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Electrochemical and molecular simulation studies on the corrosion inhibition of L-glutamine monolayers on an iron surface

ZHE ZHANG[1], SHENHAO CHEN[1,2]*, YUANYUAN FENG[3], YUNQIAO DING[1], JUANJUAN ZHOU[1] and HENGLEI JIA[1]

[1]*Department of Chemistry, Shandong University, Jinan 250100,* [2]*State Key Laboratory for Corrosion and Protection, Shenyang 110016 and* [3]*Department of Chemistry Qufu Normal University, Qufu 273165, P.R. China*

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Abstract: L-Glutamine was used to form monolayers for the inhibition of the corrosion of iron in 0.50 mol dm^{-3} H_2SO_4. The protection ability of the films was examined by electrochemical impedance spectroscopy. The mechanism of adsorption is discussed using quantum chemical calculations and molecular simulations. Scanning electron microscopy was applied to confirm the formation of L-glutamine monolayers and the inhibitive effect. The results indicate that the molecules of L-glutamine are able to form films on the surface of iron and longer immersion time of the iron electrode in the solution results in a stronger inhibition ability of the films. The films are formed spontaneously by the adsorption of L-glutamine with a specific affinity of its head-group to the iron surface, hence, the densely and ordered monolayers can be considered as self-assembled.

Keywords: L-glutamine; iron; corrosion; self-assembled monolayer; EIS.

INTRODUCTION

Self-assembled monolayers (SAMs) have been intensively studied in the past two decades because of their applications in corrosion prevention, metal ion sensors and biosensors.[1–4] SAMs are able to adsorb spontaneously on the metal surface and form compact and stable films which protect the metal from corrosion.[5] Many attempts have been made to enhance the resistance of iron and Cu against corrosion in a corrosive environment.[6–10] Iron is a widely used metal with extensive industrial application because of its interesting properties, such as electrical conductivity, malleability, ductility, *etc*. Hence, work aimed at investigating its corrosion mechanism is very important in order to prevent it from corrosion.

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* Corresponding author. E-mail: shchen@sdu.edu.cn

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Felhosi *et al.*[11] studied the kinetics of self-assembled monolayers formation on iron. Much work has been performed on the use alkanethiols and alkanamine SAMs on iron and stainless steel surfaces for corrosion protection.[12–13] However, a large number of the effective inhibitors are toxic, hence there has recently been a growing trend to study environment friendly inhibitors. L-Glutamine is an amino acid, just like a protein. It is the most abundant free amino acid in muscle tissue and it plays a principal role in protein metabolism and anti-catabolism. It is a kind of innocuous compound; however, few related literature on the adsorption of the amino-group in amides monolayers on iron surface have been reported.

In this work, L-glutamine monolayers were prepared on an iron surface. The structural formula of L-glutamine is shown in Fig. 1. Electrochemical impedance spectroscopy was performed to study the inhibition ability of the films in 0.50 mol dm^{-3} H_2SO_4. Scanning electron microscopy was used to examine the inhibitive effect of the films on the iron surface. Quantum chemical calculations and molecular simulations were used to discuss the adsorption mechanism and structure of the molecules on the iron surface.

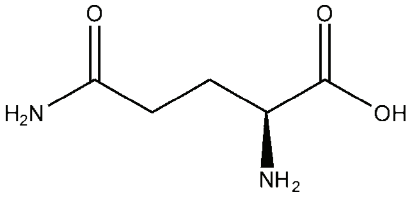

Fig. 1. Molecular structure of the L-glutamine.

EXPERIMENTAL

Electrochemical measurements

The reagents in this experiment were all analytical grade chemicals. L-Glutamine was dissolved in anhydrous ethanol to form a solution with the concentration of 1.0×10^{-4} mol dm^{-3}. The electrolyte solution was 0.50 mol dm^{-3} H_2SO_4, which was prepared with ultra pure water.

The electrochemical measurements were performed using a conventional three-electrode cell. The working electrode was made of an iron rod (Aldrich, 99.9 %, 2.0 mm diameter), which was embedded in epoxy resin, leaving only its cross-section exposed. The reference electrode was a saturated calomel electrode (SCE) and the counter electrodes were two platinum foils (1 cm×1.8 cm). Before each experiment, the exposed surface was polished with 1600# and 2000# emery paper until its surface became smooth and mirror-like bright, then it was cleaned with ultra pure water and anhydrous ethanol as quickly as possible and dried in a stream of pure nitrogen gas. Subsequently, the iron electrode was immersed in L-glutamine solution to form monolayers. The assembly time ranged from 0.50 to 38 h. The iron electrode was immersed in 0.50 mol dm^{-3} H_2SO_4 for 20 min for stabilization before each electrochemical impedance spectroscopy (EIS) test.

