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The Effects of Organic Compounds on Inhibition of Hydrogen **The Effects of Organic Compounds on Inhibition of Hydrogen** Permeation Through a Mild Steel Membrane **Permeation Through a Mild Steel Membrane**

H. A. Duarte,t D. M. See, B. N. Popov,** and R. E. White** **H. A. Duarte,* D. M. See, B. N. Popov,** and R. E. White****

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ABSTRACT ABSTRACT

The effectiveness of 5-(4-pyridyl)-2,7-nonadiene, and 1 phenyl-2-propyn-ol (PP) on inhibition of the hydrogen evolution reaction on a 1010 steel membrane and on the degree of hydrogen ingress into the membrane was determined
Hydrogen evolution rates and permeation currents were monitored as a function of time at different applied pot ed by 98 and 95%, respectively. lution reaction on a 1010 steel membrane and on the degree of hydrogen ingress into the membrane was determined. Hydrogen evolution rates and permeation currents were monitored as a function of time at different applied potentials. In the presence of 0.5 g/liter PP in the electrolyte, the hydrogen discharge and permeation current density were inhibited by 98 and 95%, respectively.

Introduction **Introduction**

Hydrogen can cause embrittlement of metals and alloys $\frac{1000}{60}$ during electroplating, cathodic protection, and corrosion assumed of metals.1-4 Various method have been proposed to decrease hydrogen embrittlement.⁵⁻⁹ However, it is usually $\mathcal{L}_{\text{the step}}$ impossible to reduce hydrogenation of metals and alloys to $\frac{d\ln x}{d\ln x}$ a level that eliminates the possibility of hydrogen cracking. According to our earlier studies, $10-18$ an alloy surface was v modification with underpotentially deposited metals (Zn, Bi, Pb) or deposited Zn or Bi inhibits the hydrogen dis-
charge reaction and reduces drastically the degree of drastically hydrogen ingress in the substrate. hydrogen ingress in the substrate. of metals.1 - ⁴ Various method have been proposed to decrease hydrogen embrittlement.⁵⁻⁹ However, it is usually a level that eliminates the possibility of hydrogen cracking. According to our earlier studies,¹⁰⁻¹⁸ an alloy surface modification with underpotentially deposited metals (Zn, Bi, Pb) or deposited Zn or Bi inhibits the hydrogen discharge reaction and reduces drastically the degree of

Corrosion inhibitors were also used to decrease the hy-Corrosion inhibitors were also used to decrease the hydrogen permeation and embrittlement effects.¹⁹⁻²² Martin²³ he can found that all three states of H in steels, mobile, reversibly $\frac{\text{the cut}}{\text{electron}}$ trapped, and irreversibly trapped were minimized in electroly quantity when inhibitors were used to mitigate corrosion. According to Wilhelm *et al.*²⁴ diamines with long carbon ping sit chains were most effective in reducing the corrosion rate $\frac{ap^{\text{pure}}}{\text{norm}}$ and hydrogen adsorption.

and hydrogen adsorption.
The objective of this study was to investigate the effect $\frac{W_N}{f_N}$ of two organic compounds 1-phenyl-2-propyn-1-ol (PP) and 5-(4-pyridyl)-2,7-nonadiene (PN) on the hydrogen at const permeation through a mild steel membrane. permeation through a mild steel membrane. and 5-(4-pyridyl)-2,7-nonadiene (PN) on the hydrogen

Experimental **Experimental**

The Devanathan-Stachurski permeation technique^{25,26} refilm
was used to investigate the rate of hydrogen permeation sole of completion through a 1010 steel with an area of approximately 0.4 cm² $\frac{\text{kinetic}}{\text{kinetic}}$ with thickness of 0.03 cm. The experiments were carried $\frac{\text{KilleUC}}{0.5 \text{MHz}}$ out in a system with two compartments, separated by a $\frac{0.5 \text{MHz}}{0.5 \text{MHz}}}$ bipolar membrane made of 1010 steel. Prior to the experi-bipolar membrane made of 1010 steel. Prior to the experiment, the membrane was prepared by polishing with $\frac{overpoint}{\text{on the }c}$ 0.5 μ m high purity alumina powder and cleaning in an $\frac{0.5}{10}$ in the C ultrasonic cleaning bath. Just prior to placing the mem-
brane in the permeation cell, it was etched for 20 s in a membra
methanol solution containing 1% H_2SO_4 , rinsed with ditions deionized water; and then dried in the air. deionized water, and then dried in the air. The Devanathan-Stachurski permeation technique 25,26 out in a system with two compartments, separated by a ultrasonic cleaning bath. Just prior to placing the membrane in the permeation cell, it was etched for 20 s in a methanol solution containing 1% H_2SO_4 , rinsed with

The electrolyte on the cathodic side of the cell was 0.5 M The electrolyte on the cathodic side of the cell was 0.5 *M* HC1. The rate of hydrogen permeation through the alloy in HC1. The rate of hydrogen permeation through the alloy in the absence and presence of 0.5 g/liter of PN or PP was the absence and presence of 0.5 g/liter of PN or PP was recorded continuously as a function of time. The electrolyte on the anodic side of the cell was $0.2 \text{ } M$ NaOH. To (iii) for keep electrolyte impurities at the lowest possible level, the memb solutions for the anodic and cathodic compartments were pre-electrolyzed at least 24 h in a separate electrolytic cell

prior to introduction into the compartment. The potential

of the "diffusion side" of the membrane (the side from
 $\frac{j_t - j_o}{j_x - j_o} = 1 - \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{$ which the hydrogen emerged) was set at a value that cor-
responded to a practically zero concentration of the $\frac{1}{10}$ absorbed atomic hydrogen on the surface.²⁶ This condition sity, j_x was maintained by the instantaneous ionization of all density, hydrogen atoms that diffused through the membrane and $\frac{tD/L^2}{dt}$, where emerged on the diffusion side. emerged on the diffusion side. pre-electrolyzed at least 24 h in a separate electrolytic cell prior to introduction into the compartment. The potential which the hydrogen emerged) was set at a value that corwas maintained by the instantaneous ionization of all hydrogen atoms that diffused through the membrane and

