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ORIGINAL PAPER

Arginine self-assembled monolayers against copper corrosion and synergistic effect of iodide ion

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Abstract Self-assembled monolayers (SAMs) of arginine (Arg) were formed on copper surface. The corrosion protection properties of the Arg SAMs were examined by electrochemical impedance spectroscopy and polarization techniques in 0.5 M HCl solution. The results show that Arg SAMs have limited protection effect. The protective efficiency increased with an increase of self-assembly time and reached maximum protection at 6 h. When iodide ion was added to the Arg-containing solution, the ability of the corrosion inhibition of the mixed SAMs improved significantly. The corrosion protection mechanism of Arg SAMs is discussed based on AM1 quantum-chemical calculations.

Keywords Copper · Self-assembled monolayers · Arginine · Iodide ion · Synergistic effect

1 Introduction

Self-assembled monolayers (SAMs) formed spontaneously by chemical adsorption and self-organization on the surface of the metal offer great flexibility for the control of surface structure and interfacial properties [1]. Substances with a long alkyl chain, which form dense and ordered monolayer on metal surface, can stop the corrosion of the base metal [2, 3]. Amino acid compounds are nontoxic, biodegradable, relatively cheap, and completely soluble in aqueous media. The number of publications about the corrosion inhibition effect of amino acids is increasing [4–10]. However, amino acid SAMs for controlling metal corrosion are seldom reported. Amino acids contain two functional groups of carboxyl and amino bonded to the same carbon atom. This is beneficial to their molecular modification and structural assembling. The formation and organization of functionalized amino acid on the metal surfaces is of considerable importance for the development of new assembled system for corrosion inhibition.

In this paper, we describe the study of the protection efficiency of arginine (Arg) self-assembled monolayers on copper surface in 0.5 M hydrochloric acid (HCl) solution at room temperature. The influence of iodide ions on the protection properties of Arg SAMs was also investigated in order to ascertain the specific mode (ionic or molecular) in which the compound exerts its inhibiting action. The adsorption mechanism of Arg on copper surface is elucidated by quantum-chemical calculations.

2 Experimental procedures

2.1 Chemicals

The reagents used in this experiment were all analytical-grade chemicals. HCl solution (0.5 M) was prepared by dilution of analytical-grade 36–38% HCl with deionized water. Arg (Yuanju Bio-Tech Co., Ltd., Shanghai, China) was dissolved in deionized water to form the different concentrations of aqueous solution. KI was dissolved in

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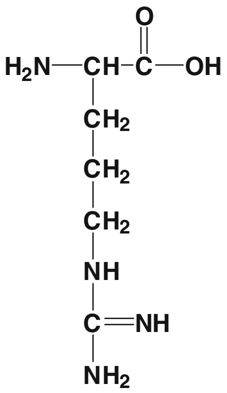
Fig. 1 Molecular structure of Arg



Arg aqueous solution to form Arg/KI mixed aqueous solution. The structure of Arg is shown in Fig. 1.

2.2 Formation of SAMs

Copper samples prepared from rectangular copper (99.9%) were embedded in epoxy resin so that only the cross section (0.4 cm^2) was exposed. The copper electrode was gradually polished with different grades of emery paper (#1, #3, and #6), then thoroughly rinsed with anhydrous ethanol and deionized water as soon as possible. The copper electrode was immersed in Arg solution or Arg/KI mixed solution immediately to form the Arg or Arg/KI SAMs film at room temperature, and then the electrode was rinsed with enough anhydrous ethanol and deionized water in order to get rid of the physically adsorbed Arg and KI molecules.

2.3 Apparatus

Electrochemical measurements were performed in a three-electrode cell using a PARC M273A potentiostat (EG&G) with a PC. A PARC M5210 frequency response analyzer was also used for electrochemical impedance spectroscopy (EIS) measurements. M352 and M398 software packages were used to obtain the polarization curves and electrochemical impedance spectra, respectively.

2.4 EIS and potentiodynamic curve measurements

The reference electrode was a saturated calomel electrode (SCE), and a platinum electrode was used as auxiliary electrode. The working electrode (WE) was the copper electrode covered with or without SAMs on its surface. All reported potential values are referred to SCE. After 0.5 h immersion, the measurements were carried out in 0.5 M HCl solution without deaeration or agitation. EIS experiments were performed at open-circuit potential over a frequency range from 0.02 Hz to 100 kHz. The sinusoidal potential perturbation was 5 mV in amplitude. Polarization studies were carried out in the potential range ±250 mV versus corrosion potential (E_{corr}) at scan rate of 1 mV s^{-1}.

