

## Conversion Coating Treatment for Zinc Surface by a Vanadate Solution

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In this work, chemical conversion coating on zinc surfaces was performed by immersion in a solution containing vanadate. Corrosion behaviour of zinc surfaces was investigated using electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy. According to the results, the vanadium-treated layer significantly improved the corrosion resistance of zinc surfaces in contact with 3.5 % NaCl solution. In comparison of the chromium-treated layer, the vanadium-treated layer also exhibits better corrosion resistance. The treated zinc surface mainly consists of vanadium and oxygen, which mainly exist as  $V_2O_5$ ,  $VO_2$ , and its hydrates.

**Key Words:** Vanadium, Chemical conversion coating, Corrosion resistance.

### INTRODUCTION

Surface treatments based on the use of chromates have been successfully applied on a large number of metal and alloys<sup>1</sup>. However, hexavalent chromium has been leading to legislation that will soon prohibit these treatments. Therefore, new alternative and more environmentally friendly surface treatments need to be developed. Many studies have been conducted in recent decades to find a suitable friendly anticorrosive alternative to chromate<sup>2</sup>.

At present, vanadium solution is usually used as the corrosion resistant inhibitor for the paint or pigment systems. However, only a few works are reported on the application of vanadium-based coatings on aluminum alloys<sup>3-7</sup> and magnesium alloys<sup>8</sup>. Herein, we study the corrosion properties of the vanadium-treated layer on zinc surfaces by using electrochemical impedance spectroscopy (EIS). The surface composition of the film was investigated by using X-ray photoelectron spectroscopy (XPS). The results for vanadium-treated layer were compared with untreated and conventional chromium-treated layers on zinc surfaces.

### EXPERIMENTAL

Commercially available zinc was degreased and etched by immersion in 3 %  $HNO_3$  for 10 s, then the untreated zinc was immersed in the solution containing  $NaVO_3$  with concentration of 200 mM for 30 s at 20 °C and pH 6.0, at last rinsed in distilled water and dried with compressed air, the vanadium-treated zinc sample was obtained. The untreated zinc was immersed in the solution containing 5 g/L  $CrO_3$  and 2 g/L

$ZnSO_4$  solution for 30 s at 20-25 °C and pH 1.5, then rinsed in distilled water and dried with compressed air, the chromium-treated zinc sample was obtained.

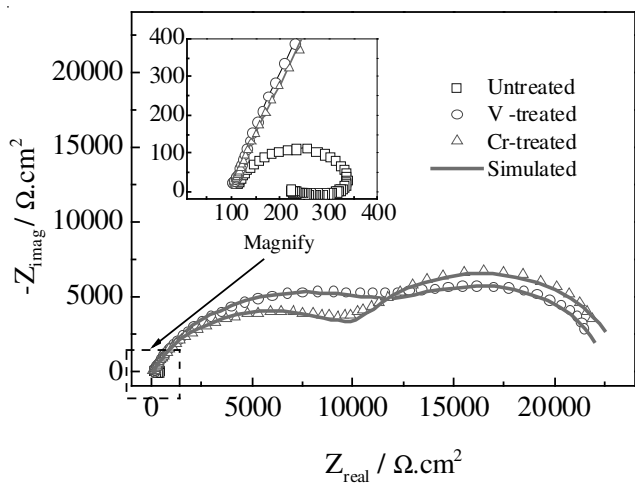
Electrochemical impedance spectroscopy were measured by immersion the samples (0.785 cm<sup>2</sup> of exposed area) into a 3.5 % NaCl solution at pH 6.8 with an EG and G PAR273 potentiostat. This equipment comprised three electrodes, the sample is the working electrode, platinum is the counter electrode and the saturated calomel electrode (SCE) as the reference electrode. Electrochemical impedance spectroscopy was recorded for frequency range from  $10^4$ - $10^{-2}$  Hz, with the amplitude equal to 5 mV rms.

Chemical composition of the film was analyzed by X-ray photoelectron spectroscopy, using a PHI-5700 ESCA system (Perkin-Elmer). The position of the  $C_{1s}$  peak at 284.5 eV was used to calibrate the spectra. The XPS data analysis was performed with XPSPeak4.1 program<sup>9</sup>.