To avoid passivation or dissolution of the metal, the To avoid passivation or dissolution of the metal, the anodic side of the steel membrane was always electroplat-anodic side of the steel membrane was always electroplated with a thin layer (0.15 to 0.2 µm) of palladium. It was
assumed in this work that this thin film of palladium would not affect the permeation rate of hydrogen through would not affect the permeation rate of hydrogen through the steel membrane because it is well known that hydro-the steel membrane because it is well known that hydrogen diffuses rapidly through palladium. The deposition was carried out in an electrolyte containing $2\,\times\,10^{-6}\,$ M sodium tetranitropalladium $[Na_2Pd(NO_2)_4]$ using a current density of 200 $\mu A/cm^2$ for 4 h. Then, the electrolyte was drained off, and the compartment was washed with deionized water and filled with 0.2 M NaOH. The solution was ized water and filled with 0.2 M NaOH. The solution was kept at —0.3 V vs. Hg/HgO reference electrode until the kept at -0.3 V *vs.* Hg/HgO reference electrode until the background current was reduced below $0.03 \mu A/cm^2$. Then the cathodic compartment was filled with a supporting the cathodic compartment was filled with a supporting electrolyte containing 0.5 M HC1. The membrane was then electrolyte containing 0.5 *M* HC1. The membrane was then saturated with hydrogen to fill possible irreversible trap- ping sites in the membrane by keeping the cathodic side ping sites in the membrane by keeping the cathodic side applied potential of —0.8 V vs. SCE until the measured applied potential of -0.8 V *vs.* SCE until the measured permeation current was constant. Prepurified nitrogen was bubbled through both compartments to keep them was bubbled through both compartments to keep them free of dissolved oxygen. All experiments were carried out free of dissolved oxygen. All experiments were carried out at constant volume, inhibitor concentration, temperature, pressure, and substrate surface area. assumed in this work that this thin film of palladium was carried out in an electrolyte containing 2×10^{-6} *M* sodium tetranitropalladium $[Na_2Pd(NO_2)_4]$ using a current saturated with hydrogen to fill possible irreversible trappermeation current was constant. Prepurified nitrogen pressure, and substrate surface area.

Results and Discussion **Results and Discussion**

Permeation experiments were performed to clarify the Permeation experiments were performed to clarify the role of organic inhibitors (PP and PN) on hydrogen entry
kinetics in acidic media. To determine the hydrogen entry kinetics into C-1010 steel, experiments were carried out in 0.5 M HC1 to measure the cathodic current density and the permeation current density as a function of the applied permeation current density as a function of the applied overpotential. In these experiments, the alloy membrane on the cathodic site of the cell was polarized potentiostat-on the cathodic site of the cell was polarized potentiostatically. The hydrogen permeation transient into a bipolar membrane in a diffusion mode can be presented by the fol-membrane in a diffusion mode can be presented by the following equations obtained for two typical boundary con- ditions: (i) for the case where the hydrogen concentration ditions: *(i)* for the case where the hydrogen concentration at the entry side of the membrane is constant²⁷ role of organic inhibitors (PP and PN) on hydrogen entry 0.5 *M* HC1 to measure the cathodic current density and the overpotential. In these experiments, the alloy membrane ically. The hydrogen permeation transient into a bipolar lowing equations obtained for two typical boundary con-

$$
\frac{j_{\rm t}-j_{\rm o}}{j_{\rm x}-j_{\rm o}}=1+2\sum_{n=1}^{\infty}(-1)^{n}e^{-n^{2}\pi^{2}\tau}
$$
 [1]

(ii) for the case where the flux of the hydrogen entering the *(ii)* for the case where the flux of the hydrogen entering the m embrane is constant²⁸

$$
\frac{j_{\rm t}-j_{\rm o}}{j_{\rm x}-j_{\rm o}}=1-\frac{4}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^n}{(2n+1)}e^{\frac{-(2n+1)^2\pi^2\tau}{4}}\qquad \qquad [2]
$$

where j_t is the transient hydrogen permeation current density, f. is the steady-state hydrogen permeation current sity, *j,* is the steady-state hydrogen permeation current density, j_0 is the initial hydrogen current density, and $\tau =$ tD/L2, where t is time, L is the membrane thickness, and D *tD/L2 ,* where *t* is time, *L* is the membrane thickness, and *D* is the hydrogen diffusivity.

is the hydrogen diffusivity. Equations 1 and 2 are compared in Fig. 1 to our experi- mental permeation curve for a 1010 steel membrane mental permeation curve for a 1010 steel membrane (obtained in the absence of inhibitor in the electrolyte). As (obtained in the absence of inhibitor in the electrolyte). As shown in Fig. 1 the experimental permeation curve is clos-Equations 1 and 2 are compared in Fig. 1 to our experi-