2.5 Calculation method

Theoretical calculations were based on the restricted Hartree–Fock (RHF) level using semiempirical AM1 method in the MOPAC 7.0 program. All the calculations were carried out with the help of complete geometry optimization. Initial estimates of the geometry data were obtained from the Pcmodel 6.0 program, and subsequent AM1 calculations were done by using a Pentium personal computer.

3 Results and discussion

3.1 Electrochemical impedance measurements

3.1.1 Arg SAMs with different self-assembly time and concentrations

Figure 2 shows Nyquist plots of the naked electrode and the SAMs-modified electrodes which assemble in 10 mM Arg solution for different times, and Fig. 3 shows Nyquist plots of the naked electrode and the SAMs-modified electrodes which assemble in different concentrations of Arg for 6 h. As shown in Figs. 2 and 3, each of them has an obvious capacitive loop in high frequency and a straight line (Warburg impedance) in low frequency. The capacitive loop is attributed to the relaxation time constant of the charge-transfer resistance (R_{ct}) whose value is approximately equal to the diameter of the capacitive loop and the double-layer capacitance (C_{dl}) at the copper/electrolyte interface. The Warburg impedance reflects the anodic

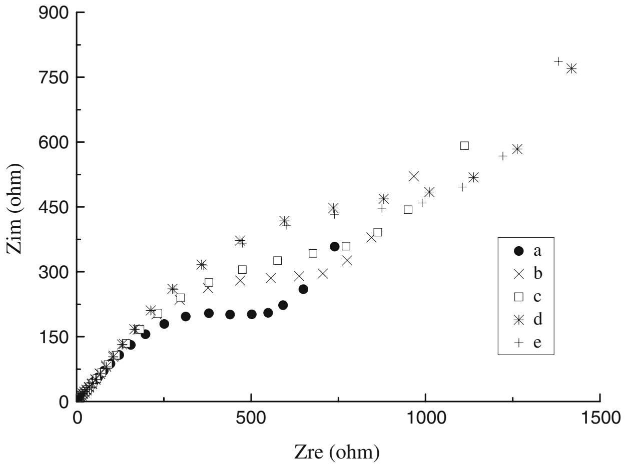


Fig. 2 Nyquist plots of the naked electrode and the copper electrode modified by SAMs immersed in 10 mM Arg solution for different times: (a) naked copper, (b) 2 h, (c) 4 h, (d) 6 h, and (e) 12 h

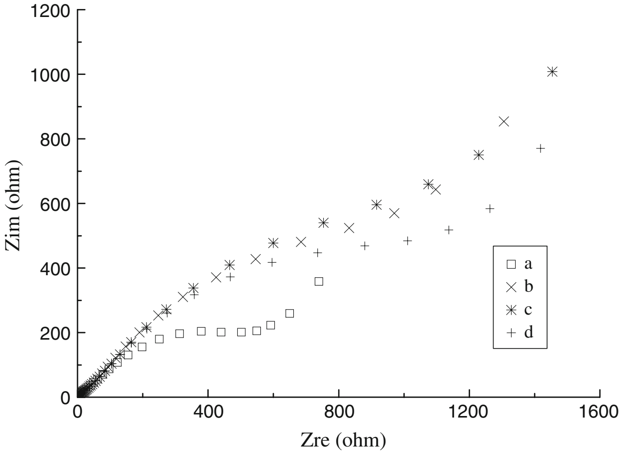


Fig. 3 Nyquist plots of the naked electrode and the copper electrode modified by SAMs immersed in different concentrations of Arg for 6 h: (a) naked copper, (b) 0.1 mM, (c) 1 mM, and (d) 10 mM

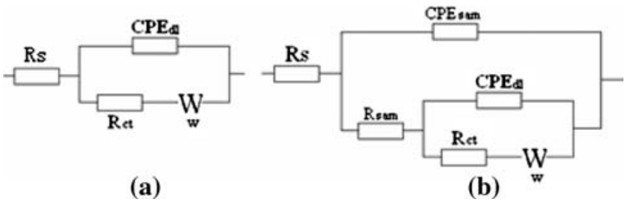


Fig. 4 Equivalent circuit model for the corrosion of copper: **a** naked electrode, and **b** the SAMs-covered electrode

