Electrochemical and AFM Study of Corrosion Inhibition with Respect to Application Method

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The aim of this work was to investigate how the efficiency of a corrosion inhibitor and the mechanism of its inhibiting action depend on the inhibitor application method. Studies were performed on copper in 0.5 M NaCl solution for two imidazole derivatives. Studied compounds were either added to the corrosive solution or the inhibitor film was formed prior to immersion in the corrosive solution.

The investigations were conducted by means of electrochemical methods and atomic force microscopy.

The results obtained indicate that the method of inhibitor application may determine the mechanism of inhibition and the efficiency of an inhibitor. When the inhibitors were adsorbed on the metal surface from the organic solvent, they acted primarily as cathodic corrosion inhibitors. On the other hand, when they were added to the aqueous solution, both anodic and cathodic reaction rates slowed down.

AFM studies have also confirmed changes in the inhibition mechanism due to the application method. All experimental methods have confirmed that the studied imidazole compounds can control the corrosion processes more efficiently when they are dissolved in a chloride solution than when used in nanolayers.

Key words:
Copper, corrosion inhibition, imidazoles, chloride medium

Introduction

One of the most important methods for the corrosion protection of metals is the use of organic inhibitors. Corrosion inhibitors are commonly applied by either adding them directly to the corrosive media or by forming a protective inhibitor film prior to the exposure of metal to the corrosive environment. The choice between these two methods usually depends on the properties of the inhibitor and on the type of the corrosive media.

Imidazole derivatives were found to be efficient copper corrosion inhibitors in various corrosive environments.[1–4] Previous research has shown that their inhibiting action depends on the anion and pH value of the solution.[5] This work examines the relationship between the inhibitor application method and the inhibiting effect. The goal was to find the optimal application technique to obtain higher efficiency of the inhibitor by varying the method of its application.

Two imidazole compounds were studied: 4-methyl-1-phenyl imidazole (PMI) and 4-methyl-1-(*p*-tolyl) imidazole (TMI). The molecular struc-
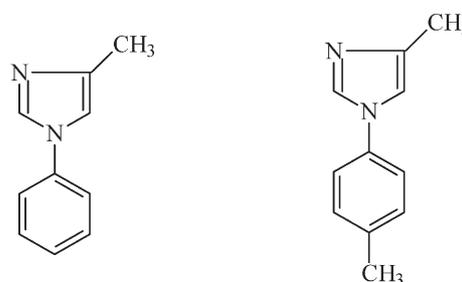
4-methyl-1-phenyl imidazole
(PMI)   4-methyl-1-(*p*-tolyl) imidazole
(TMI)

F i g . 1 – *Molecular structure of the investigated imidazoles*

tures of these compounds are given in Fig. 1. Their efficiency as copper corrosion inhibitors was examined in chloride media. The inhibitors were either added to corrosive solution or the inhibitor film was formed prior to immersion in the corrosive solution.

The first approach (i.e. addition of inhibitor in corrosive medium) is mostly used for closed systems.[6] The second approach is to form a coating of mono- or multimolecular-layers of molecules on metal surfaces. This is done by nanocoating techniques performed either by Langmuir-Blodgett (LB) film deposition or by the self-assembling method.[7–9]

Experimental details

Testing solutions were prepared from analytical grade NaCl and redistilled water. The inhibitors, 4-methyl-1-phenyl imidazole (PMI) and 4-methyl--1-(p-tolyl) imidazole (TMI), were synthesized specially for this research.

The working electrode and disc for AFM measurements were of pure copper (99.98 % purity). The working electrode, of area 1.54 cm², prior to each measurement was abraded with emery paper to a 2000 metallographic finish, polished with alumina (α-Al$_2$O$_3$ 0.1 µm), rinsed in redistilled water and degreased in ethanol. A saturated calomel electrode (SCE) with a Luggin capillary was the reference, and a Pt plate was the counter electrode. All potentials are reported vs. SCE.

Electrochemical measurements were conducted after 1 hour immersion in 0.5 M NaCl solution with or without inhibitor. The solution was stirred by a magnetic stirrer.