- * Electrochemical Society Student Member. * * Electrochemical Society Active Member. * Electrochemical Society Student Member. ** Electrochemical Society Active Member.
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.1 Electrochem. Soc., Vol. 144, No. 7, July 1997 The Electrochemical Society, Inc. 2313 *J.* Electrochem. Soc., Vol. 144, No. 7, July 1997 *©* The Electrochemical Society, Inc. 2313

Fig. 1. The comparison of the experimental transient of hydrogen **Fig. 1. The comparison of the experimental transient of hydrogen** permeation current density with Iwo typical theoretical solutions. **permeation current density with two typical theoretical solutions.**

er to the theoretical curve given by Eq. 1. The diffusion $\frac{1}{n}$ inhibit coefficient was evaluated by two different methods. In the \mathbb{P}^P m first method, Eq. 1 was fitted using a computer program to $\overline{}^{electro}$ the experimental data to find $D = 7.2 \times 10^{-7} \text{ cm}^2/\text{s}$, using The hy
 $j_x = 223 \mu\text{A/cm}^2$, and $j_0 = 50 \mu\text{A/cm}^2$ from Fig. 1, and $L =$ presence 0.03 cm. The second method, which consisted in using 0.03 cm. The second method, which consisted in using $t_{1/2} = 0.138L^2/D$,²⁹ where $t_{1/2}$ (172 s) is the time correspond-
potential was ing to half rise of the permeation curve, yielded the same $\frac{\text{potential}}{\text{partial}}$ value for the hydrogen diffusivity. The diffusion coefficient $\hskip1cm ^{-1}$ valued obtained in this work is consistent with the previ-valued obtained in this work is consistent with the previously obtained value for the hydrogen diffusion coefficient ^{re} in AISI 4340 steel.¹² $j_0 = 223 \mu A/cm^2$, and $j_0 = 50 \mu A/cm^2$ from Fig. 1, and $L =$

The effect of the inhibitors on the cathodic current den-The effect of the inhibitors on the cathodic current density at different applied potentials is shown in Fig. 2, hydroge which shows that the cathodic current density is much that lower in the presence of 0.5 g/liter of PP or 0.5 g/liter of PP PN in the electrolyte. Our previous studies using a rotat-PN in the electrolyte. Our previous studies using a rotating disk electrode have shown that the optimum concen-ing disk electrode have shown that the optimum concentration for corrosion inhibition of $C-1010$ steel for both Fig. 5, t inhibitors is 0.5 g/liter.³⁰ At -0.9 V *vs.* SCE, the hydrogen presence cathodic current density in the presence of 0.5 g/liter of PP permeat is 2 mA/cm² compared with 90 mA/cm² measured on a bare 150μ alloy membrane. The inhibition efficiencies of 0.5 g/liter of P PP and PN at different applied potentials are presented in PP and PN at different applied potentials are presented in Fig. 3. The inhibitor inhibition efficiency is defined as $P_i =$ **Clube 1 Exercise** $(i_c - i_l)/i_c$, where i_c is the cathodic current density meas-
ured in the absence of the inhibitor and i_i is the cathodic current current density measured in the presence of inhibitor. As $\frac{0 \text{ t} \text{ in}}{1 \text{ h}}$ shown in Fig. 3, the hydrogen discharge current at -0.6 V the applied v_s . SCE was reduced by 80 and 98% in the presence of PN v_s brane. At \neg (and PP, respectively. The results indicated that both the electron of the elec inhibitors adsorb on the surface of the electrode and tion effic sity at different applied potentials is shown in Fig. 2, ured in the absence of the inhibitor and i_i is the cathodic

Fig. 2. The effect of PN and PP on the cathodic current density as **Fig. 2. The effect of PN and PP on the cathodic current density as** a function of the applied cathode cell potential. $\mathsf{C_{\textsf{PN}}} = 0.5$ g/liter, C, = 0.5 g/liter in 0.5 M HCl. **Cp = 0.5 g/liter in 0.5 M HCI.**

Fig. 3. The cathodic current inhibition efficiency of PN and PP vs. **Fig. 3. The cathodic current inhibition efficiency of PN and PP vs.** applied potential E. **applied potential E.**

inhibit the hydrogen discharge reaction. Adsorbed PN and PP molecules decrease the cathodic reaction sites of the inhibit the hydrogen discharge reaction. Adsorbed PN and electrode. electrode. PP molecules decrease the cathodic reaction sites of the