diffusion process of soluble copper species ($CuCl_2^-$) from the surface of the electrode to the bulk solution and the cathodic diffusion process of dissolved oxygen from the bulk solution to the surface of the electrode. The plot of the naked electrode can be simulated by the equivalent circuit with the ZSIMPWIN software in Fig. 4a and the others by the equivalent circuit in Fig. 4b, where W stands for the Warburg impedance, R_s the solution resistance, R_{ct} the charge-transfer resistance, R_{sam} the transfer resistance of electrons or ion through the monolayers, which reflects the protective properties of the SAMs, and CPE_{sam} and CPE_{dl} represent the capacitance of the SAMs and the double layer capacitance, respectively. Admittance of a CPE is described as [11]:

$$Y_Q = Y_0(j\omega)^n, \tag{1}$$

where Q is a CPE, Y_0 the modulus, j the imaginary root, ω the angular frequency ($\omega = 2\pi f$, where f is the frequency in Hz) and n the exponential term of the admittance formula of CPE. The value of n is related to the surface roughness of the electrode [12, 13]. When n has a value of 0, 0.5, and 1, the impedance of the CPE would be that of a pure resistance, Warburg impedance, and a pure capacitor, respectively [14, 15]. The results are shown in Table 1, and the total polarization resistance R_p, which is simply the sum of R_{ct} and R_{sam}, can be used to calculate the corrosion rate [16, 17]. The protection efficiency (PE %) of copper corrosion can be calculated according the following formula [17]:

$$\text{PE\%} = \frac{R_p - R_p^0}{R_p} \times 100, \tag{2}$$

where R_p^0 is the total polarization resistance of the naked electrode and R_p is the total polarization resistance of the SAMs-covered electrode (the sum of R_{ct} and R_{sam}).

The protection efficiency (PE %) is shown in Table 1. It can be seen that the total polarization resistance R_p of the naked electrode has the lowest value. When the electrode surface is covered by Arg film, the value of R_p will increase. For self-assembly time of 2, 4, 6, and 12 h in 10 mM Arg solution, the protection efficiency (PE %) of the SAMs is 20%, 38%, 54% and 52%, respectively. When the self-assembly concentrations are 0.1, 1, and 10 mM for 6 h, the protection efficiency (PE %) of the SAMs are 54%, 63%, and 60%, respectively. The result shows that Arg SAMs have limited protection effect and cannot act as a

Table 1 Electrochemical impedance parameters in 0.5 M HCl for the copper electrode covered with SAMs

Immersion time (h)	SAMs type	Conc. (mM)	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	CPE_{dl} (μF cm^{-2})	n_1	R_{sam} (Ω cm^2)	CPE_{sam} (μF cm^{-2})	n_2	W Ω cm^2	PE %
Naked electrode		–	1.11	672	743	0.57	–	–	–	7.1×10^{-3}	–
2	Arg	10	2.35	810	546	0.62	28.7	69.8	0.79	5.0×10^{-3}	20
4	Arg	10	2.27	1052	630	0.60	30.2	50.1	0.82	4.2×10^{-3}	38
6	Arg	10	1.66	1413	519	0.61	38.2	37.4	0.84	3.5×10^{-3}	54
12	Arg	10	2.43	1359	504	0.61	36.5	36.6	0.83	3.4×10^{-3}	52
6	Arg	0.1	1.63	1651	779	0.60	28.0	42.9	0.84	3.0×10^{-3}	60
6	Arg	1.0	1.60	1799	730	0.59	29.0	40.1	0.84	2.3×10^{-3}	63
2	Arg/KI	5/5	4.72	4933	254	0.53	162	15.8	0.85	1.8×10^{-3}	87
2	KI	10	2.69	917	399	0.65	43.3	43.2	0.81	5.5×10^{-3}	30

practical inhibition method against copper corrosion. The film formed in 1 mM Arg solution for 6 h had the best protection effect.

3.1.2 Synergistic effect of iodide ion

Figure 5 shows Nyquist plots of the copper electrodes in 0.5 M HCl solution. The copper electrodes were self-assembled in aqueous solution containing 5 mM Arg and 5 mM KI for 2 h. The impedance spectra can be analyzed with the equivalent circuit in Fig. 4b and the obtained results are summarized in Table 1. The values of the protection efficiency (PE %) were estimated according to Eq. 2. The results show that the protection efficiency (PE %) of Arg/KI SAMs has improved markedly to 87% compared with the protection efficiency (PE %) of Arg SAMs or KI SAMs alone. Arg/KI SAMs have better inhibition effect than Arg SAMs because the adsorption of the amino acid can be enhanced in presence of halide ions [18, 19]. I^- ions adsorbed on the metal surface form interconnecting bridges between the copper surface and the positive center in Arg molecules, thus facilitating the adsorption process [14]. When iodide ion was added to the Arg-containing solution, the corrosion inhibition ability of the mixed SAMs improved significantly.

