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The Role of Thallium as a Hydrogen Entry Promoter on Cathodically Polarized HY-130 Steel

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ABSTRACT

Hydrogen permeation experiments were carried out to investigate the effect of thallium on hydrogen entry into HY-130 steel. These experiments show that the presence of thallium ions in an electrolyte drastically increase the hydrogen entry rate. The hydrogen entry efficiency and hydrogen surface coverage were increased by a factor of 10 and 6, respectively. In order to fit the permeation experimental data, the Iyer-Pickering-Zamanzadeh (I-P-Z) hydrogen permeation model was modified by including a mass-transfer term in the discharging equation. The relationship between hydrogen permeation and the hydrogen evolution reaction were investigated and new relationships were obtained.

Certain elements, particularly those of Group V-A (As, Sb, F) and VI-A (S, Se) kinetically increase the rate of hydrogen entry into iron, steel, and ferritic alloys. Very small additions of these elements, referred to as “promoters” or “poisons” poison the hydrogen evolution reaction and consequently promote hydrogen absorption. Other species, which increase the hydrogen entry, are cyanide ions in alkaline solutions, halide ions in acidic solutions, and, under some circumstances (with much weaker effects), suites of heavy metals, such as Hg, Sn, and Pb. Extensive literature can be found on promoters. However, the results presented and the suggested reaction mechanism by different authors are conflicting. Shuler and Laidler suggest that the promoter action could be due to an increasing of the strength of the M-H bond so that the activation energy for hydrogen recombination increased. Contrary to Shuler and Laidler’s mechanism Bockris et al., Newman and Shreir, and Kovba and Bagatskaya suggest that the metal to hydrogen bond is reduced in the presence of the promoting species. The kinetic effect can be described by the decreased metal hydrogen bond energy which has a lower activation energy for the absorption process relative to the energy barrier for the recombination process. According to Smialowski, Szklarska-Smialowska et al. the enhanced hydrogenation effect, in the presence of promoters, involves the formation of a stable hydride. By using various promoters in 1 N H2SO4 and measuring the elongation of hydrogen-charged iron wires or coils, they found that the relative effectiveness of the promoter element correlated well with increasing bond strength and stability of the hydride (H2S > PH3 > AsH3). Newman and Shreir reached the same conclusion as Smialowski. They galvanostatically charged high-strength steel specimens for 24 h and measured the hydrogen content afterwards. According to Newman and Shreir, an enhanced hydrogen permutation occurs in the case of stable hydrides, such as AsH3, PH3, H2S, and H2Se. Smialowski’s explanation was also supported by McGraw et al. and Fontana and Stachkie. It is assumed that the hydrides first chemisorbed and then dissociated on the metal surface and have the ability to transmit hydrogen atoms through the electrolyte/metal boundary. However, Redekrishnan and Shreir found that AsH3, produced outside their permeation cell, did not enhance the hydrogen permeation rate when bubbled into the cell. The discrepancy in the necessity of the presence of arsine in these two papers was confirmed by McCright and Stahle. They found that the reduction of arsenate to elemental arsenic suppresses the hydrogen re-action and promotes the entry of hydrogen into steel structures during cathodic polarization. According to these authors the rate of entry of hydrogen does not depend on arsine (AsH3) formation. The greatest relative permeation occurred in the potential range where arsenic is the stable phase. Some authors suggested that the promoter interferes with the recombination step by increasing the average residence time of H on the surface which increases the surface coverage of adsorbed hydrogen. Alikin and Beloglazov and Polukarov have postulated that colloidal particles, which are formed during electrolysis promote hydrogen entry and that in the presence of poisons, hydrogen enters the metals as protons.

As shown in previous publications, the mechanism of promoter action is highly controversial. In this work, hydrogen permeation experiments were carried out to investigate the effect of thallium on hydrogen entry into HY-130 steel. We have established the atomic thallium rather than its hydride has a significant effect on hydrogen entry.