The hydrogen permeation current was measured in the The hydrogen permeation current was measured in the presence and absence of inhibitors. At the beginning of the permeation experiment, the cathodic side of the mem-
brane was held at a potential of -0.6 V *vs*. SCE. The
potential was then stepped to more negative values $-0.7, -0.8,$ and $-0.9 \text{ V } vs. \text{ SCE}$ and the steady-state permeation curve was recorded as a function of time. The meation curve was recorded as a function of time. The resulting permeation transients obtained at —0.6, —0.7, —0.8, and —0.9 V vs. SCE are shown in Fig. 4. With -0.8, and -0.9 V *vs.* SCE are shown in Fig. 4. With inhibitors present on the surface of the electrode, the inhibitors present on the surface of the electrode, the hydrogen permeation current decreases drastically at all hydrogen permeation current decreases drastically at all tested potentials. The effect of 0.5 g/liter PN and 0.5 g/liter tested potentials. The effect of 0.5 g/liter PN and 0.5 g/liter PP on the hydrogen permeation current is presented in PP on the hydrogen permeation current is presented in Fig. 5 as a function of the applied potential. The lines rep-
resent the linear regression fit to the data. As shown in
Fig. 5, the hydrogen permeation current is lower in the presence of inhibitors. At -0.9 V $vs.$ SCE, the hydrogen permeation current in the absence of inhibitors was $150~\rm \mu A$. In the presence of 0.5 g/liter of PN and 0.5 g/liter PP the hydrogen permeation currents were: 97 and 5μ A, respectively. The permeation current inhibition efficien-respectively. The permeation current inhibition efficienrespectively. The permeation current inhibition efficien-
cies of PN and PP were defined as $P_j = (j_t - j_i)/j_i$, (where j_t
is the transition normaation current in the observed of is the transition permeation current in the absence of is the transition permeation current in the absence of inhibitor and j_i is the permeation current in the presence of inhibitor), and are presented in Fig. 6 as a function of the applied potential at the cathodic side of the membrane. At —0.9 V vs. SCE in the presence of PN and PP in brane. At -0.9 V *vs.* SCE in the presence of PN and PP in the electrolyte, the hydrogen permeation current inhibi-the electrolyte, the hydrogen permeation current inhibition efficiencies are 35 and 95%, respectively. PN inhibits tion efficiencies are 35 and 95%, respectively. PN inhibits the permeation current more efficiently at lower applied the permeation current more efficiently at lower applied potentials. As shown in Fig. 6, at —0.6 V vs. SCE the PN potentials. As shown in Fig. 6, at -0.6 V *vs.* SCE the PN presence and absence of inhibitors. At the beginning of the permeation experiment, the cathodic side of the membrane was held at a potential of -0.6 V $vs.$ SCE. The potential was then stepped to more negative values of resulting permeation transients obtained at $-0.6, -0.7$, Fig. 5 as a function of the applied potential. The lines represent the linear regression fit to the data. As shown in presence of inhibitors. At -0.9 V $vs.$ SCE, the hydrogen inhibitor and j_i is the permeation current in the presence

Fig. 4. Hydrogen permeation transients through a 1010 steel **Fig. 4. Hydrogen permeation transients through a 1010 steel** membrane at different applied potentials in the absence and pres-**membrane at different applied potentials in the absence and pres**ence of inhibitors. The membrane thickness is 0.03 cm. **ence of inhibitors. The membrane thickness is 0.03 cm.**

Fig. 5. The effect of the inhibitors on the hydrogen permeation **Fig. 5. The effect of the inhibitors on the hydrogen permeation** transients as a function of the applied cell potential. **transients as a function of the applied cell potential.**

permeation current inhibition efficiency increases up to tial regi 55%. 55%.

An attempt was made using the IPZ model to quantify value $=$ the effect of the organic inhibitor on the hydrogen perme-the effect of the organic inhibitor on the hydrogen permeation process. The mechanistic model of Iyer *et al.*^{9,31} was anist used to determine the surface concentration and the hy-used to determine the surface concentration and the hydrogen surface coverage, the hydrogen absorption, dis-
charge, and recombination rate constants as well as HER state perm coverage-dependent transfer coefficient, α, and the ex-
change current density *i₀* from a knowledge of the steadychange current density i_0 from a knowledge of the steadystate hydrogen permeation current, cathodic current, hy-state hydrogen permeation current, cathodic current, hydrogen surface coverage, the hydrogen absorption, disdrogen diffusivity, and hydrogen overvoltage.

drogen diffusivity, and hydrogen overvoltage. The IPZ model assumes that (i) the hydrogen reaction The IPZ model assumes that *(i)* the hydrogen reaction occurs via the coupled discharge-recombination mechan-occurs via the coupled discharge-recombination mechanism, (*ii*) the recombination step of hydrogen is not rate-
determining so that the hydrogen atom oxidation can be neglected, $\overline{(n} \gg RT/F)$, *(iii)* the Langmuir isotherm is used $\overline{140}$ to describe the hydrogen coverage of the substrate, (iv) the to describe the hydrogen coverage of the substrate, *(iv)* the intermediate hydrogen adsorption-absorption reaction is intermediate hydrogen adsorption-absorption reaction is in local equilibrium, and (v) the hydrogen permeation $\left[\begin{matrix} 0 & 0 \\ 0 & 1 \end{matrix}\right]$ process is described by a simple diffusion model through $\frac{2}{3}$ ¹⁰⁰. the membrane. With these assumptions one can derive the $\frac{1}{2}$ so following relationships \int ism, *(ii)* the recombination step of hydrogen is not rate-

$$
i_{\rm c} = i'_{0}(1 - \theta_{\rm H})e^{-a\alpha\eta}
$$
 [3]

$$
i_{\rm r} = F k_3 \theta_{\rm H}^2 \tag{4}
$$

$$
j_x = \frac{k''\theta_H}{b}
$$
 [5]
$$
0.00 \t 0.05 \t 0.10 \t 0.00
$$

$$
j_x = \frac{k''}{b\sqrt{Fk_3}}\sqrt{i_x} \tag{6}
$$

Fig. 6-The permeation current inhibition efficiencies of PN and PP vs. E. **Fig. 6. The permeation current inhibition efficiencies of PN and PP vs. E.**

$$
i_{\rm c}e^{\rm a\alpha\eta} = -\frac{bi_0'}{k''}j_{\rm x} + i_0' \qquad [7]
$$