Electrochemical measurements were performed using EG&G potentiostat/galvanostat Model 263A and Frequency Response Detector 1025. Polarization measurements were controlled with PARC corrosion analysis software M 352/252 SoftCorr. Potential scan was performed from the most negative potentials up to the most positive potentials in the range E_{corr} ± 150 mV. Electrochemical impedance measurements were controlled with Power Sine software. EIS experiments were performed with a 10 mV rms ac-amplitude-signal perturbation with a frequency scan range from 100 kHz to 10 mHz. The impedance data were then analyzed with software based on a Simplex parameter regression method.

Studies were performed following one of the following procedures:

A) inhibitor was added in 0.5 M NaCl in previously determined optimum concentration[1] *(untreated + inhibitor)*

B) formation of inhibitor film in 10^{-2} M inhibitor solution in THF (tetrahydrofurane) during one hour. Samples are referred to as *pretreated*. After pretreatment the copper sample was immersed in 0.5 M NaCl solution

C) pretreated copper electrode immersed in corrosive solution containing inhibitor (*pretreated + inhibitor*).

Atomic force microscopy (AFM): Polished copper samples immersed in test solutions for one hour were *ex situ* scanned and visualized by NanoScope III (Digital Instrument). Images taken in contact mode were used without further procedures except autoflattening.

Results and discussion

The influence of inhibitor addition on copper corrosion in 0.5 M NaCl was studied by polarization measurements as presented in Fig. 2 for 4-methyl-1-phenyl imidazole (PMI). It can be seen that with the addition of the studied imidazole compound the polarization curves of copper shifted towards lower current densities, which indicates decrease of the copper corrosion rate. When the inhibitor was added in a low concentration (10^{-4} mol dm^{-3}) it had influenced mostly the cathodic corrosion reaction, while the influence on anodic process was less pronounced. This has resulted in a shift of the corrosion potential towards more negative values. The increase in inhibitor concentration influenced a decrease in the rate of anodic corrosion reaction, which resulted in a shift of the corrosion potential towards more positive values. Similar behavior was observed for the second inhibitor examined 4-methyl--1-(p-tolyl) imidazole (TMI).[1]
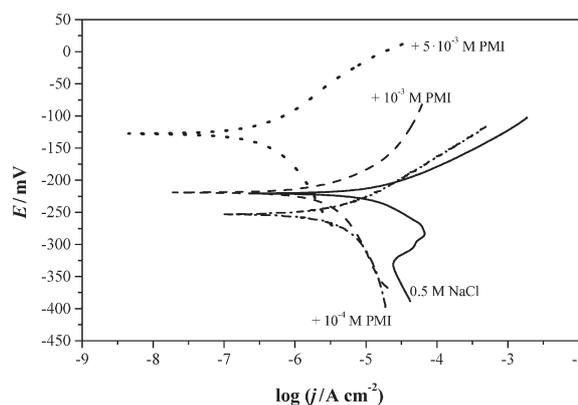

F i g . 2 – *Polarization curves of copper in 0.5 M NaCl and with the addition of different concentrations of 4-methyl-1-phenyl imidazole*

In order to determine the best application method for the studied inhibitors, polarization measurements were conducted for three different inhibitor application methods (as explained in experimental conditions). Fig. 3 shows polarization curves of copper in 0.5 M NaCl solution with and without the addition of 4-methyl-1--phenyl imidazole, and the polarization curve of copper electrode covered by 4-methyl-1-phenyl imidazole film formed in organic solvent. A decrease in corrosion rate was observed for both inhibitor application methods. From the corrosion current densities, determined by the Tafel extrapolation method, inhibiting efficiency was calculated according to the relation:

$$IE = \frac{j_0 - j_i}{j_0} \cdot 100\,\% \qquad (1)$$

Inhibiting efficiency (*IE*) was found to be 93 % when PMI was added into the solution and 71 % when pretreatment was applied. (Table 1)
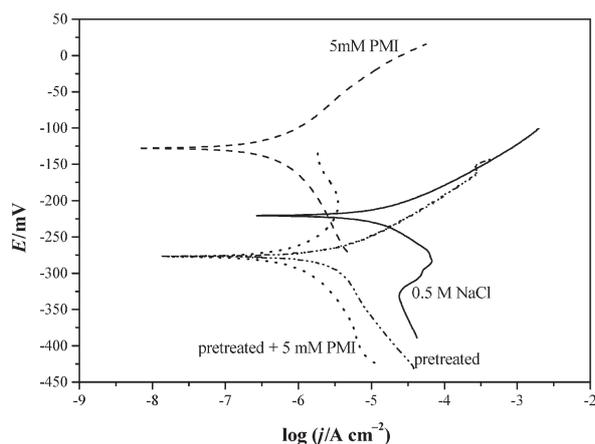
F i g . 3 – *Polarization curves of copper in blank 0.5 M NaCl, and for three PMI application methods*

