

Research Article

Inhibition Effect of Benzohydrazide Derivatives on Corrosion Behaviour of Mild Steel in 1 M HCl

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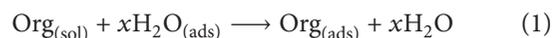
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The inhibiting effect of N-benzylidenebenzohydrazide (BBH) and N¹-(3-phenylallylidene) benzohydrazide (PABH) on the corrosion inhibition of mild steel in 1 M HCl solutions were determined by weight loss and electrochemical methods. These inhibitors were adsorbed on the surface according to Langmuir adsorption isotherm. Both BBH and PABH have offered inhibition efficiencies upto 97%. The free energy of activation for the corrosion process has suggested the participation of these molecules in the corrosion process. The adsorbed inhibitor complex has offered barrier protection and prevented the corrosion. The dissolution of iron was also retarded thereby they inhibited corrosion. The surface morphology analysis confirmed the presence of a film on the surface.

1. Introduction

Acidizing inhibitors are added to reduce base metal corrosion [1]. Most of the acid corrosion inhibitors are organic compounds such as those containing N, S, O, and aromatic rings. They adsorb on the metal surface. In most of the studies, the formation of donor-acceptor surface complexes between free or π electrons of an inhibitor and vacant d-orbital of metal atoms was proposed [2–4]. The adsorption of organic inhibitors at the metal/solution interface takes place through the replacement of water molecules by organic molecules according to the following process [5]:



where $\text{Org}_{(\text{sol})}$ and $\text{Org}_{(\text{ads})}$ are organic molecules in the solution and adsorbed on the steel surface, respectively, x is the number of water molecules replaced by the organic molecules. The Schiff base of cinnamaldehyde and p-anisidine gave 65% inhibition [6] in acid solutions at 55°C. Other Schiff base compounds have offered better inhibition than their amines and aldehydes [7–12]. Benzimidazole molecule and their derivatives have been exploited as corrosion inhibitors, as the molecule has two anchoring sites available for surface bonding which are the nitrogen atom

with its lonely sp^2 electron pair and the aromatic rings [13–16]. Triazoles, substituted triazoles adsorb on steel surfaces and inhibit corrosion [17–19]. Substituted thioamides were found to offer inhibition by forming Fe-inhibitor complex on the surface [20]. The search for environmental friendly corrosion inhibitor has resulted in the development of triazole derivatives [21]. The inhibition action of hydrazone derivatives was performed via adsorption on the surface obeying Frumkin adsorption isotherm [22].

In this paper, inhibitive action of BBH and PABH compounds on mild steel corrosion in 1 M HCl was studied using weight loss study and electrochemical techniques. The effect of temperature on the corrosion behaviour of mild steel in 1 M HCl with optimum concentration of inhibitor was studied in the temperature ranging 303–383 K.

2. Experimental Details

Mild steel coupons composed of 0.760% C, 0.019% Mn, 0.050% Cr, 0.026% Si, 0.012% P, 0.023% Al, 0.135% Cu, 0.050% Ni, and remainder being iron were used. Mild steel, strips coated with lacquer with an exposed area of 1 cm^2 were used. BBH and PABH inhibitors were newly synthesized by condensation of benzohydrazide with appropriate aldehydes. These compounds were characterized through their spectral

TABLE 1: Names and structural formulae of compounds benzohydrazide derivatives.

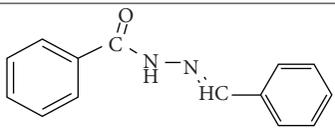
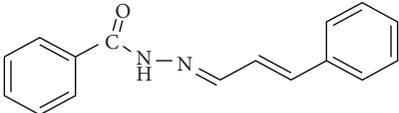
Compound	Structure	Name and abbreviation
1		N'-benzylidene benzohydrazide (BBH)
2		N'-(3-phenylallylidene) benzohydrazide (PABH)

TABLE 2: Corrosion parameters derived from weight loss measurements in 1 M HCl containing N'-benzylidenebenzohydrazide (BBH) at 303 K.