where $i_r = i_c - j_x$ is the hydrogen recombination current
donaity *i*, is the esthedia current donaity $h = I/ED$. I is density, i_c is the cathodic current density, $b = L/FD$, L is the membrane thickness, F is the Faraday constant, D is the membrane thickness, *F* is the Faraday constant, *D* is the hydrogen diffusion coefficient, $a = F/RT$, α is the transfer coefficient, η is the overpotential, R is the gas constant, *T* is temperature, and θ_H is the hydrogen surface cov-
erage, k_3 is the recombination rate constant, $i'_0 = i_0/(1 - \theta_e)$, erage, k_3 is the recombination rate constant, $i'_0 = i_0/(1 - \theta_e)$,
where i_0 is the exchange current density, θ_e is the equilib-
rium hydrogen coverage, and k'' is the thickness-dependent adsorption-absorption constant, defined as $k_{\rm abs}/(\overline{k}_{\rm ads} +$ D/L) where k_{abs} is the absorption rate constant for hydrogen into the metal and k_{ads} is the desorption constant for hydrogen from the metal.⁹ where i_0 is the exchange current density, θ_e is the equilibgen into the metal and $k_{\text{\tiny ads}}$ is the desorption constant for ${\rm\thinspace h}$ ydrogen from the metal. $^{\rm g}$

The dependence of the steady-state hydrogen perme- ation current upon the overpotential provided in this ation current upon the overpotential provided in this study is a diagnostic criterion for the identification of the study is a diagnostic criterion for the identification of the mechanism of the discharge of hydrogen ions on the steel mechanism of the discharge of hydrogen ions on the steel membrane. The experiments were carried out at a poten-membrane. The experiments were carried out at a potential region where $\eta \gg RT/F$. In this region it was found that the slope of $-\partial \eta / \partial \log (j_{\infty}) = 290 \text{ mV}$ [theoretical value = 273 mV/decade = 2.3 \times 4RT/F (T = 298.15 K)] which indicates a coupled discharge-recombination mechanism, 32 which is one of the assumptions for the applicability of the model. bility of the model. The dependence of the steady-state hydrogen permevalue = 273 mV/decade = $2.3 \times 4RT/F$ (T = 298.15 K)] which indicates a coupled discharge-recombination mech-

Figures 7, 8, and 9 show the dependence of the steady-
state permeation current upon the square root of the recombination current density in the absence of inhibitor
and in the presence of 0.5 g/liter PN and 0.5 g/liter PP,
respectively. The linear regression curves are shown as
continuous lines in the figures and indicate state permeation current upon the square root of the and in the presence of 0.5 g/liter PN and 0.5 g/liter PP, respectively. The linear regression curves are shown as continuous lines in the figures and indicate that the per-

Fig. 7. The steady-state hydrogen permeation current density, i_{ω} ,
 $^{[6]}$ for the bare iron vs. the square root of the recombination current density, √ *i_r.* Fig. 7. The steady-state hydrogen permeation current density, i_{∞} ,

Fig. 8. The steady-state hydrogen permeation current density, $i_{\rm s}$,
obtained in the presence of 0.5 g/liter PN vs. the square root of the recombination current density, J4. **recombination current density, ir.**

2316

Fig. 9. The steady-state hydrogen permeation current density, $f_{\text{av}} = 8.0114$
obtained in the presence of 0.5 g/liter PP vs. the square root of the 0.5 g recombination current density, $\sqrt{\textit{i}}$. **Fig. 9. The steady-state hydrogen permeation current density,** ,

meation rate is significantly lower when inhibitors were adsorp present in the electrolyte. The observed linear relationship mechar of hydrogen permeation current upon the square root of A^A the recombination current in the absence and presence of $\frac{b}{b}$ inhibitors is consistent with Eq. 6. inhibitors is consistent with Eq. 6.

The permeation current densities, j_x , *vs.* the charging shown is function, *i_ce^{acn}*, in the absence and presence of PN are presented in Fig. 10. Figure 11 shows the same relationship ence of $\frac{1}{2}$ but in the presence of PP in the electrolyte. Using the density slopes and intercepts in Fig. 7 through 11 and Eq. 6 and 7, $\frac{a}{a}$ but in the presence of PP in the electrolyte. Using the

Fig. 10. The steady-state hydrogen permeation current density, $i_{\rm s}$, $^{-3}$
vs. charging function, $i_{\rm e}^{\cos f/R}$ obtained in the absence of inhibitor and in the presence of 0.5 g/liter PN. **and in the presence of 0.5 g/liter PN.**

Fig. 11. The steady-state hydrogen permeation current density, I_{av} , vs. charging function, $i_{\text{c}}e^{\alpha n f / R t}$ obtained in the presence of the presence **Fig. 11. The steady-state hydrogen permeation current density, , vs. charging function,** *ie- F/RT* **obtained in the presence of 0.5 g/liter PP.**

Table I. IPZ model results. **Table . IPZ model results.**

Electrolyte/Parameter i_0' (A cm ⁻²) k'' (mol cm ⁻³) k_2 (mol cm ⁻² s ⁻¹)		
$0.5 \, M \, HCl$ $0.5 \, M \, HCl$	7.3×10^{-6} 7.02×10^{-5}	1.07×10^{-6}
$+$ 0.5 g/liter PP $0.5 \, \text{M HCl}$	4.7×10^{-8} 1.93 $\times 10^{-6}$	7.43×10^{-9}
$+$ 0.5 g/liter PN	1.6×10^{-6} 3.51 $\times 10^{-5}$	2.79×10^{-7}