F i g . 4 – *Polarization curves of copper in blank 0.5 M NaCl, and for three TMI application methods*

When the inhibitor was first adsorbed from organic solvent on the metal surface (*pretreated sample*) mainly the cathodic corrosion reaction was retarded. The polarization curve obtained was very similar to the one observed when the inhibitor was added to the solution in low concentration (Fig. 2). Such behavior could be attributed to the fact that there was no inhibitor in the solution, the adsorption-desorption equilibrium had shifted towards desorption of inhibitor, and therefore a low inhibiting effect was observed. To verify this assumption the pretreated sample was immersed in 0.5 M NaCl containing $5 \cdot 10^{-3}$ mol dm^{-3} PMI. As can be seen (Fig. 3 and Table 1) in this case the inhibiting effect observed was similar to that of the untreated sample in the solution containing inhibitor, where both corrosion reactions were retarded. Still there was a big difference in the corrosion potential (150 mV) and there were some differences in the shape of the anodic curve.

According to these results, it may be assumed that there are certain differences in the mechanism of the adsorption of PMI from organic solvent and water solution, which reflect differences in corrosion inhibition mechanism.

Polarization studies have also been conducted with another inhibitor investigated 4-methyl-1--(*p*-tolyl) imidazole (TMI). Measurements were performed for all three methods of inhibitor application (Fig. 4). Upon pretreatment, only the cathodic reaction slowed down, as observed for PMI. Inhibiting efficiency was much higher (Table 2) when inhibitor was present in the corrosive solution. As in the case of PMI, it may be noticed that there is a difference in the corrosion potential between the pretreated and non-pretreated sample.

To learn more about the structure of inhibiting layers formed by adsorption from the organic and aqueous solution, an AFM study of metal surface was conducted. (Fig. 5)

Fig. 5a and b show the differences in morphology of samples prepared by two techniques (i.e. in the first case the inhibitor was dissolved in NaCl solution, in the second, the experiment was carried out on copper with a previously formed inhibitor layer). Formation of polymer-like structures was observed in the case when inhibitor was directly added to chloride solution, but not when the inhibitor film was previously formed in organic solvent. On the pretreated samples, traces of the corrosion attack can be seen clearly, pits and corrosion products are scattered on the surface, which is consistent with the results obtained by polarization measurements, where the current density is higher than in the presence of the dissolved inhibitor.

T a b l e 1 – *Corrosion parameters of copper in blank 0.5 M NaCl and for three 4-methyl-1-phenyl imidazole application methods, determined by Tafel extrapolation method*

Sample	E_{corr} mV	$-b_c$ mV dec^{-1}	b_a mV dec^{-1}	j_{corr} µA cm^{-2}	IE %
Untreated	−255	247	56	10.01	–
+5 mM PMI	−127	160	85	0.68	93
Pretreated	−276	140	51	2.88	71
Pretreated + 5 mM PMI	−277	140	108	1.07	89

T a b l e 2 – *Corrosion parameters of copper in blank 0.5 M NaCl and for three 4-methyl-1-(p-tolyl) imidazole application methods, determined by Tafel extrapolation method*

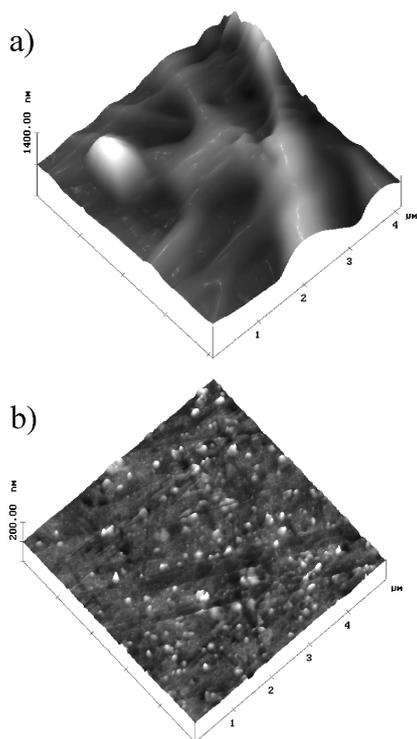| Sample	E_{corr} mV	$-b_c$ mV dec^{-1}	b_a mV dec^{-1}	j_{corr} µA cm^{-2}	IE %
Untreated	−255	247	56	10.01	–
+1 mM TMI	−197	105	76	0.83	92
Pretreated	−281	125	61	2.36	76
Pretreated + 1 mM TMI	−247	140	90	0.76	93

a)

b)