C (mM)	Corrosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (%)
0.00	332.28	—	—
0.46	37.56	0.89	88.69
0.89	21.05	0.93	93.66
1.34	16.09	0.95	95.15
1.78	11.05	0.96	96.52
2.23	8.87	0.97	97.32

TABLE 3: Corrosion parameters derived from weight loss measurements in 1 M HCl containing PABH at 303 K.

C (mM)	Corrosion rate (mmpy)	Surface coverage (θ)	IE (%)
0.00	332.28	—	—
0.40	41.27	0.88	87.57
0.80	32.76	0.90	90.24
1.20	26.41	0.92	92.04
1.60	18.16	0.94	94.53
2.00	7.84	0.97	97.43

TABLE 4: Effect of 2.23 mM of BBH and 2.00 mM of PABH on corrosion in 1 M HCl at different temperatures (weight loss method)—1 hour immersion.

Temp. (K)	Corrosion rate (mmpy)			IE (%)	
	Blank	BBH	PABH	BBH	PABH
303	644.55	79.68	71.88	87.6	88.84
323	768.38	188.69	184.69	75.45	76.03
343	935.25	364.13	349.39	61.06	62.64
363	1222.85	648.36	581.21	49.43	52.47
383	1551.69	1008.44	935.51	34.97	38.54

data. Their purity was confirmed by TLC. Table 1 presents the structural formulae of these compounds.

A conventional three-electrode cell containing platinum foil as counter electrode, saturated calomel electrode (SCE) provided with the Luggin capillary as reference electrode, and a mild steel specimen as working electrode were used.

Experiments were performed using EG & G Electrochemical analyzer (model 6310) at 303 K. Electrochemical impedance spectroscopy measurements were carried out between 100 kHz–10 mHz frequency range at steady open circuit potential with an amplitude of 10 mV. The protective film formed on the surface of the mild steel specimens was investigated by SEM.

3. Results and Discussion

3.1. Weight Loss Studies. Corrosion inhibition efficiencies (%) offered by N'-benzylidenebenzohydrazide at 303 K after 3 hours immersion are given in Table 2. IE % was increased with increase of concentration BBH. Table 3 presents the % IE efficiency offered by N'-(3-phenylallylidene) benzohydrazide. 2.00 mM concentration of PABH has offered 97.43% IE. Corrosion inhibition studies were carried out for different temperatures after immersing the steel specimens for an hour. At different temperature studies, BBH and PABH have offered good corrosion inhibition. However, the inhibition efficiencies were decreased with rise in temperatures (Table 4). High inhibition efficiency of these compounds were attributed to the presence of extensively delocalized π electrons of the phenyl rings, planarity and the presence of lone pair of electrons on N atoms, which favored greater adsorption of BBH and PABH on the metal surface at 303 K [23].

3.2. Electrochemical Methods. Polarization experiments were studied in 1 M HCl solution containing different concentrations of BBH and PABH (Figures 1 and 2). The linear segments of the anodic and cathodic polarization curves were extrapolated to the corrosion potentials to calculate corrosion currents. The Tafel slopes were determined from Tafel region of current-potential curves. The corrosion current densities were calculated by extrapolation of linear parts of these curves to corresponding corrosion potentials. The electrochemical parameters that is, corrosion potential (E_{corr}) anodic (b_a) and cathodic (b_c) Tafel slopes, corrosion current densities (i_{corr}) and inhibition efficiencies (IE%) determined from polarization curves are presented in Tables 5 and 6. In both the solutions, corrosion potentials became nobler. It can be seen from Tables 5 and 6 that, although E_{corr} and b_c values are nearly remained the same, b_c values of PABH shifted to lower values as inhibitor concentration

TABLE 5: Electrochemical parameters derived from potentiodynamic polarization curves for mild steel in 1 M HCl containing BBH at 303 K.

C (mM)	E_{corr} (mV versus (SCE))	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	I_{corr} (mA/cm ²)	IE (%)
0.00	-468	111	55	1.597	—
0.45	-498	107	72	0.212	86.17
0.89	-494	143	65	0.141	91.16
1.34	-504	89	82	0.966	93.95
1.78	-478	125	81	0.899	94.37
2.23	-477	128	64	0.688	95.69

TABLE 6: Electrochemical parameters derived from potentiodynamic polarization curves for mild steel in 1 M HCl containing PABH at 303 K.