the values of i'_0 , k'' , and k_3 were calculated and are presented in Table I. Substituting the recombination constant, k3, and the experimentally measured recombination stant, *k3,* and the experimentally measured recombination current into Eq. 3, the hydrogen surface coverage was cal-current into Eq. 3, the hydrogen surface coverage was calculated and is presented in Fig. 12. The points were calcu-culated and is presented in Fig. 12. The points were calculated from the IPZ model results at the experimentally lated from the IPZ model results at the experimentally tested overpotentials. As shown in Fig. 12, the hydrogen tested overpotentials. As shown in Fig. 12, the hydrogen surface coverage decreases drastically in the presence of 0.5 g/liter of PP. The inhibitors cause a suppression of hydrogen surface coverage by adsorbing on the surface hydrogen surface coverage by adsorbing on the surface thus decreasing the substrate electroactive area for hydro-thus decreasing the substrate electroactive area for hydrogen discharge reaction. As a consequence, the hydrogen gen discharge reaction. As a consequence, the hydrogen adsorption process is altered without changing the adsorption process is altered without changing the mechanical or physical properties of the substrate. mechanical or physical properties of the substrate. the values of i'_0 , k'' , and k_3 were calculated and are presurface coverage decreases drastically in the presence of

According to Eq. 5, the hydrogen permeation flux may be reduced by decreasing the hydrogen surface coverage by decreasing the absorption-adsorption constant. As by decreasing the absorption-adsorption constant. As shown in Table I, both the exchange current density and shown in Table I, both the exchange current density and the adsorption-absorption constant decrease in the pres-the adsorption-absorption constant decrease in the presence of inhibitors. The decrease in the exchange current ence of inhibitors. The decrease in the exchange current density accounts for the decrease in the cathodic current density accounts for the decrease in the cathodic current and consequently in a decrease of the hydrogen perme- ation current. PN reduces the hydrogen permeation rate ation current. PN reduces the hydrogen permeation rate by reducing the amount of hydrogen that discharges at the electrode surface, while PP reduces both the exchange electrode surface, while PP reduces both the exchange current density and the adsorption-absorption constant. current density and the adsorption-absorption constant. Thus, the presence of PP in the electrolyte decreases the Thus, the presence of PP in the electrolyte decreases the hydrogen discharge current and hydrogen permeation hydrogen discharge current and hydrogen permeation even at high cathodic potentials, up to 98 and 95%, respec-even at high cathodic potentials, up to 98 and 95%, respectively. The observed decrease of the hydrogen discharge and permeation currents in the presence of PP at high and permeation currents in the presence of PP at high cathodic potentials indicates the potential for the use of According to Eq. 5, the hydrogen permeation flux may be reduced by decreasing the hydrogen surface coverage and consequently in a decrease of the hydrogen permeby reducing the amount of hydrogen that discharges at the tively. The observed decrease of the hydrogen discharge PP in cathodic protection systems.

PP in cathodic protection systems. Our interpretation of the experimental data is that the Our interpretation of the experimental data is that the model assumptions were reasonable in the potential region model assumptions were reasonable in the potential region in which the inhibitors were studied. Despite the model in which the inhibitors were studied. Despite the model limitations, we believe it is possible to compare the kinet-limitations, we believe it is possible to compare the kinetic parameters in the presence and the absence of the ic parameters in the presence and the absence of the inhibitors to quantify their effect. It is important to point out that the values of the calcu-It is important to point out that the values of the calcuinhibitors to quantify their effect.

lated model dependent parameters are valid as long as the assumptions of the IPZ model are applicable. This inter-lated model dependent parameters are valid as long as the pretation is also restricted to the potential area in which pretation is also restricted to the potential area in which the parameters were estimated. the parameters were estimated. assumptions of the IPZ model are applicable. This inter-

Fig. 12. The hydrogen surface coverage, $\theta_{\rm H}$, vs. applied potential,
E, estimated in the absence of inhibitor and in the presence of 0.5 g/liter PN and 0.5 g/liter PP. **0.5 g/liter PN and 0.5 g/liter PP. E, estimated in the absence of inhibitor and in the presence of**

Conclusions **Conclusions**

The Devanathan-Stachurski permeation technique was \overrightarrow{n} over used to determine the hydrogen entry kinetics through an $\overrightarrow{\theta}$ expansion iron membrane in the presence and absence of PN and PP les inhibitors. Hydrogen evolution rates and hydrogen perme-inhibitors. Hydrogen evolution rates and hydrogen permeation rates were followed as a function of time at different $\qquad \tau$ applied potentials. The hydrogen discharge current at —0.6 V vs. SCE was reduced by 80 and 98% in the presence -0.6 V *vs.* SCE was reduced by 80 and 98% in the presence of PN and PP, respectively; hydrogen permeation current density was reduced by 55 and 95%, respectively. At $-0.9 \text{ V } vs. \text{SCE}$ in the presence of PN and PP in the electrolyte, the hydrogen permeation current inhibition was trolyte, the hydrogen permeation current inhibition was 35 and 95%, respectively and the discharge current densi-35 and 95%, respectively and the discharge current density were reduced by 55 and 95%. It was found, according to $\frac{1}{4}$ the IPZ model, that PN reduces the hydrogen permeation $\frac{4}{5}$. R. F rate by reducing the amount of hydrogen that discharges $\frac{5.5}{5.1}$ at the electrode surface, while PP reduces both, the $\frac{5.5}{r}$ exchange current density and the hydrogen adsorption-
absorption constant. The Devanathan-Stachurski permeation technique was applied potentials. The hydrogen discharge current at of PN and PP, respectively; hydrogen permeation current density was reduced by 55 and 95%, respectively. At -0.9 V *vs.* SCE in the presence of PN and PP in the elecrate by reducing the amount of hydrogen that discharges absorption constant.