The EIS measurements were performed using a Zahner IM6 electrochemical workstation. The sinusoidal potential perturbation was 5 mV in amplitude and frequencies ranged from 60 kHz to 20 mHz. The whole measurement process was accomplished in a still electrolyte system at room temperature (25±1°C).

Scanning electron microscopy (SEM)

Samples for SEM experiments were iron sheets (8 mm×8 mm×1 mm). The polishing procedure was the same as that mentioned above. The immersion time was 4 h. A Jeol JSM-6700F field emission scanning electron microscope was used to observe the morphology of the iron sheets, including the bare iron sheet and the L-glutamine modified iron sheet after corrosion in 0.50 mol dm^{-3} H_2SO_4 for 2 h.

Quantum chemical calculations and molecular simulations

In order to investigate the adsorbate–surface interaction, theoretical calculations of the L-glutamine films on an iron surface were performed using *ab initio* quantum chemical calculations and molecular simulations of the molecular mechanics. The geometrical structures were optimized at the HF/6-311+G (*d,p*) basic levels and then the Natural Bond Orbital (NBO) method was used to analyze the natural atomic charge of the L-glutamine molecule.[14,15] These calculations were performed using the GAUSSIAN03 program passage. The interaction of the L-glutamine molecule with an iron surface was simulated using molecular dynamics simulation through the COMPASS force field. The molecular simulations were performed using the C2 package.[16]

RESULTS AND DISCUSSIONS

Electrochemical impedance spectroscopy

A lot of useful information about a metal corrosion process can be obtained through EIS measurements, such as the charge-transfer resistance, the polarization resistance, the double-layer capacitance and the pseudo-capacitance.[17] The Nyquist impedance spectra for the bare and L-glutamine-modified iron electrodes and the equivalent circuit used to analyze and fit the whole impedance spectra are represented in Fig. 2. In the circuit, R_s is the resistance of solution between the

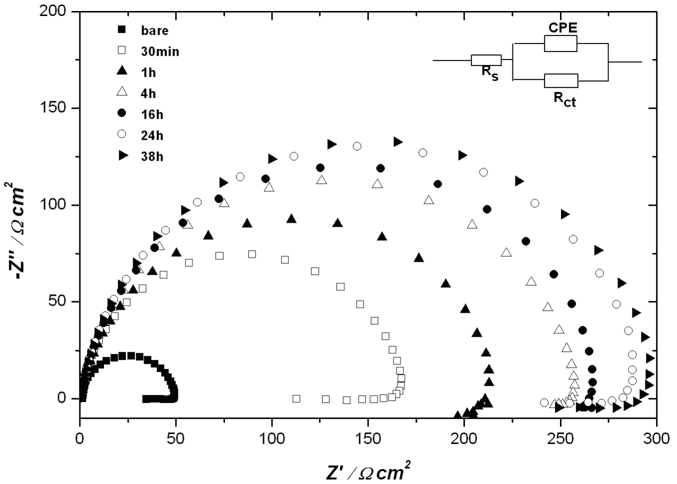

Fig. 2. Nyquist impedance spectra for the bare iron electrode and L-glutamine-modified iron electrodes in 0.50 mol dm^{-3} H_2SO_4 with increasing immersion time in 1.0×10^{-4} mol dm^{-3} L-glutamine and the equivalent circuit for fitting.

iron electrode and the reference electrode and R_{ct} is the charge-transfer resistance, corresponding to the corrosion reaction at the metal substrate/solution interface.[18] The double-layer usually behaves as a constant phase element (CPE) rather than a pure capacitor. The CPE is substituted for a pure capacitor so that it fits the impedance spectra better. The admittance and impedance of a CPE are, respectively, defined as:

$$Y_{\mathrm{CPE}} = Y_0 (j\omega)^n \text{ and } Z_{\mathrm{CPE}} = \frac{1}{Y_0}(j\omega)^{-n} \tag{1}$$

where Y_0 is the modulus, ω is the angular frequency and n is the phase. The depression degree of the impedance loops depend on the phase of the CPE.[19]

The protection efficiency was calculated using the following equation:

$$PE = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \tag{2}$$

where R_{ct} and R'_{ct} represent the charge-transfer resistance of bare electrode and L-glutamine-modified electrodes, respectively.