F i g . 5 – *AFM images of copper electrode after 60 min immersion in 0.5 M NaCl containing 5 mM PMI (a), and after 60 min of inhibitor formation in THF followed by 60 min immersion in 0.5 M NaCl (b)*

a)

b)

F i g . 6 – *AFM images of copper electrode after 60 min immersion in 0.5 M NaCl containing 1mM TMI (a), and after 60 min of inhibitor formation in THF followed by 60 min immersion in 0.5 M NaCl (b)*

Investigations performed with the other inhibitor (4-methyl-1-(*p*-tolyl) imidazole) have also shown differences in the structure of the copper surface in inhibitor containing chloride solution and the pretreated sample exposed to NaCl. Although no polymer-like structures were observed for TMI, untreated copper surface (Fig. 6a) was covered with a thin layer, presumably inhibitor layer, and no significant traces of corrosion were visualized. On the other hand, on the pretreated sample, traces of corrosion attack may be clearly observed (Fig. 6b).

For further clarification of inhibiting mechanisms of the studied compounds electrochemical impedance spectroscopy measurements (EIS) were conducted.

Results obtained for 4-methyl-1-phenyl imidazole are presented in Fig. 7. The diameter of the impedance loop for pretreated sample was only slightly bigger than the one measured for the untreated sample. The impedance loop obtained for pretreated sample in inhibited chloride solution was twice larger than the one obtained in uninhibited 0.5 M NaCl. For the untreated sample in inhibited solution, significantly higher impedance was observed. Impedance data were analyzed with an equivalent electrical circuit presented in Fig. 8.

Equivalent circuit consists of three time constants representing three processes. The origin of the elements of the equivalent circuit is as follows:
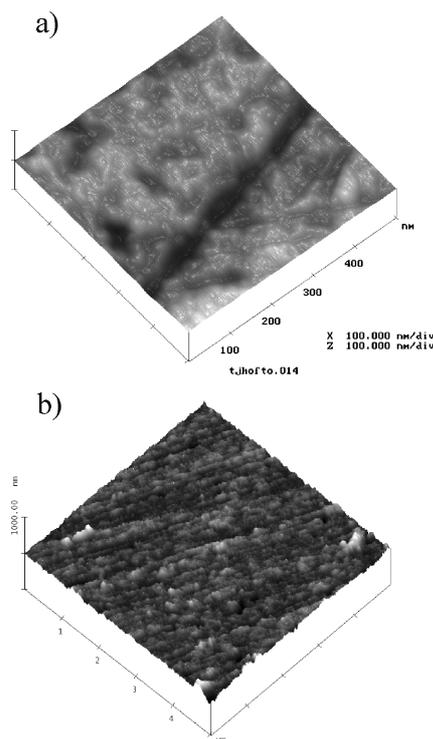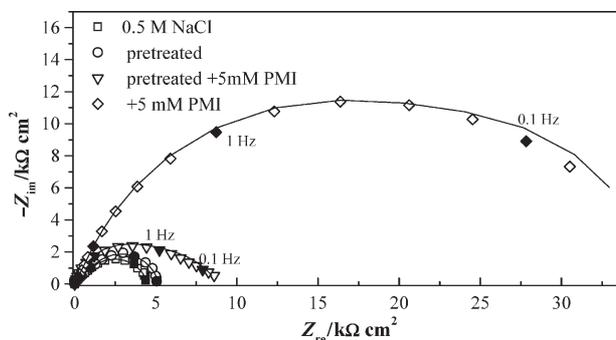