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LIST OF SYMBOLS LIST OF SYMBOLS

- a F/RT, a constant, V^{-1}
- b $L/(F\acute{D})$ *a F/RT*, a constant, V⁻¹
b L/(FD), a constant, (A cm)⁻¹
C_H hydrogen surface concentration, mol cm⁻³
- $b\qquad L/(FD)$, a constant, ${\rm (A\ cm)}^{-1}$ and $C_{\rm H}$ and $D_{\rm C}$ is a maximum hydrogen surface concentration, mol cm⁻³ and 17 and 1
- b_H maintain hydrogen barrace concer. a F/RT , a constant, V^{-1}
 b $L/(FD)$, a constant, $(A \text{ cm})^{-1}$
 C_H hydrogen surface concentration, mol cm⁻³
 D_H^{max} maximum hydrogen surface concentration
 E_{oc} open-circuit potential, V
 E_c^{co} cat
- *Eoc* open-circuit potential, V
- open-circuit potential, V
cathodic potential, V *E,* cathodic potential, V
- Faraday constant, 96487 C/eq mol current density, A/cm2 *F* Faraday constant, 96487 C/eq mol
i current density, A/cm²
-
- i_c cathodic current density, A/cm²
- i_r hydrogen recombination current density, A/cm² 21
- i_0 exchange current density, A/cm^2
- i_i cathodic current density measured in the presence $\frac{23}{24}$ of inhibitor, A/cm2 of inhibitor, A/cm² $\begin{bmatrix} i_c \ i_r \ i_0 \end{bmatrix}$
- $i_{\rm 0}/(1\,$ $\theta_{\rm c})$, A/cm 2
- steady-state hydrogen permeation current density
 $(j_x = FDC_{\text{H}}/L)$, A/cm² *i;* i $\begin{array}{lll} i'_0& i_0/(1-\theta_c), \ {\rm A/cm}^2\ \end{array}$ steady-state hydrogen permeation current density $(j_{\infty} = FDC_{\text{H}}/L)$, A/cm²
- j_o initial hydrogen permeation current density, A/cm² ^{26.} M
- transition hydrogen permeation current density in *ji* transition hydrogen permeation current density in $\frac{j_{\rm o}}{j_{\rm i}}$ the presence of inhibitor, A/cm2
- the presence of inhibitor, A/cm^2 i_t transition hydrogen permeation current density,
 A/cm^2 j_t transition hydrogen permeation current density,
A/cm²
- k_3 recombination rate constant, mol $(\text{cm}^2 \text{ s})^{-1}$
- thickness dependent absorption-adsorption constant, mol cm2 *k"* thickness dependent absorption-adsorption constant, mol cm⁻
- membrane thickness, cm L
- *L*₁ membrane thickness, cm $\left(i_c i_l\right)/i_c$, dimensionless P_l inhibitor efficiency $(i_c i_l)/i_c$, dimensionless $\left(i_l i_l\right)$ \overline{P}_{1}
- P_j permeation current inhibitor efficiency $(j_c j_i)/j_c$, Corros.
dimensionless 31. R. N. Iyer dimensionless
- R gas constant, 8.3143 J (mol K)⁻¹
time, s R gas con
t time. s
-
- tume, s time, s the corresponding to the half rise of the permeation $t_{1/2}$ time corresponding to the half rise of the permeation $\frac{c_1}{c_2}$ curve, s ¹² curve, s

T temperature, K
-

Greek Greek

- α transfer coefficient, dimensionless

m overpotential, V

a coujibrium bydrogen surface coverage din
- θ_e overpotential, V
 θ_e equilibrium hyd
- $\theta_{\rm e}$ equilibrium hydrogen surface coverage, dimensionless less
- θ_H hydrogen surface coverage, dimensionless τ ^{*tD/L²*, dimensionless time}

