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# **Supporting Information**

#### 1. Experimental section

# 1.1 Configuration of electrolyte

The electrolytes used were 0.1 mM acetic acid solutions containing various corrosion inhibitors (Table S1). All reagents are analytical pure and purchased from Sinopharm Chemical Reagent Ltd.

Table S1 Electrolyte containing various corrosive media at 25 °C.

Code	Electrolyte
HAc	0.10 mM acetic acid (HAc)
HAc-C <sub>6</sub> H <sub>7</sub> N	0.10 mM acetic acid + 1 mM aniline ( $C_6H_7N$ )
$HAc-CH_4N_2S$	0.10 mM acetic acid + 1 mM thiourea ( $CH_4N_2S$ )
HAc-C <sub>4</sub> H <sub>9</sub> OH	0.10 mM acetic acid + 1 mM n-butanol ( $C_4H_9OH$ )

#### 1.2 Electrochemical system

The electrochemical system for testing consisted of a working electrode, a reference electrode, a counter electrode, and an electrolyte.

The platinum black electrode was used as the counter electrode, and the saturated calomel electrode (SCE) was used as the reference electrode. The potential of SCE at 25 °C was 0.228 V (relative to the standard hydrogen electrode).

The aluminum electrodes as working electrode with the working surface of 1 cm  $\times$  1 cm were cut from the radiator of high voltage direct current (HVDC) systems. The grade of aluminum was Model 3003, and composed of Si (0.57 wt%), Fe (0.63 wt%), Cu (0.14 wt%), Mn (1.27 wt%), Zn (0.09 wt%), Li (0.03 wt%), and Al (97.31 wt%). All of the surfaces other than the 1 cm<sup>2</sup> working surface were coated with epoxy resin. Before testing, the working electrode was polished with the emery paper of 500, 1000 mesh, and nano alumina powder with 50 nm diameter, washed, and cleaned in distilled water and anhydrous ethanol, and dried in a vacuum drying box.

## 1.3 Electrochemical tests

The potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests were conducted with a CHI660D electrochemical workstation.

The potential scanning rate of PDP was 1 mV s<sup>-1</sup>, and the potential range was 0.8 V (ranging from 0.4 V lower than the stable potential to 0.4 V higher than the stable potential). The corrosion potential and corrosion current density were obtained from the polarization curves with CHI660D software.

The corrosion characteristics of the aluminum surface were determined from the results of EIS analysis that was performed over a frequency range of  $10^{-1}$ – $10^{5}$  Hz, with an amplitude of 5 mV. The EIS raw data was fitted using Zsimpwin software to obtain the corresponding parameters.

The electrolyte temperature for all electrochemical tests was 25 °C. During testing, the electrochemical systems

were kept in a shielding box.

## 1.4 Physical characterization

Before the tests, the aluminum electrodes after immersion in HAc, HAc- $C_6H_7N$ , HAc- $C_4H_9OH$ , HAc- $CH_4N_2S$  at 25 °C for 5 days, were washed with distilled water and anhydrous ethanol, and then dried in a vacuum drying box at 25 °C to prevent oxidation.

The scanning electron microscopy (SEM) test instrument was a SU8010 ultrahigh-resolution field emission scanning electron microscope. The attenuated total reflectance infrared spectroscopy (ATR-IR) was carried out on Nicolet iS50 Fourier transform infrared (FT-IR) spectrometer at wave-numbers ranging of 4000–400 cm<sup>-1</sup>. Elemental and valence state analysis were determined using X-ray photoelectron spectroscopy (XPS) with Al Kα radiation source. The binding energy of C1s (284.8 eV) was set as a reference.

#### 1.5 Theoretical calculation

Density functional theory (DFT) with the exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) with the spin-polarization scheme was used for the electronic structure calculations. The core electrons were described by the projector augmented wave (PAW) method, and the valence orbitals were represented with a plane-wave basis set with a cutoff energy of 400 eV. Electronic energies were calculated using a self-consistent-field (SCF) with the tolerance of  $10^{-4}$  eV. By theoretical calculation, the optimization results of the exposed surface of aluminum, i.e. the exposed surface of aluminum with the lowest energy, was obtained. Al (001) had the lowest energy, so Al (001) was chosen as the substrate for the adsorption model. The surface was fully equilibrated prior to small organic molecule (C<sub>6</sub>H<sub>7</sub>N, C<sub>4</sub>H<sub>9</sub>OH, CH<sub>4</sub>N<sub>2</sub>S) adsorption except the bottom 2 layers, which were kept fixed during our simulation, until the total energy of the system converged to within  $10^{-3}$  eV. The Brillouin zone integration was treated with a 2×2×1 Monkhorst-Pack *k*-point mesh. All calculations were performed using the Vienna ab initio simulation package (VASP).

The interaction energies ( $\Delta E_{int}$ ) between organic molecule and the Al (001) surface were calculated using the following correlation:

$$\Delta E_{\rm int} = E_{\rm complex} - E_{\rm slab} - E_{\rm mol} \tag{S1}$$

where  $E_{\text{complex}}$ ,  $E_{\text{slab}}$  and  $E_{\text{mol}}$  are the total energies of the organic molecule-Al (001) complex, Al (001) slab system and the organic molecule, respectively.