All impedance spectra exhibited a capacitive loop and all loops were not regular semicircles but depressed to some extent, which is defined by a dispersing effect and is concerned with the state of electrode surface.[20] The diameter of the semicircle represents the charge-transfer resistance. The bare iron electrode had a small charge transfer resistance, because iron reacts with hydrogen ions quickly in acidic solution. After modified with L-glutamine, the electrodes showed a larger charge-transfer resistance than that of the bare electrode, which means that the monolayers block the transfer of the electrons from the iron surface to the solution. By comparing the loops of iron electrode at different immersion time, it was shown that longer immersion times lead to larger loops and higher protection efficiency. It can be seen from Table I that the R_{ct} of the L-glutamine-modified iron electrode was larger than that of the bare iron, which indicates that L-glutamine monolayers were formed and the presence of the monolayers could effectively protect iron from corrosion. With longer immersion times, the L-glutamine-

TABLE I. Equivalent circuit parameters determined by fitting the impedance spectra in Fig. 2 and the calculated values of the protection efficiency (*PE*)

Self-assembly time, h	CPE		R_{ct} / Ω cm^2	*PE* / %
	Y_0 / 10^{-6} Ω^{-1} cm^{-2} s^n	*n*		
0	0.860	0.93	48.10	–
0.50	0.730	0.92	169.0	71.5
1.0	1.13	0.90	215.8	77.7
4.0	0.810	0.91	258.6	81.4
16	0.810	0.90	272.1	82.3
24	0.910	0.91	295.3	83.7
38	0.790	0.91	301.9	84.1

-modified iron electrodes had larger loops and, accordingly, the monolayer had higher protection abilities. It was also found that when the immersion time was prolonged after 4 h, the protection efficiency of L-glutamine did not increase as fast as during the first 4 h because the films became very packed after long immersion times. The maximal protection efficiency obtained in these experiments was approximately 84 %.

There are two controversial processes at the electrode surface, the adsorption and desorption of L-glutamine molecules. At the beginning of the immersion, more and more L-glutamine molecules adsorb on the iron surface. With increasing immersion time, the films become denser and more stable, the adsorption/desorption process attains equilibrium. This might be the reason that the increase of the PE was not so obvious after 4 h of immersion. After the films were formed, the electrode was rinsed with ethanol and ultra pure water and dried in a stream of nitrogen. Thus, only the chemisorbed L-glutamine molecules remained on the iron surface. The L-glutamine molecule can be adsorbed on the iron surface through lone pair electrons entering into the empty orbital of iron, hence, the monolayers formed on the iron surface could be considered as self-assembled.

SEM Analysis

SEM was applied to confirm that the self-assembled films on the iron surface can protect the metal from corrosion. The SEM surface morphologies of the bare and L-glutamine-modified iron sheets after corrosion for 2 h in 0.50 mol dm^{-3} H_2SO_4 solutions are shown in Fig. 3. It can be observed that there are distinct differences between the two microphotographs. The former one had suffered more severe corrosion than the latter one. The surface of the bare iron sheet was completely damaged, while the L-glutamine-modified iron sheet was not so severely damaged. This means the presence of L-glutamine films can effectively protect iron from corrosion.