F i g . 7 – *Experimental (□) and fitted (–) impedance spectra for copper in 0.5 M NaCl and for three 4-methyl-1-phenyl imidazole application methods examined*
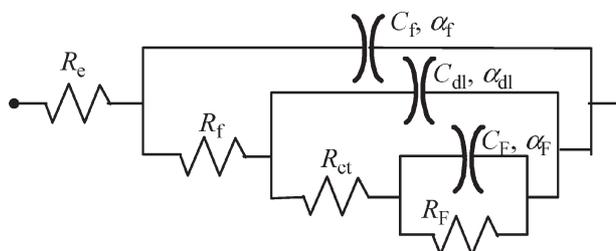

F i g . 8 – *Equivalent circuit used for parameter regression calculation*

R_f – C_f – these elements are observed in the high frequency domain. They correspond to the surface film resistance and the capacitance of the sur-

face film. This layer may be formed of oxide or oxide with adsorbed inhibitor.

$R_{ct} - C_{dl}$ – their contribution will exhibit a capacitive loop in the medium frequency domain. They correspond to charge transfer resistance and double layer capacitance.

$R_F - C_F$ – are faradaic resistance and capacitance that correspond to a redox process involving corrosion products.

α – represents a depressed feature in the Nyquist diagram according to the following equation:

$$Z(\omega) = \frac{R}{1 + (j \cdot \omega \cdot R \cdot C)^{\alpha}} \text{ where } 0 < \alpha \leq 1 \quad (2)$$

R_e – represents electrolyte resistance

The EIS parameters obtained by regression calculation with the simplex method are presented in Table 3. It can be seen that no matter which PMI application method was used it did not affect much the surface film resistance (R_f). Surface capacitance (C_f) decreased only when the inhibitor was present in the chloride solution. This leads to the assumption that only when the PMI was present in the solution it was adsorbed on the copper surface in a significant amount. Charge transfer resistance (R_{ct}) increased for all three methods of PMI application, but the highest was for the untreated sample in inhibited solution. From the charge-transfer resistance values it follows that copper dissolution decelerates significantly when inhibitor is only added into the chloride solution and no pretreatment is applied.

It may be seen that only for the untreated sample in inhibited solution faradic resistance (R_F) and capacitance (C_F) have significantly changed in comparison with the unprotected sample. The values obtained can be related to the presence of a complex 3D layer (Fig. 5a) that consists not only of
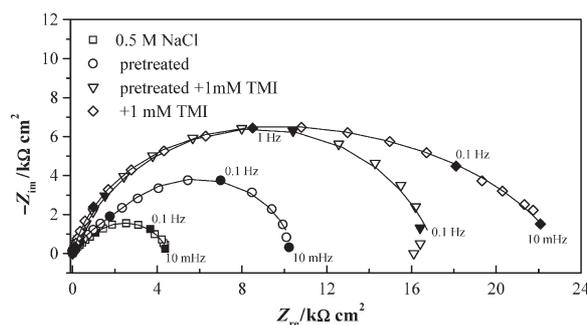

F i g . 9 – *Experimental (□) and fitted (–) impedance spectra for copper in 0.5 M NaCl and for three 4-methyl-1-(p-tolyl) imidazole application methods examined*

inhibitor but also of corrosion products[4] that give rise to faradic capacitance.

The influence of the second studied inhibitor TMI on impedance spectra of copper is presented in Fig. 9. Diameters of the impedance loops increase in the same order as observed for PMI: blank chloride solution < pretreated sample < pretreated sample in solution containing inhibitor < untreated sample in solution containing inhibitor. For TMI the difference in corrosion parameters (Table 4) between the last two cases is not as stunning as for PMI, which can be related to the fact that in the presence of TMI formation of complex 3D structures was not observed.

The impedance data presented above confirm the results obtained by polarization measurements. Both studied imidazole compounds can protect copper better when added directly into the corrosive chloride media than when applied in nanolayer on the metal surface prior to exposure to aggressive environment. It was also found that these differences are not only due to desorption of the inhibitor from the pretreated sample surface as there were differences in the protection efficiency when the inhibitors were used only in dissolved form and applied in combination, i.e. as nanocoating and as dissolved inhibitor.