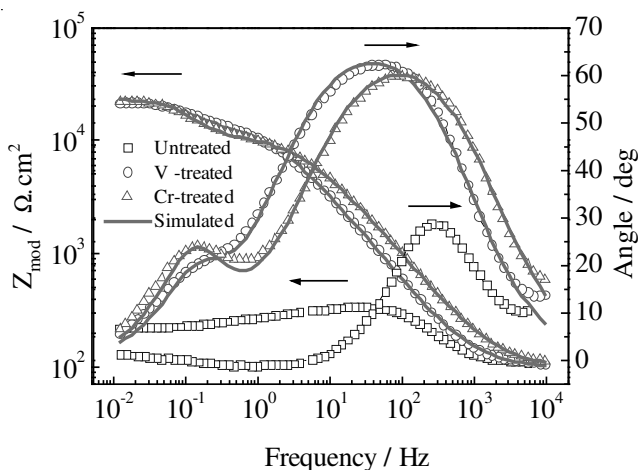
### RESULTS AND DISCUSSION

Fig. 1 exhibit Nyquist (a) and Bode (b) plots for the samples after 1 h of immersion in 3.5 % NaCl solution at pH 6.8. As Fig. 1(a) shows, Nyquist plot of the untreated zinc surface presents a depressed semicircle, at the higher frequencies, accompanied by a capacitive loop at the lower frequencies, which resembles an inductive-type loop over the real axis. The semicircle at high and intermediate frequencies can be attributed to charge transfer process, while the pseudo-inductive loop could be related to the effect of the corrosion rate's increasing during the measurement more than a real process. The shape of the Nyquist plots is similar for the vanadium-treated and

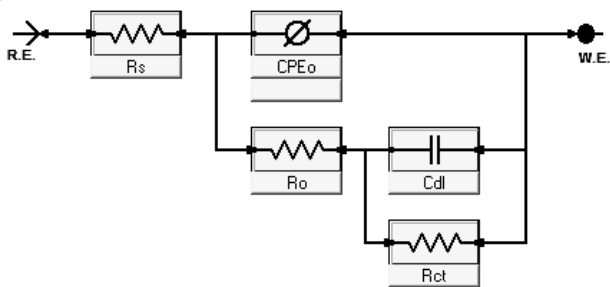
chromium-treated zinc surfaces, showing two depressed semi-circles at the higher and the lower frequencies. The two coupled semicircles can be more clearly distinguished in the Bode angle diagram [Fig. 1(b)], in which two maxims are differentiated. The process that appears at the higher frequencies would be associated to the presence of the vanadium-treated layer generated on the surface. The second semicircle of the Nyquist diagram, at lower frequencies, would be associated to the double layer of zinc surface.



(a)



(b)



(c)

Fig. 1. Nyquist (a) and Bode (b) plots for the samples after 1 h of immersion in 3.5 % NaCl solution at pH 6.8. Scatters: the experimental data; solid curves: the simulated data according to the equivalent circuit (c)

In this case, the simulation fitting procedure was performed using the equivalent circuit of Fig. 1(c) for the vanadium-treated and chromium-treated zinc surfaces. In the circuit,  $R_s$  corresponds to the resistance of the electrolyte;  $R_{ct}$  is the charge transfer resistance, which represents the corrosion resistance of the whole material and  $C_{dl}$  is the capacity associated with the double layer of the metal;  $R_o$  and  $CPE_o$  represent resistance and capacity of the treated layer resistance, respectively. CPE is not a normal capacitance but a non-ideal (dispersive) capacitance.

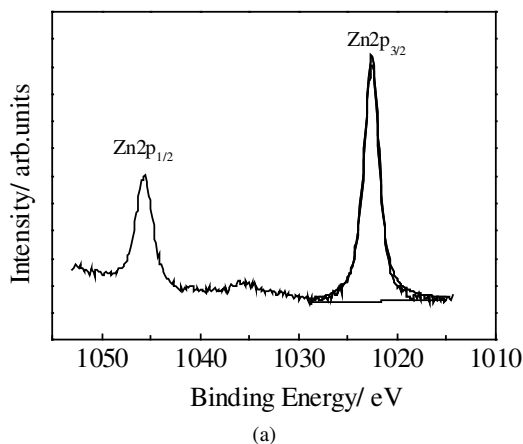
The parameters presented in Table-1 were used in fitting procedure of experimental data. As shown in Fig. 1(1) and (2), excellent agreement between experimental and simulated data is observed.

