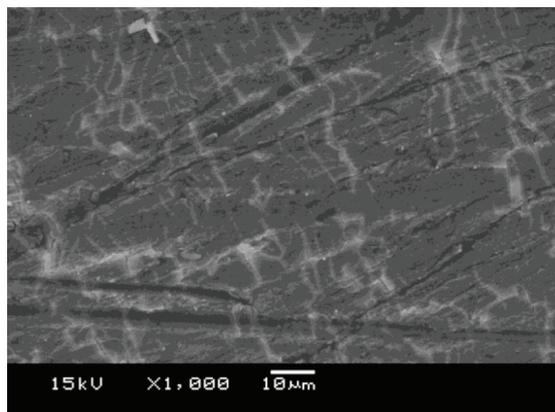


Fig. 5. SEM image of the CTAB/porous SiO<sub>2</sub> coating, 2 layers

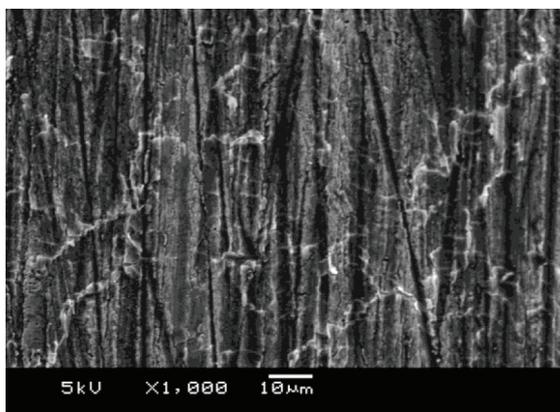


Fig. 6. SEM image of the Pluronic/porous SiO<sub>2</sub> coating, 2 layers

Tab. 2. Open-circuit potential (OCP) and polarization resistance ( $R_p$ ) of Zn and SiO<sub>2</sub>-coated Zn samples ( $R$  = correlation coefficient;  $N$  = number of points)

Sample	OCP [V vs. Ag/AgCl]	$R_p$ [ $\Omega\text{cm}^2$ ]	R/N
Zn	-0.994	98.5	0.9991/ 28
compact SiO <sub>2</sub> , 2 layers	-0.934	1649.3	0.9996/ 50
compact SiO <sub>2</sub> , 4 layers	-0.927	1804.0	0.9990/ 27
CTAB/porous SiO <sub>2</sub> , 1 layer	-0.948	709.2	0.9992/ 24
CTAB/porous SiO <sub>2</sub> , 2 layers	-0.910	2147.3	0.9990/ 27
Pluronic/porous SiO <sub>2</sub> , 1 layer	-0.956	900.9	0.9993/ 22
Pluronic/porous SiO <sub>2</sub> , 2 layers	-0.943	1633.0	0.9992/ 25

of the SiO<sub>2</sub> layers and points out to the importance of the preparation method and of the ingredients used for the obtaining of sol-gel coatings.

In Figure 7 a), b) and c) the electrochemical response of different SiO<sub>2</sub> coated Zn samples are compared with that of

uncoated zinc. The polarization curves were recorded in a  $\pm 200$  mV potential range around the OCP. The Tafel plots were used to extract the corrosion potential ( $E_{\text{corr}}$ ), the corrosion current density ( $i_{\text{corr}}$ ) and the Tafel slopes values. The obtained results are presented in Table 3.