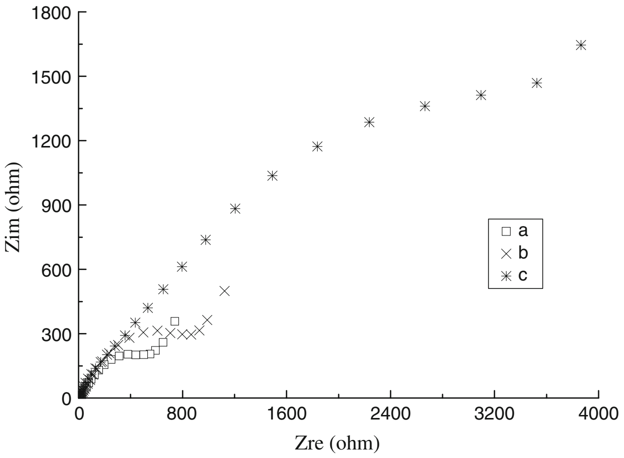


Fig. 5 Nyquist plots of the copper electrode self-assembled in the aqueous solution containing: (a) the naked copper; (b) 5 mM KI; (c) 5 mM Arg + 5 mM KI

3.2 Polarization curve measurements

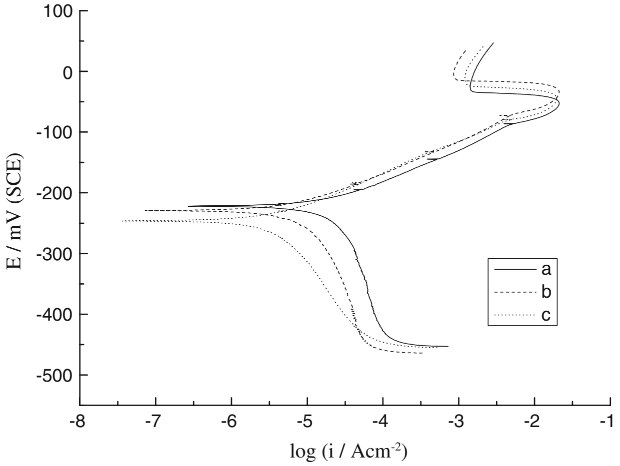


Fig. 6 Polarization curves measured in 0.5 M HCl. (a) The naked electrode; (b) covered with Arg SAMs (self-assembly in 1 mM Arg for 6 h); (c) covered with Arg/KI SAMs (self-assembly in 5 mM Arg and 5 mM KI for 2 h)

The polarization curves in 0.5 M HCl for the naked electrode and the copper electrodes covered with Arg, Arg/KI SAMs are shown in Fig. 6. The copper electrodes were self-assembled in the aqueous solution containing 1 mM Arg for 6 h or 5 mM Arg and 5 mM KI for 2 h. It is well known that the anodic reaction of copper is the dissolution of copper due to oxidation of Cu to Cu^+ and then Cu^+ to Cu^{2+} [20]:

$$Cu \rightarrow Cu^+ + e^- \quad (\text{fast}) \tag{3}$$

$$Cu^+ \rightarrow Cu^{2+} + e^- \quad (\text{slow}). \tag{4}$$

So the reaction mechanism of copper has two steps in 0.5 M HCl [12, 21]:

$$Cu^+ + Cl^- \rightarrow CuCl \tag{5}$$

$$CuCl + Cl^- \rightarrow CuCl_2^-. \tag{6}$$

The cathodic corrosion reaction is as follows:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O. \tag{7}$$

According to the reported studies [17, 22, 23], the total corrosion reaction of copper in acidic chloride solutions is as follows:

$$2Cu + 4H^+ + 4Cl^- + O_2 \rightarrow 2Cu^{2+} + 4Cl^- + 2H_2O. \tag{8}$$

From Fig. 6, one can see that cathodic currents of the copper electrodes covered with Arg and Arg/KI SAMs only reduced significantly, while the corrosion potential (E_{corr}) is negatively shifted. This implies that Arg or Arg/KI SAMs mainly function by retarding the oxygen diffusion (Eq. 7). The corrosion current density (i_{corr}) was calculated from the polarization curves by extrapolating the Tafel line to the corrosion potentials. Protection efficiency (PE %) was calculated from the polarization data as [24]:

$$PE\% = \frac{i_{coor} - i'_{corr}}{i_{corr}} \times 100, \tag{9}$$

where i'_{corr} and i_{coor} are, respectively, the corrosion current densities in the presence and absence of SAMs. The