#### 2. Supplementary figures and tables

For fitted data of PDP curves (Figure 1a, Table S2),  $E_{corr}$  was the corrosion potential,  $I_{corr}$  was the corrosion current density, and  $\beta_a$  and  $\beta_c$  were slope of anodic and cathodic polarization curve, respectively. Based on corrosion current density from PDP curves, the corrosion inhibition rates (*IE*) was calculated with Equation S2 [1].

$$IE\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100\%$$
(S2)

where  $I_{\text{corr (inh)}}$  were the corrosion current densities without and with inhibitors, respectively.

Table S2 Fitted data from PDP curves for aluminum corrosion in HAc, HAc-C<sub>6</sub>H<sub>7</sub>N, HAc-C<sub>4</sub>H<sub>9</sub>OH, HAc-CH<sub>4</sub>N<sub>2</sub>S at 25 °C for 5 days.

Electrolyte	Corrosion potential $E_{corr}(V)$	Corrosion current density $I_{corr}$ ( $\mu$ A cm <sup>-2</sup> )	Slope of anodic polarization curve $\beta_{a}$ (V dec <sup>-1</sup> )	Slope of cathodic polarization curve $\beta_{c}$ (V dec <sup>-1</sup> )	IE (%)	<i>IE</i> <sub>RT</sub> (%)
HAc	-1.305	1.347	0.491	-0.482		
HAc-C <sub>6</sub> H <sub>7</sub> N	-1.088	0.719	0.513	-0.459	46.62 %	67.59 %
HAc-C <sub>4</sub> H <sub>9</sub> OH	-1.102	0.680	0.526	-0.557	49.52 %	73.39 %
HAc-CH <sub>4</sub> N <sub>2</sub> S	-1.332	0.473	0.530	-0.513	64.88 %	77.41 %

The EIS curves, fitting data, and corresponding equivalent circuit of the aluminum electrodes are shown in Figure 1b, Table S3.  $R_s$  represented the solution resistance between the reference electrode Lujin capillary mouth and the aluminum electrode,  $C_f$  represented the capacitance of the oxide film on the surface of the aluminum electrode,  $R_f$  represented the resistance of the oxide film on the surface of the aluminum electrode, the surface of the surface of the aluminum electrode, and  $R_{dl}$  represented the surface of the aluminum sheet,  $R_{ct}$  represented the charge transfer resistance of the aluminum sheet, and W represented the liquid phase transfer impedance.

Through charge transfer resistance of EIS, the inhibition rate ( $IE_{RT}$ ) was also be calculated with Equation S3 [2, 3].

$$IE_{\rm RT}\% = \frac{R_{p(inh)} - R_{p}}{R_{p(inh)}} \times 100\%$$
(S3)

where  $R_{p (inh)}$  and  $R_{p}$  were the polarization transfer resistors with and without corrosion inhibitors, respectively, which was equivalent to the sum of  $R_{ct}$  and  $R_{f}$  [4].

Table S3 EIS fitting parameters of aluminum after immersion in HAc, HAc- $C_6H_7N$ , HAc- $C_4H_9OH$ , HAc- $CH_4N_2S$  at 25 °C for 5 days.

Electrolyte	$R_{\rm s}$	$C_{ m f}$	$R_{\rm ct}$	$C_{ m dl}$	$R_{ m f}$	W	R <sub>p</sub>
	$(k\Omega \ cm^2)$	$(nF cm^{-2})$	$(k\Omega \ cm^2)$	$(\mu F \text{ cm}^{-2})$	$(\Omega \text{ cm}^2)$	$(\mu\Omega~cm^{-2})$	$(k\Omega \ cm^2)$
HAc	0.345	13.946	2.944	1.926	2.251	10.220	2.946
HAc-C <sub>6</sub> H <sub>7</sub> N	1.151	23.571	9.084	16.430	8.333	10.741	9.092
HAc-C <sub>4</sub> H <sub>9</sub> OH	1.459	19.780	11.060	20.260	9.978	11.757	11.072
HAc-CH <sub>4</sub> N <sub>2</sub> S	1.853	19.520	13.030	11.570	10.570	14.980	13.041



Figure S1 XPS spectra for corrosion surfaces of aluminum after immersion in (a) HAc, (b) HAc-C<sub>6</sub>H<sub>7</sub>N, (c) HAc-CH<sub>4</sub>N<sub>2</sub>S, (d) HAc-C<sub>4</sub>H<sub>9</sub>OH at 25 °C for 5 days.



Figure S2 Adsorption model of the inhibitors on Al (001) surface, (a, b) aniline, (c, d) thiourea, (e, f) n-butanol.

Inhibitor	$E_{\text{complex}}(\text{eV})$	$E_{\rm mol}(eV)$	$\Delta E_{\rm int}(eV)$	$\Delta G_{ m ads} ({ m kJ} { m mol}^{-1})$
Aniline	-313.710	-88.129	-0.850	-81.940
Thiourea	-270.313	-44.615	-0.967	-93.219
N-butanol	-305.336	-79.903	-0.702	-67.673

Table S4 Interaction energy of the corrosion inhibitor molecules on Al (001) surface.

## References

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