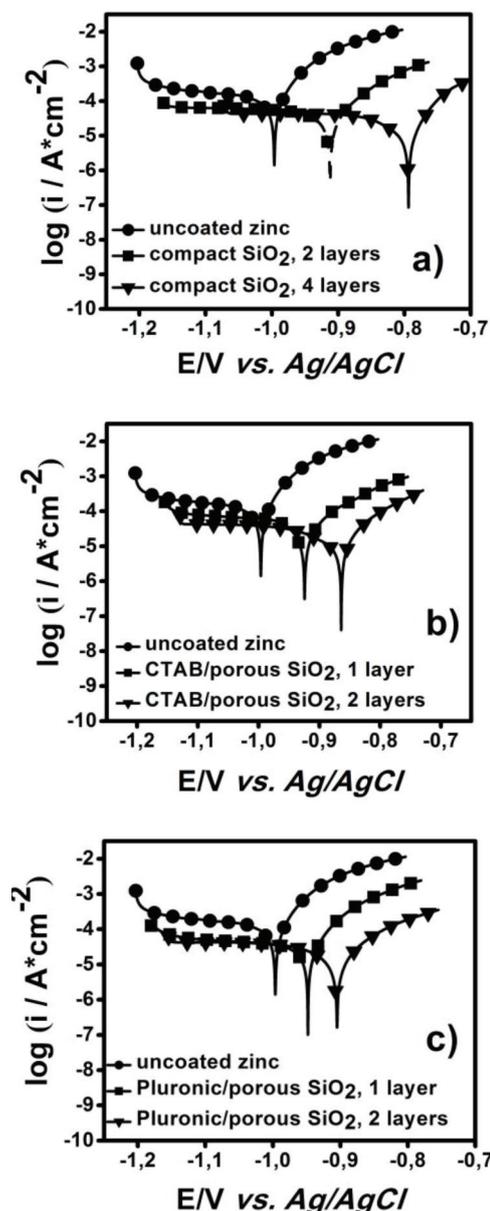


Fig. 7. Tafel plots of the polarization curves recorded for uncoated Zn substrates (circles) and for different type silica coatings: a) compact silica coatings (2 layers: squares, 4 layers: triangles); b) porous SiO<sub>2</sub> sol-gel coatings templated with CTAB (1 layer: squares, 2 layers: triangles); c) porous SiO<sub>2</sub> sol-gel coatings templated with Pluronic PE 10300 (1 layer: squares, 2 layers: triangles) (*i* = current density, *E* = potential).

It can be observed that the corrosion current density of the coated samples decreased with an order of magnitude in comparison with the uncoated Zn samples and the polarization resistance increased correspondingly. This effect could be correlated with the physical properties of the coatings, which act as a barrier between the corrosion medium and the zinc substrate.

The protection efficiency increases with the number of layers. As expected, multilayered coatings are more efficient than single ones but, surprisingly, the porous coatings provide better protection than compact ones. The reason for the unexpected efficiency of the porous layers can be due to an improved

Tab. 3. Corrosion parameters extracted from Tafel plots for uncoated Zn and SiO<sub>2</sub> coated samples (*i*<sub>corr</sub> = corrosion current density, *E*<sub>corr</sub> = corrosion potential, *b*<sub>a</sub> = anodic activation coefficient, *b*<sub>c</sub> = cathodic activation coefficient, *v*<sub>corr</sub> = corrosion rate)

Sample	<i>i</i> <sub>corr</sub> [A/cm <sup>2</sup> ]	<i>E</i> <sub>corr</sub> [V vs. Ag/AgCl]	<i>b</i> <sub>a</sub> [V <sup>-1</sup> ]	<i>b</i> <sub>c</sub> [V <sup>-1</sup> ]	<i>v</i> <sub>corr</sub> [mm/year]
Zn	1.215*10 <sup>-5</sup>	-0.996	0.020	0.036	1.81*10 <sup>-1</sup>
compact SiO <sub>2</sub> , 2 layers	1.819*10 <sup>-6</sup>	-0.859	0.029	0.026	2.712*10 <sup>-2</sup>
compact SiO <sub>2</sub> , 4 layers	1.871*10 <sup>-6</sup>	-0.896	0.031	0.021	2.789*10 <sup>-2</sup>
CTAB/porous SiO <sub>2</sub> , 1 layer	2.76*10 <sup>-6</sup>	-0.924	0.024	0.031	4.115*10 <sup>-2</sup>
CTAB/porous SiO <sub>2</sub> , 2 layers	1.087*10 <sup>-6</sup>	-0.859	0.018	0.013	1.62*10 <sup>-2</sup>
Pluronic/porous SiO <sub>2</sub> , 1 layer	3.832*10 <sup>-6</sup>	-0.948	0.046	0.025	5.713*10 <sup>-2</sup>
Pluronic/porous SiO <sub>2</sub> , 2 layers	1.207*10 <sup>-6</sup>	-0.905	0.021	0.022	1.799*10 <sup>-2</sup>

coating ability (wettability) of precursor sols containing surfactants as compared with the precursors without surfactants which were used for the preparation of the compact layers. It is worth mentioning that the layers prepared from precursor sols templated with CTAB were more efficient than those prepared from sols containing Pluronic PE 10300. This behaviour can be attributed to different porous structures and porosities.