Table 2 Electrochemical impedance parameters for copper self-assembled in the aqueous solution containing 1 mM Arg or 5 mM Arg + 5 mM KI

SAMs type	E_{corr} (mV)	i_{corr} (μA cm^{-2})	β_a (mV dec^{-1})	β_c (mV dec^{-1})	PE %
Naked electrode	−221.8	24.80	57.85	332.7	–
1 mM Arg	−229.1	9.439	56.84	259.4	62
Arg/KI	−246.3	3.802	54.70	161.6	85

electrochemical polarization parameters are listed in Table 2. From Table 2, i_{corr} of the naked electrode was 24.8 μA cm^{-2}. i_{corr} of the copper electrodes covered with Arg and Arg/KI SAMs was 9.439 μA cm^{-2} and 3.802 μA cm^{-2}, respectively. The protection efficiency (PE %) of Arg SAMs and Arg/KI SAMs was 62% and 85%, respectively. It is observed that the values of protection efficiency obtained are in close agreement with those determined from EIS measurements. This also indicates that KI can increase the adsorption of Arg and that the protection of Arg/KI SAMs against copper corrosion has improved significantly.

3.3 Quantum-chemical calculations and mechanism

It is understood that computational methods have a potential application towards the design and development of organic corrosion inhibitors in the corrosion field. In order to investigate the charge distribution of Arg, quantum-chemical calculations were performed by semiempirical AM1 method by using the MOPAC 7.0 packet program. In aqueous solutions, ionization of amino acids depends on pH. At the isoelectric pH (isoelectric point, pI), the molecules have no net charge, and the zwitterion structure is dominant. Below or above this isoelectric pH, the molecules are cationic or anionic, respectively [25]. The optimal structures of Arg calculated are shown in Fig. 7. Arg^0 is the structure of Arg at pH equal to pI. Arg$^+$ is the structure of Arg at pH < pI. Values of energy of the lowest unoccupied molecular orbital energies (LUMO, E_L), energy of the highest occupied molecular orbital (HOMO, E_H), dipole moments of molecules (μD), charge on oxygen (ηO), and charge on nitrogen (ηN) were calculated and the obtained results are presented in Table 3.

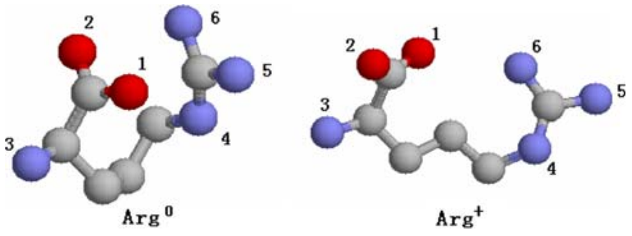


Fig. 7 Optimum conformations of Arg. Arg^0 is the structure of Arg at pH = pI, Arg$^+$ is the structure of Arg at pH < pI

It is confirmed that, the more negative the atomic partial charges of the adsorbed centre, the more easily the atom donates its electrons to the unoccupied orbital of the surface atoms of the metal [26]. In Table 3, the oxygen atomic charges are more negative than the nitrogen atomic charges, so the oxygen atoms more easily adsorbed on the copper surface. The value of pI for Arg is 10.76. The cationic Arg$^+$ is dominant at acidic or neutral pH. It is also found that there is a positive charge center (N4) in the Arg$^+$ molecule. The added I$^-$ ion can interact with the positive charge center in Arg$^+$. This enhances the adsorption of Arg$^+$ and improves the protective effect of Arg SAMs on the copper surface.

4 Conclusions

Arg can adsorb on the copper surface. Arg SAMs show limited inhibition against copper corrosion in 0.5 M HCl solution. The optimal time of self-assembly is 6 h, and the optimal concentration of self-assembly is 1 mM. However, in general, Arg SAMs cannot protect copper against corrosion practically. The addition of KI can promote the adsorption of Arg molecules and enhance the PE % of SAMs significantly. Quantum-chemical calculations show that the oxygen atoms in Arg molecule more easily adsorbed on the copper surface. The added I$^-$ ion can interact with the positive charge center in Arg$^+$.

Table 3 Quantum-chemical calculations data for Arg

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	Net atomic charges						Dipole moment/μD
			ηo		ηN				
			O 1	O 2	N 3	N 4	N 5	N 6	
Arg^0	−8.51576	−0.39259	−0.6294	−0.5484	−0.3240	−0.2846	−0.2901	−0.3168	6.348
Arg$^+$	−12.19556	−3.80104	−0.5192	−0.4844	0.0571	−0.3243	−0.3444	−0.3900	9.772

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