T a b l e 3 – *EIS data for copper in blank 0.5 M NaCl solution and for three 4-methyl-1-phenyl imidazole application methods examined*

Sample	R_f/Ω cm^2	C_f/μF cm^{-2}	α_f	R_{ct}/Ω cm^2	C_{dl}/μF cm^{-2}	α_{dl}	R_F/Ω cm^2	C_F/μF cm^{-2}	α_F
Untreated	423	15.5	0.94	1470	22.2	0.81	2953	103	0.80
+5 mM PMI	519	2.10	0.76	33805	2.82	0.77	1241	1380	1.00
Pretreated	365	17.6	0.89	1566	47.4	0.81	3247	146	0.92
Pretreated + 5 mM PMI	123	2.94	0.89	5285	1.74	0.84	3367	114	0.66

T a b l e 4 – *EIS data for copper in blank 0.5 M NaCl solution and for three 4-methyl-1-(p-tolyl) imidazole application methods examined*

Sample	R_f/Ω cm^2	C_f/μF cm^{-2}	α_f	R_{ct}/Ω cm^2	C_{dl}/μF cm^{-2}	α_{dl}	R_F/Ω cm^2	C_F/μF cm^{-2}	α_F
Untreated	423	15.5	0.94	1470	22.2	0.81	2953	103	0.80
+1 mM TMI	156	2.1	0.85	13200	2.25	0.89	9910	86	0.61
Pretreated	966	15.1	0.92	3883	33.2	0.81	5617	109	0.96
Pretreated + 1 mM TMI	431	1.79	0.86	15106	2.13	0.77	1643	34	1.00

Such behaviour may be attributed to the fact that imidazole compounds have multiple anchoring sites available.[10–11] Loo *et al.*[12] have studied the electrosorption of imidazole and imidazolium ion (ImH$^+$) on copper and silver electrodes. A flat orientation was derived for ImH$^+$ while imidazole is adsorbed by pyridine nitrogen on a copper electrode. Bukowska *et al.*[13] observed from SERS data for imidazole on silver, changes in adsorbate orientation and composition depending on pH and potential.

Inhibitors examined in this work may be adsorbed via phenyl ring as well. Therefore, it may be proposed that, from chloride solutions with low inhibitor concentration and from organic solvents, PMI and TMI adsorb on copper by different anchoring sites than from chloride solutions with higher inhibitor concentration.

The difference in the adsorption of inhibitors from organic solvent and aqueous chloride solution may also be attributed to the fact that the surface of the copper sample exposed to organic solvent is covered only with a thin layer of Cu_2O formed in the air. On the other hand, in chloride solution, chloride ions readily adsorb on copper and CuCl is formed due to the corrosion reaction. Studies on benzotriazole[14–15] and adenine[16] have suggested that the reaction between the inhibitor molecule and $CuCl_2^-$ species in the diffusion layer can result in the precipitation of a protective cuprous inhibitor complex.

For these reasons inhibitor layers formed in aqueous chloride solution and in organic solvent have different structures (as observed by AFM) and exhibit different inhibiting properties. This could explain the difference in the inhibitor layer structure on the copper surface visualized by AFM.

Conclusions

Investigations performed in this work have shown that the inhibitor application method may determine the inhibition mechanism. When the two studied inhibitors, 4-methyl-1-phenyl imidazole (PMI) and 4-methyl-1-(*p*-tolyl) imidazole (TMI), were adsorbed on the metal surface from organic solvent they acted primarily as cathodic corrosion inhibitors. On the other hand, when they were dissolved in aqueous solution, both the anodic and cathodic reaction rates decreased.

Electrochemical impedance measurements have shown that these compounds have only slight effect on the properties of the surface film (R_f and C_f); however, a significant influence on the corrosion kinetics was observed through the increased charge transfer resistance.

AFM studies have also confirmed the differences in inhibition mechanism due to the application method. Each one of the experimental methods used in this work has confirmed that the studied imidazole compounds are much more efficient when dissolved in a chloride solution than used as a nanocoating.

List of symbols

b_a – anodic Tafel slope, mV dec^{-1}

b_c – cathodic Tafel slope, mV dec^{-1}

C_f – film capacitance, μF cm^{-2}

C_F – faradaic capacitance, μF cm^{-2}

C_{dl} – double layer capacitance, μF cm^{-2}

E_{corr} – corrosion potential, mV

IE – inhibiting efficiency, %

j_{corr} – corrosion current density, μA cm^{-2}

R_e – electrolyte resistance, Ω cm^2

R_f – film resistance, Ω cm^2

R_F – faradaic resistance, Ω cm^2

R_{ct} – charge transfer resistance, Ω cm^2

Z – impedance, Ω cm^2

α – constant phase element coefficient

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