TABLE-1 PARAMETERS USED IN THE SIMULATION OF IMPEDANCE DATA			
Parameters	Untreated	Cr-Treated	V-Treated
$R_s$ ( $\Omega \text{ cm}^2$ )	94.75	96.34	96.94
$Y_0(CPE_o)$ ( $F \text{ s}^{-1} \text{ cm}^2$ )	–	7.25E-6	1.10E-5
$n$	–	0.7712	0.7898
$R_o$ ( $\Omega \text{ cm}^2$ )	–	1.15E4	1.45E4
$C_{dl}$ ( $F \text{ cm}^2$ )	3.385E-6	1.483E-4	1.834E-4
$R_{ct}$ ( $\Omega \text{ cm}^2$ )	195.7	7961	11670

As Table-1 shows, the charge transfer resistance ( $R_{ct}$ ) of vanadium-treated zinc is much higher than that of untreated zinc and slightly lower than that of chromium-treated zinc, which indicates that both vanadium-treatment and chromium-treatment seem to have a significant improvement on corrosion resistance of zinc in contact with 3.5 % NaCl solution and the efficiency of vanadium-treatment is the highest.

After 5 min of argon-ion sputtering, the vanadium layer on zinc was analyzed by XPS. The chemical composition of the layer determined by integration of the peak area in the spectrum is V 31.32, O 60.11, Zn 4.63, C 3.94 (atom %).

Fig. 2 shows high resolution XPS spectrum of Zn 2p, V2p and O1s. The Zn2p<sub>3/2</sub> spectrum consists of a peak corresponding to zinc in form of ZnO at 1022.1 eV [Fig. 2(a)]. It comes from the zinc surface, which suggests that the distribution of vanadium layer is not even. Fig. 2(b) presents the two peaks at about 516.4 and 523.5 eV, which represent V2p<sub>3/2</sub> and V2p<sub>1/2</sub>, respectively. After deconvolution with Gaussian functions, the V2p region is decomposed in two contributions corresponding



(a)

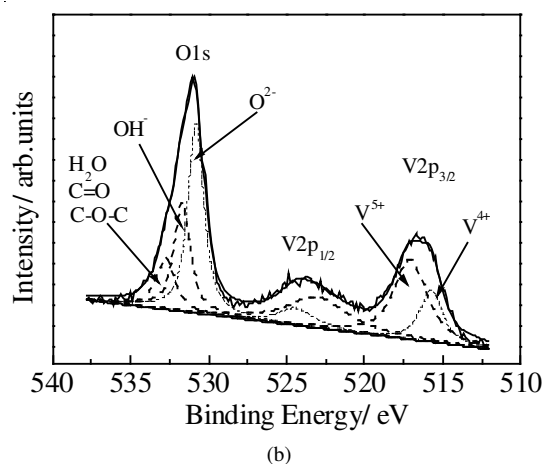


Fig. 2. High resolution XPS spectra of (a) Zn2p, (b) V2p and O1s for the vanadium-treated zinc

to the different oxidation states of vanadium. Each contribution consists of a doublet between the  $2p_{3/2}$  and  $2p_{1/2}$  peaks. The dominant doublet composed of two peaks located at 517.11 eV ( $V2p_{3/2}$ ) and 524.44 eV ( $V2p_{1/2}$ ) is assigned to  $V^{5+}$ . The peaks of the minor doublet are located at 515.75 eV ( $V2p_{3/2}$ ) and 523.08 eV ( $V2p_{1/2}$ ) and assigned to  $V^{4+}$ . The O1s region consists of three peaks [Fig. 2(b)]; the dominant peak at 531.70 eV is attributed to  $OH^-$  existing as V-OH. The second one at

530.81 eV is attributed to  $O^{2-}$ . The third one at 532.74 eV is attributed to adsorbed water and C-OH, C=O, C-O-C of the contaminants.

### Conclusion

As described above, the vanadium-treated and the chromium-treated layers present a significant improvement on corrosion resistance, which are much better than that provided by the untreated zinc when exposed to the 3.5 % NaCl solution and V-treatment provides better effectiveness. XPS analyzed that the vanadium layer was made on the zinc surface, consisting largely of  $V_2O_5$ ,  $VO_2$  and its hydrates such as  $V_2O_5 \cdot nH_2O$ ,  $VO(OH)_2$ .

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