#### 4 Conclusions

Based on the above-mentioned results, some conclusions can be drawn:

- all SiO<sub>2</sub> coatings provided corrosion protection to zinc
- the open-circuit potentials of the SiO<sub>2</sub> coated samples are more positive than for pure Zn, and the corrosion current density on the coated samples decreased with an order of magnitude, proving the protection ability of the SiO<sub>2</sub> layers
- multi-layered coatings are more efficient than single ones and the porous coatings provide better protection than compact ones
- the layers prepared from precursor sols templated with CTAB were more efficient than those prepared from sols containing Pluronic PE 10300 as a result of different porous structures and porosities
- the reason for the unexpected efficiency of the porous layers can be an improved coating ability of precursor sols containing surfactant due to the better wetting ability of surfactant solutions

The interpretation of the experienced effects requires further investigations that are in progress in our laboratories.

## Acknowledgement

The authors thank E. Hild, K. Molnár, D. Blejan, A. T. Gaál and B. Kiss for their help in this work. The financial support of the Hungarian Scientific Research Fund (OTKA CK 78629), of NKTH - A\*STAR Hungarian - Singaporean Bilateral S&T International Co-operation (BIOSPONA), of the New Széchenyi Plan (TÁMOP-4.2.1/B-09/1/KMR-2010-0002) and of the National Development Agency (Hungarian-French Bilateral Co-operation, PHONOSEL, Tét\_11-2-2012-0008 and Hungarian-Romanian Bilateral Co-operation, SOLGELCOR, (Tét\_12\_RO-1-2013-0011; 664/2013) is gratefully acknowledged.