REFERENCES REFERENCES

- 1. R. A. Oriani, *Ann. Rev. Mater. Sci.,* 8, 327 (1978).
- 1. R. A. Oriani, Ann. Rev. Mater. Sci., 8, 327 (1978). 2. J. O'M. Bockris and A. K. N. Reddy, Modern Electrochemistry, Vol. 2, p. 1231, Plenum Press, New York 2. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry,* Vol. 2, p. 1231, Plenum Press, New York (1970).
- (1970). 3. J. O'M. Bockris and P. K. Subramanyan, Elect rochim. 3. J. O'M. Bockris and P. K. Subramanyan, *Electrochim. Acta,* 16, 2169 (1971).
-
- Acta, 16, 2169 (1971). 4. R. H. Song and S. Pyun, This Journal, 137, 1051 (1990). 5. B. E. Wilde and T. Shimada, Scr. Metall., 22, 551 (1988). 4. R. H. Song and S. Pyun, *This Journal,* 137, 1051 (1990). 5. B. E. Wilde and T. Shimada, *Scr. Metall.,* **22,** 551 (1988).
- 6. P J. Grobner, D. L. Sopnseller, and D. E. Diesburg, Cor-6. P J. Grobner, D. L. Sopnseller, and D. E. Diesburg, *Corrosion,* **35,** 240 (1979).
- rosion, 35, 240 (1979). 7. M. Manohar, Ph.D. Thesis, Ohio State University, 7. M. Manohar, Ph.D. Thesis, Ohio State University,
- Columbus, OH (1990).
8. B. E. Wilde and I. Chattoraj, *Scr. Metall.*, **26,** 627 (1992).
9. R. N. Iyer, H. W. Pickering, and M. Zamanzadeh, *This* 8. B. E. Wilde and I. Chattoraj, *Scr. Metall.,* 26, 627 (1992). 9. R. N. Iyer, H. W. Pickering, and M. Zamanzadeh, *This*
- Journal, 136, 2463 (1989). 10. B. N. Popov, G. Zheng, and R. E. White, Corrosion, 50, 10. B. N. Popov, G. Zheng, and R. E. White, *Corrosion,* **50,** *Journal,* 136, 2463 (1989).
- 613 (1994). 11. B. N. Popov, G. Zheng, and R. E. White, ibid., 51, 429 11. B. N. Popov, G. Zheng, and R. E. White, *ibid.,* **51,** 429 613 (1994).
- (1995). 12. B. N. Popov, G. Zheng, and R. E. White, This Journal, 12. B. N. Popov, G. Zheng, and R. E. White, *This Journal,* (1995).
- 140, ³¹⁵³ (1993). 13. G. Zheng, B. N. Popov, and P. E. White, ibid., 141, 1220 13. G. Zheng, B. N. Popov, and R. E. White, *ibid.,* 141, 1220 140, 3153 (1993).
- (1994). 14. G. Zheng, B. N. Popov, and R. E. White, ibid., 141, 1526 14. G. Zheng, B. N. Popov, and R. E. White, *ibid.,* 141, 1526 (1994) .
- (1994). 15. B. N. Popov, G. Zheng, and P. E. White, Corros. Sci., 36, 15. B. N. Popov, G. Zheng, and R. E. White, *Corros. Sci.,* 36, (1994) .
- 2139 (1994). 16. G. Zheng, B. N. Popov, and P. E. White, J. Appl. Elec-16. G. Zheng, B. N. Popov, and R. E. White, *J. Appl. Elec-*2139 (1994).
- trochem., 25, 212 (1995). 17. G. Zheng, B. N. Popov, and P. E. White, This Journal, 17. G. Zheng, B. N. Popov, and R. E. White, *This Journal, trochem.,* **25,** 212 (1995).
- 142, 154 (1995).
- 142, 154 (1995).
18. D. H. Coleman, G. Zheng, B. N. Popov, and R. E. White, ibid., 143, 1871 (1996). 19. R. L. Martin, Mater Perform., 19, 20 (1980). 19. R. L. Martin, *Mater Perform.,* **19,** 20 (1980). *ibid.,* 143, 1871 (1996).
-
- 20. K. van Gelder, M. J. Simon Thomas, and C. J. Kroese, 20. K. van Gelder, M. J. Simon Thomas, and C. J. Kroese, Corrosion, **42,** 36 (1986).
21. R. L. Martin, *Mater. Perform.*, **13,** 19 (1974). *Corrosion,* 42, 36 (1986).
- 21. R. L. Martin, *Mater Perform.,* **13,** 19 (1974).
- 22. P. L. Martin, ibid., 22, 33 (1986). 22. R. L. Martin, *ibid.,* **22,** 33 (1986).
-
- 23. R. L. Martin, Corrosion, 49, 694 (1993). 24. 5. M. Wilhelm and D. Abayarathna, ibid., 50, 152 23. R. L. Martin, *Corrosion,* 49, 694 (1993). (1994). 25. M. A. V Devanathan and Z. Stachurski, Proc. R. Soc. 25. M. A. V. Devanathan and Z. Stachurski, *Proc. R. Soc.* 24. S. M. Wilhelm and D. Abayarathna, *ibid.,* 50, 152 (1994).
- *London, Ser. A,* 270, 90 (1962).
- London, Ser A, 270, 90 (1962). 26. M. A. V Devanathan and Z. Stachurski, This Journal, 26. M. A. V. Devanathan and Z. Stachurski, *This Journal,* 110, 886 (1963).
- 110, 886 (1963). 27. M. A. V Devanathan, Tech. Rep. ONR/551/22NR-036- 028, Office of Naval Research, Washington, DC 27. M. A. V. Devanathan, *Tech. Rep. ONR/551/22NR-036- 028,* Office of Naval Research, Washington, DC (1961).
- (1961). 28. N. Boes and H. Zuchner, J. Less-Common Met., 49, 223 28. N. Boes and H. Zuchner, *J. Less-Common Met.,* 49, 223 (1976).
- (1976). 29. B. S. Chaudhari and T P Radakrishnan, Corros. Sci., 29. B. S. Chaudhari and T. P Radakrishnan, *Corros. Sci.,* 30, 1219 (1990).
- 30, 1219 (1990).
30. H. A. Duarte, G. Zheng, B. N. Popov, and R. E. White, Corros. Sci., Submitted. *Corros. Sci.,* Submitted.
- 31. R. N. Iyer and H. W Pickering, Ann. Rev. Mater Sci., 20 31. R. N. Iyer and H. W. Pickering, *Ann. Rev. Mater. Sci.,* 20 (1990). 32. P Subramanyan, Comprehensive Treatise of Electro-32. P Subramanyan, *Comprehensive Treatise of Electro-*(1990).
- $chemistry,$ Vol. 4, J. O 7 M. Bockris, B. E. Conway, E. A. Yeager, and P. E. White, Editors, p. 411, Plenum Press, Inc., New York (1981). Press, Inc., New York (1981). *chemistry,* Vol. 4, J. O'M. Bockris, B. E. Conway, E. A. Yeager, and R. E. White, Editors, p. 411, Plenum