C (mM)	E_{corr} (mV versus (SCE))	b_a (mV dec ⁻¹)	b_c (mV dec ⁻¹)	I_{corr} (mA/cm ²)	IE (%)
0.00	-468	111	55	1.597	—
0.40	-484	108	86	0.296	87.10
0.80	-482	120	93	0.159	89.24
1.20	-474	75	70	0.150	90.38
1.60	-450	70	95	0.136	91.57
2.00	-486	66	64	0.108	93.23

TABLE 7: Electrochemical parameters derived from Nyquist diagrams for mild steel in 1 M HCl containing BBH at 303 K.

C (mM)	R_{ct} (Ωcm^2)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE (%)
0.00	20	492.00	—
0.45	167	83.43	88
0.89	311	68.51	93
1.34	708	41.02	97
1.78	1102	24.16	98
2.23	1570	15.58	98

TABLE 8: Electrochemical parameters derived from Nyquist diagrams for mild steel in 1 M HCl containing PABH at 303 K.

C (mM)	R_{ct} (Ωcm^2)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE (%)
0.00	20	492.00	—
0.40	135	92.12	85
0.80	191	74.57	89
1.20	341	47.64	94
1.60	733	35.02	97
2.00	1108	21.08	98

is increased. Corrosion current densities decreased with increase between increase inhibitor concentrations. Corrosion inhibition increased upto 95% for BBH and 93% for PABH, respectively.

The Nyquist plots of mild steel obtained in 1 M HCl solution in the absence and presence of various concentrations of inhibitors and the data obtained are given in Figures 3 and 4. The related electrochemical parameters were calculated and are shown in Tables 7 and 8 at open circuit potential in presence and absence of different concentrations of BBH and PABH (Figures 3 and 4). Single distorted semicircles were

observed in Nyquist plots suggesting a simple R - C circuit. Increase the BBH and PABH concentrations decreased the double layer capacitance values (Tables 7 and 8). In inhibitor free solution the observed capacitance values $492 \mu\text{F cm}^{-2}$ was due to the pseudocapacitance. This capacitance would have been due to the adsorption of corrosion products on the surface of steel. Higher charge transfer resistances indicate the decreases in corrosion current densities. The percentage of inhibition efficiencies increased with BBH and PABH concentrations. The values of double layer capacitance (C_{dl}) were decreased and the charge transfer resistance (R_{ct}) increased with inhibitor concentration. The appearance of depressed semicircle is due to high frequency dispersion [24] or due to surface heterogeneity or corrosion products covering the surface at random sites [25, 26]. Both the electrochemical methods offered nearly same % IE values for both inhibitors.

3.3. Surface Examination. The surface morphologies of iron after 3 h immersion in the solution containing inhibitor and inhibitor free conditions are shown. A polished mild steel surface (Figure 5(a)) became covered with corrosion products at selected sites (Figure 5(b)) in 1 M HCl solutions. Smooth surfaces were seen for mild steel specimens after immersion in 1 M HCl solutions containing inhibitors as shown in Figures 5(c) and 5(d).

3.4. Adsorption Isotherms. BBH and PABH molecules have adsorbed on the mild steel surface due to Vander Waals forces. The presence of extensively delocalized π electrons of the phenyl rings and presence of lone pair of electrons on N-atoms have favoured greater adsorption [26]. Adsorptions of these organic molecules have displaced the water molecules from the metal surface. The interaction between the organic