## References

- 1 Araujo W. S., Margarit I. C. P., Ferreira M., Mattos O. R., Lima Neto P., *Undoped polyaniline anticorrosive properties*. *Electrochimica Acta*, 46(9), 1307-1312 (2001).  
DOI: [10.1016/S0013-4686\(00\)00726-X](https://doi.org/10.1016/S0013-4686(00)00726-X)
- 2 Wilson B., Fink N., Grundmeier G., *Formation of ultra-thin amorphous conversion films on zinc alloy coatings: Part 2: Nucleation, growth and properties of inorganic-organic ultra-thin hybrid films*. *Electrochimica Acta*, 51(15), 3066-3075 (2006).  
DOI: [10.1016/j.electacta.2005.08.041](https://doi.org/10.1016/j.electacta.2005.08.041)
- 3 Klimow G., Fink N., Grundmeier G., *Electrochemical studies of the inhibition of the cathodic delamination of organically coated galvanised steel by thin conversion films*. *Electrochimica Acta*, 53(3), 1290-1299 (2007).  
DOI: [10.1016/j.electacta.2007.05.045](https://doi.org/10.1016/j.electacta.2007.05.045)
- 4 Hosseini M., Ashassi-Sorkhabi H., Yaghoobkhani Ghiasvand H. A., *Corrosion Protection of Electro-Galvanized Steel by Green Conversion Coatings*. *Journal of Rare Earths*, 25(5), 537-543, (2007).  
DOI: [10.1016/S1002-0721\(07\)60558-4](https://doi.org/10.1016/S1002-0721(07)60558-4)
- 5 Tiwari S. K., Sahu R. K., Pramanick A. K., Singh R., *Development of conversion coating on mild steel prior to sol gel nanostructured  $Al_2O_3$  coating for enhancement of corrosion resistance*. *Surface and Coatings Technology*, 205(21-22), 4960-4967 (2011).  
DOI: [10.1016/j.surfcoat.2011.04.087](https://doi.org/10.1016/j.surfcoat.2011.04.087)
- 6 Wang D., Bierwagen G.P., *Sol-gel coatings on metals for corrosion protection*. *Progress in Organic Coatings*, 64(4), 327-338 (2009).  
DOI: [10.1016/j.porgcoat.2008.08.010](https://doi.org/10.1016/j.porgcoat.2008.08.010)
- 7 Pepe A., Aparicio M., Cere S., Duran A., *Synthesis of hybrid silica sol-gel coatings containing Zn particles on carbon steel and Al/Zn coated carbon steel*. *Materials Letters*, 59(29-30), 3937-3940 (2005).  
DOI: [10.1016/j.matlet.2005.07.037](https://doi.org/10.1016/j.matlet.2005.07.037)
- 8 Deflorian F., Rossi S., Fedel M., Motte C., *Electrochemical investigation of high-performance silane sol-gel films containing clay nanoparticles*. *Progress in Organic Coatings*, 69(2), 158-166 (2010).  
DOI: [10.1016/j.porgcoat.2010.04.007](https://doi.org/10.1016/j.porgcoat.2010.04.007)
- 9 Schem M., Schmidt T., Gerwann J., Wittmar M., Veith M., Thomson G. E., Molchan I. S., Hashimoto T., Skeldon P., Phani A. R., Santucci S., Zheludkevich M. L.,  *$CeO_2$ -filled sol-gel coatings for corrosion protection of AA2024-T3 aluminium alloy*. *Corrosion Science*, 51(10), 2304-2315 (2009).  
DOI: [10.1016/j.corsci.2009.06.007](https://doi.org/10.1016/j.corsci.2009.06.007)
- 10 Montemor M. F., Trabelsi W., Lamaka S. V., Yasakau K. A., Zheludkevich M. L., Bastos A. C., Ferreira M. G. S., *The synergistic combination of bis-silane and  $CeO_2$ • $ZrO_2$  nanoparticles on the electrochemical behaviour of galvanised steel in NaCl solutions*. *Electrochimica Acta*, 53(20), 5913-5922 (2008).  
DOI: [10.1016/j.electacta.2008.03.069](https://doi.org/10.1016/j.electacta.2008.03.069)
- 11 Söptei B., Baranyai P., Kovács A. L., Hörvölgyi Z., *Preparation and characterization of Thioflavin T doped silica nanoparticles*. *Periodica Polytechnica Chemical Engineering*, 53(2), 49-54 (2009).  
DOI: [10.3311/pp.ch.2009-2.03](https://doi.org/10.3311/pp.ch.2009-2.03)
- 12 Vaishnavi T. S., Haridoss P., Vijayan C., *Optical properties of zinc oxide nanocrystals embedded in mesoporous silica*. *Materials Letters*, 62(10-11), 1649-1651 (2008).  
DOI: [10.1016/j.matlet.2007.09.051](https://doi.org/10.1016/j.matlet.2007.09.051)
- 13 Hild E., Deák A., Naszályi L., Sepsi Ö., Ábrahám N., Hörvölgyi Z., *Use of the optical admittance function and its WKB approximation to simulate and evaluate transmittance spectra of graded-index colloidal films*. *Journal of Optics A: Pure and Applied Optics*, 9(10), 920-930 (2007).  
DOI: [10.1088/1464-4258/9/10/023](https://doi.org/10.1088/1464-4258/9/10/023)
- 14 Hinczewski D. S., Hinczewski M., Tepehan F. Z., Tepehan G. G., *Optical filters from  $SiO_2$  and  $TiO_2$  multi-layers using sol-gel spin coating method*. *Solar Energy Materials and Solar Cells*, 87(1-4), 181-196 (2005).  
DOI: [10.1016/j.solmat.2004.07.022](https://doi.org/10.1016/j.solmat.2004.07.022)
- 15 Press W. H., Flannery B. P., Teukolsky S. A., Vetterling W. T., *Numerical Recipes in C: The Art of Scientific Computing*. Cambridge University Press, New York (1988).
- 16 Lorenz L. V., *Annalen der Physik und Chemie*, 11, 70 (1880)
- 17 Lorentz H. A., *Theory of Electrons*. Second edition. Teubner. Leipzig, Germany. (1916).
- 18 Grigoriev D., Gorin D., Sukhorukov G. B., Yashchenok A., Maltseva E., Möhwald H., *Polyelectrolyte/magnetite Nanoparticle Multilayers: Preparation and Structure Characterization*. *Langmuir*, 23(24), 12388-12396 (2007).  
DOI: [10.1021/la700963h](https://doi.org/10.1021/la700963h)