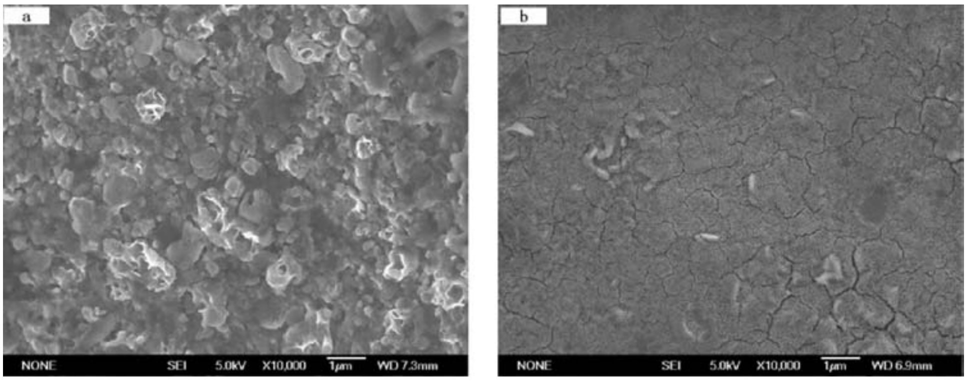

Fig. 3. SEM Images of iron electrodes after corrosion in 0.50 M H_2SO_4 for 2 h. Bare iron electrode (a); L-glutamine modified iron electrode (b).

Quantum chemical calculations and molecular simulations

The optimized structure of L-glutamine is shown in Fig. 4a. The Arabic numbers on the atoms are the natural charges obtained using the Natural Bond Orbital (NBO) analysis of the B3LYP method at 6-311+G (*d*,*p*) basic levels.[21,22] For comparison, the same calculation was performed for the *n*-hexylthiol molecule because alkanethiols can be intensely adsorbed on a metal surface.[23] The optimized structure of *n*-hexylthiol is shown in Fig. 4b. Comparing the two molecules, it can be seen that the N or O atoms in L-glutamine bear much more negative charges than the S atom in *n*-hexylthiol, which indicates the structure of the former is more preferable to interact with the iron surface than that of the latter. Two N atoms and two O atoms in the L-glutamine molecule cannot only interact with an iron surface through lone pair electrons entering into the empty 3*d* orbital of iron but also through the π-electrons in the molecule inserting into the empty 3*d* orbital.

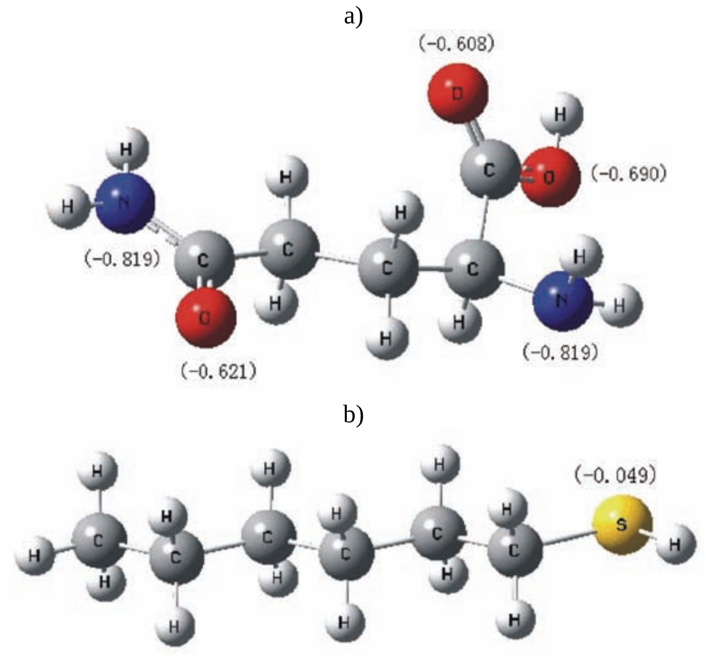

Fig. 4. Optimized structures of L-glutamine (a) and *n*-hexylthiol (b).

To verify the above prediction, a series of molecular dynamics simulations were performed in the next stage. Docking L-glutamine onto an optimized three-layer Fe (110) surface was the calculation model. An L-glutamine molecule was placed onto the surface according to five possible models and the five interaction configurations of L-glutamine with the Fe (110) surface were obtained by minimization using COMPASS force field. The minimization algorithm used by default is the Smart algorithm; it is a cascade of methods using successively steepest descent and conjugate gradient algorithms. As shown in Fig. 5, the models I, II, III and VI are the adsorption models of L-glutamine on an iron surface adsorbing through different N and O atoms; model V is adsorption by the simultaneous action of N and O atoms and the π-electrons with the metal surface.