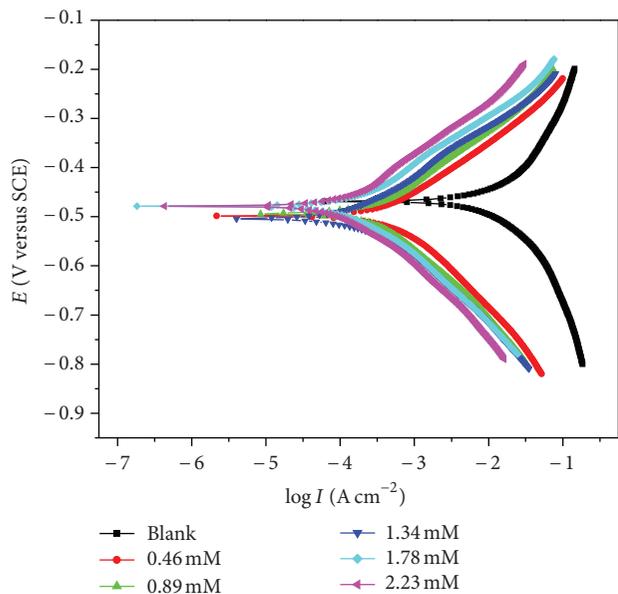


FIGURE 1: Polarization curves for mild steel in 1 M HCl with different concentrations of BBH.

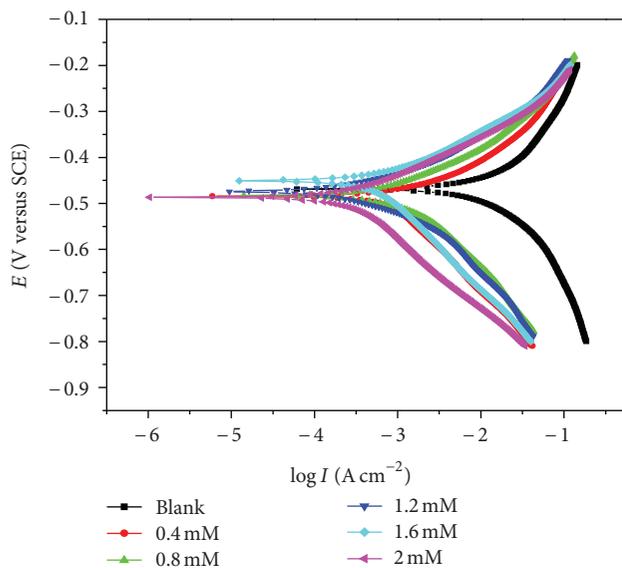


FIGURE 2: Polarization curves for mild steel in 1 M HCl solution without and with PABH.

molecules and the metal surfaces are obtained from various isotherms. Percentage inhibition efficiency was obtained from weight loss measurements as surface coverage (θ). According to the Langmuir adsorption isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} = C, \quad (2)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process. Figure 6 presents the plot of C/θ versus C for both the inhibitors. A straight line fit with a correlation

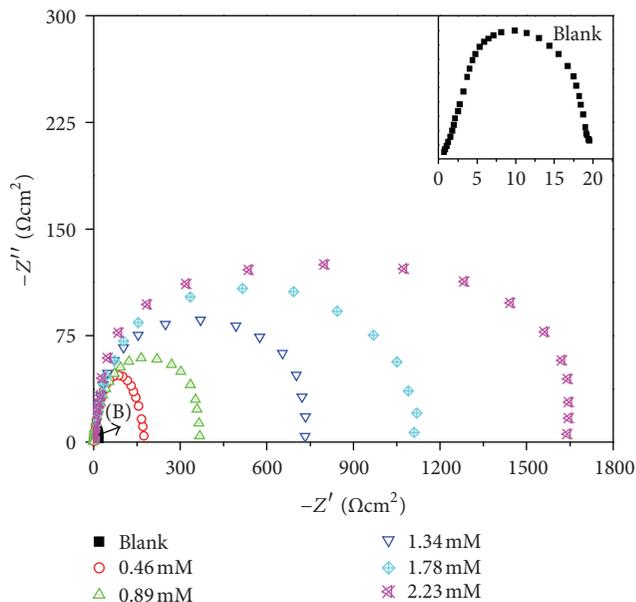


FIGURE 3: Nyquist diagrams for mild steel in 1 M HCl with different concentration of BBH.