Experimental

Using the Devanathan-Stachurski permeation technique, the rate of hydrogen permeation through HY-130 steel membrane was measured continuously as a function of time. The permeation experiments were carried out in a system with two compartments separated by a bipolar HY-130 steel membrane. The permeation rate through a thin membrane of thickness 0.15 mm was measured by setting 

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the potential on the “diffusion side” of the membrane (the side from which the hydrogen emerges) at a fixed value (-0.5 V vs. Hg/HgO). This value corresponds to almost a zero concentration of absorbed atomic hydrogen on the surface. This condition occurred when all hydrogen atoms which have diffused through the membrane and emerged on the diffusion side have been instantaneously ionized. The hydrogen permeation rate was directly proportional to the applied current, which can be measured conveniently with a high degree of accuracy and sensitivity. The steel membrane on the cathodic side of the cell was polarized potentiostatically. Prior to the permeation studies the steel membrane was cleaned in an ultrasonic cleaning bath and saturated with hydrogen in a 0.1M H2SO solution maintaining the solution at cathodic current densities of 10 mA/cm² for 1 h. Then, the membrane was removed from the cell, etched for 20 s in a solution containing methyl alcohol and 1% H2SO4, rinsed with deionized water, dried in air, and fitted into the permeation cell.

To avoid possible passivation, the anodic side of the membrane was electroplated with a thin layer (0.15 to 0.20 μm) of palladium. The deposition was carried out in an electrolyte containing 2 x 10⁻⁶ M Na₂Pd(NO₂)₄ using a current density of 1.0 μA/cm² for 2 h. Then, the electrolyte was drained off, and the compartment was washed with deionized water and filled with the anodic solution (0.2M NaOH). To keep the electrolyte impurities at the lowest possible level, the anodic solution was pre-electrolyzed for at least 24 h in a separate electrolytic cell before putting it in the permeation cell. In the anodic compartment, the electrolyte was kept at -0.3 V vs. Hg/HgO reference electrode until the background current was reduced to below 3 μA/cm². Then, the cathodic compartment was filled with a supporting electrolyte containing 0.5M Na₂SO₄ and 0.5M H₂SO₄. Prepurified nitrogen was bubbled through both compartments in order to keep the system free of dissolved oxygen. All potentials were reported vs. SCE unless otherwise mentioned.

Results and Discussion

Hydrogen permeation studies on cathodically polarized HY-130 steel.—Permeation experiments were performed to clarify the relationship between thallium and hydrogen entry kinetics. Thallium was predeposited on a HY-130 steel membrane from electrolytes containing 0.5M Na₂SO₄ and 0.5M H₂SO₄ and 2 x 10⁻³M Tl⁺. At cathodic potentials, more negative than -0.70 V, a visible deposition of thallium occurred on the steel surface. The open-circuit potential of the membrane with a predeposited thallium was -0.70 V. At potentials more positive than -0.70 V no bulk deposition of thallium was observed. Thus, in order to avoid bulk deposition of thallium on steel, most of the permeation experiments were performed at potentials more anodic than -0.70 V. The permeation experiment were also carried out on membranes with predeposited thallium on the surface and the results were compared with those obtained for underpotential deposited thallium.

The experiments were performed at different cathodic potentials in a solution containing 0.5M Na₂SO₄ and H₂SO₄ which is free of thallium ions. Initially, the membrane was charged at a potential of -0.5 V and then charged at more negative potentials using steps of 50 mV until the potential reached a value of -0.65 V. Thus, the applied potentials were: -0.50, -0.55, -0.60, and -0.65 V. After the permeation rate stabilized, at an applied potential of -0.65 V, the potential was switched off, and the decaying curve was created. The atomic hydrogen permeation current density was determined at different potentials plotted in Fig. 1. Figure 1 shows that the steady-state hydrogen permeation current increased with the increasing of the applied cathodic potential. The hydrogen diffusivity through HY-130 membrane was calculated by fitting the whole hydrogen permeation transient obtained experimentally for Eweep = -0.55 V.