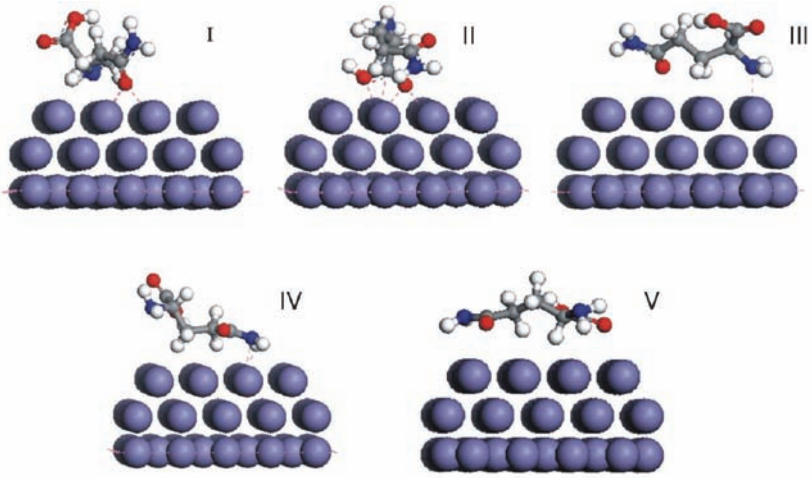

Fig. 5. Adsorption configurations of L-glutamine with a Fe (110) surface.

Based on the optimized configuration, the interaction energy of adsorption between L-glutamine and the iron surface was calculated using the following equation:

$$E_{\mathrm{interaction}} = E_{\mathrm{total}} - (E_{\mathrm{surface}} + E_{\mathrm{L-G}}) \qquad (3)$$

where E_{total} is the energy of surface adsorption by an L-glutamine molecule, E_{surface} is the energy of the bare iron surface, and $E_{\mathrm{L-G}}$ is the energy of an L-glutamine molecule. The values of $E_{\mathrm{interaction}}$ and E_{total} are listed in Table II, which shows that configuration V is the most stable adsorption structure of the five models, the next are configurations III and IV. Configurations I and II are unstable adsorption structures because the values of $E_{\mathrm{interaction}}$ are too positive. This verifies the above prediction and shows that L-glutamine can vary easily form monolayers on an iron surface and the possible adsorption structures are configuration III, VI and V.

TABLE II. Calculated interaction energy between L-glutamine and Fe for different adsorption configurations

Configuration	I	II	III	IV	V
$E_{\mathrm{interaction}}$ / kJ mol^{-1}	1.89	105.06	-216.12	-229.38	-246.95

CONCLUSIONS

With increasing immersion time of an iron electrode in an ethanolic L-glutamine solution, more molecules assembled on the iron surface. The highest inhibition efficiency of L-glutamine in 0.50 mol dm^{-3} H_2SO_4 was 84 %. Furthermore, SEM analysis showed that L-glutamine is able to adsorb on an iron surface and the formed monolayers can effectively protect iron against corrosion. Quantum chemical calculations and molecular simulations were able to explain the experimental results to some extent.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКА ИСПИТИВАЊА И МОЛЕКУЛСКЕ СИМУЛАЦИЈЕ МОНОСЛОЈЕВА ИНХИБИТОРА КОРОЗИЈЕ L-ГЛУТАМИНА НА ГВОЖЂУ

ZHE ZHANG[1], SHENHAO CHEN[1,2], YUANYUAN FENG[3], YUNQIAO DING[1], JUANJUAN ZHOU[1] и HENGLEI JIA[1]

[1]*Department of Chemistry, Shandong University, Jinan 250100,* [2]*State Key Laboratory for Corrosion and Protection, Shenyang 110016 и* [3]*Department of Chemistry, Qufu Normal University, Qufu 273165, P.R. China*

L-Глутамин у монослоју је коришћен као инхибитор корозије гвожђа у 0,50 mol dm^{-3} H_2SO_4. Заштитна моћ слоја је испитивана спектроскопијом електрохемијске импеданције (СЕИ). Механизам адсорпције је дискутован на основу квантно-механичких израчунавања и молекулских симулација. Помоћу скенирајуће електронске микроскопије потврђено је формирање монослојева L-глутамина и њихов инхибициони ефекат. Резултати указују на то да молекули L-глутамина могу да формирају филмове на површини гвожђа и да је инхибициони ефекат филма већи уколико је гвожђе дуже уроњено у раствор L-глутамина. Филмови се формирају спонтано адсорпцијом L-глутамина чије терминалне групе поседују специфичан афинитет према површини гвожђа, те се густо паковани монослојеви могу сматрати самоуређеним типом слојева.

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