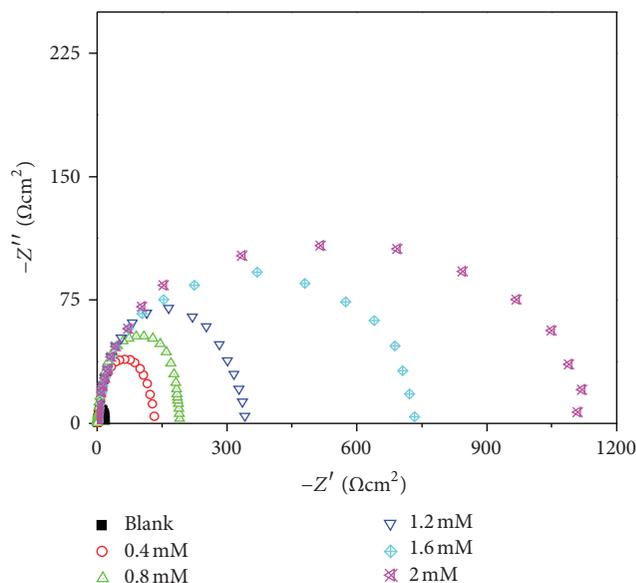


FIGURE 4: Nyquist diagrams for mild steel in 1 M HCl with different concentration of PABH.

of 0.999 suggests the adsorption obeys Langmuir adsorption isotherm. Using K_{ads} value, (ΔG_{ads}^0) was calculated:

$$\Delta G_{\text{ads}}^0 = -RT \ln(55.5 K_{\text{ads}}), \quad (3)$$

where R is the gas constant and T is the absolute temperature. The value of 55.5 is the concentration of water in solution. The values of ΔG_{ads}^0 were -32.12 and -34.56 kJ/mol for BBH and PABH, respectively. The negative value of ΔG_{ads}^0 suggests the chemisorptions of these inhibitors. This is due to electrostatic interactions between the charged molecules and the metal. The ΔG_{ads}^0 values more than -40 kJ/mole involve

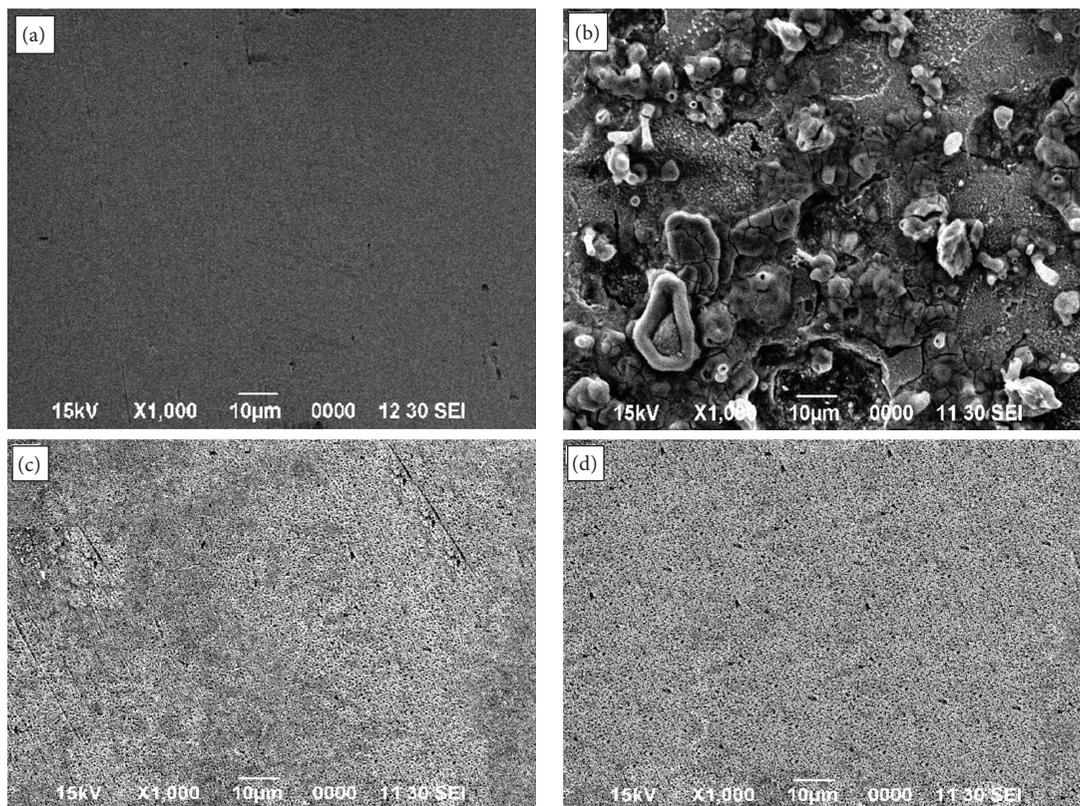


FIGURE 5: SEM photographs for mild steel (a) before immersion, (b) after immersion in 1 M HCl, (c) after immersion in 1 M HCl with 2.23 mM BBH, (d) after immersion in 1 M HCl with 2.00 mM PABH.

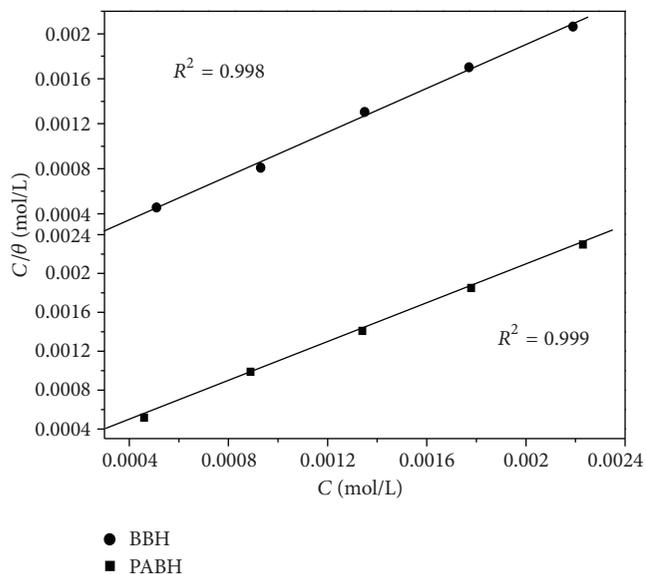
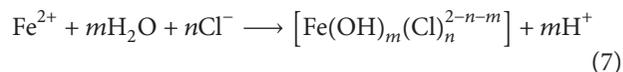
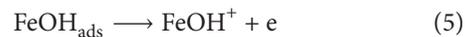
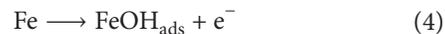


FIGURE 6: Langmuir adsorption isotherm plots for mild steel in (a) 1 M HCl containing BBH and (b) 1 M HCl containing PABH.

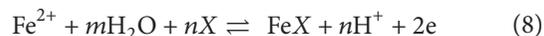
charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [27, 28]. The presence of various electrons donating groups in the inhibitor molecules and delocalized aromatic ring may also provide electrostatic adsorption.

The free energy of activation for the corrosion process was 11.23 kJ/mole which was raised to 29.26 kJ/mole by 2.23 mM of BBH and to 28.35 kJ/mole by 2.00 mM of PABH. This increase in the free energy of activation for corrosion suggests that corrosion reaction is hindered. The adsorption of these molecules led to the formation of a physical barrier which reduced the metal reactivity in the electrochemical reactions of corrosion.

3.5. Mechanism of Inhibition. In chloride solutions [29], the dissolution of iron takes place as



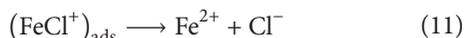
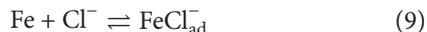
The overall reaction is



The organic inhibitor molecules (BBH and PABH) may exist either as protonated using lone pair of electrons from -NH

group or as a neutral molecule. This molecule can interact with $[\text{Fe}(\text{OH})_m(\text{Cl})_n]^{2-n-m}$ intermediate to form a surface complex containing inhibitor.

In hydrochloric acid solutions without inhibitor, chloride ions may also adsorb on the electrode to form chlorocomplex [30] as suggested



In hydrochloric acid solutions with inhibitors,



4. Conclusions

The results showed that, BBH and PABH compounds offer corrosion inhibition for mild steel in 1 M HCl solution. These compounds spontaneously chemisorbed obeying Langmuir isotherm. The free energy of activation values for corrosion process was suggested that the compounds participated in the corrosion process. The adsorbed chloro-inhibitor complex has offered better barrier protection to steel and thereby reduced corrosion. The positively charged complex was prevented; the formation of protons and retarded hydrogen evolution reaction. Surface morphology observations revealed the formation of a protective film.

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