The experimental data fits the theoretical solution for hydrogen permeation through a membrane at a constant hydrogen concentration at the entry side of the membrane with D = 2.4 x 10⁻⁷ cm²/s.

Using the mechanistic model developed by Iyer, Pickering, and Zamanadel, the I-P-Z model, the hydrogen surface coverage and the surface concentration, the hydrogen absorption, discharge, and recombination rate constants as well as the hydrogen evolution reaction (h.e.r.) coverage-dependent transfer coefficient, α, and the exchange current density i₀ may be computed from a knowledge of the steady-state hydrogen permeation current, cathodic charging current, hydrogen diffusivity, and hydrogen overvoltage. This was done by assuming that (i) the hydrogen evolution reaction is a coupled discharge-recombination process (ii) since η >> RT/F, hydrogen atom oxidation can be neglected; (iii) the Langmuir isotherm is used to describe the hydrogen coverage of the substrate; (iv) the intermediate hydrogen adsorption-absorption reaction is in local equilibrium; and (v) the hydrogen permeation process is described by a simple diffusion model through the membrane. With these assumptions, one can derive the following relationships:

\[ i_t = i_i \left( 1 - \theta_i \right) e^{-\eta_i} \]  
\[ i_c = F k_0 \theta_i \]  
\[ j_c = \frac{F D}{L} \theta_i - \frac{C_i}{b} \]  
\[ j_c = F \left[ k_s a \theta_i \right. - k_s c \left( 1 - \theta_i \right) \]  
\[ \theta_i = \frac{b j_c}{k_s} \]  
\[ j_s = \frac{k_s}{b \sqrt{F k_3}} \]  
\[ i_e = \frac{b j_c}{k_c} + i'_i \]
hydrogen surface coverage, $k_3$ is the recombination rate constant, $k^*$ is the thickness dependent adsorption–absorption constant, $i_0 = i_0(1 - \theta_s)$, where $i_0$ is the exchange current density, $k_{ads}$ is the adsorption rate constant, and $k_{ads}$ is the adsorption rate constant.

Due to the assumption that $i_e = i_s, j_s$ is linearly related to $\sqrt{n}$ (where $n$ is the overpotential). This assumption is generally true because $j_s << i_s$ for most of the cases.

The Langmuir isotherm does not always apply, especially when hydrogen starts evolving. Frumkin–Temkin isotherm corrections have been used by Iyer et al. to correct the hydrogen surface coverage for such reactions. In this case Eq. 1 and 2 become

$$i_s = i'_0 (1 - \theta_s)e^{-\alpha_0 \eta}e^{-\alpha_0 \eta}$$

and

$$i_s = Fk_{ads}^* \theta_s e^{-\alpha_0 \eta}$$

respectively. The value 4.5 for $f = \sqrt{RT}$ is used when the surface is covered by hydrogen. Substituting Eq. 7 into 10 and 11, the following modified I-P-Z relationships can be obtained

$$\ln \left( \frac{i}{i_0} \right) = \frac{\alpha_0 f_b}{k^*} j_s - \frac{bFk_i}{k^*}$$

and

$$\ln \left( \frac{i}{i_e} \right) = -\alpha_0 \eta + \ln i'_0$$

Equations 8 and 9, 12 and 13 may be used to evaluate various reactions parameters such as $k_3, k^*$, and $i'_0$ by plotting corresponding experimental data.

The steady-state hydrogen permeation current density ($j_s$) and the cathodic current density ($i_s$) are plotted vs. hydrogen overpotential ($\eta$) in Fig. 2. The permeation current density ($j_s$) vs. the square root of hydrogen recombination current density ($\sqrt{n}$) is given in Fig. 3. The measured data may satisfy the I-P-Z model under Langmuir isotherm coverage. If true, $\log i_s$ vs. $\eta$ and $\log j_s$ vs. $\eta$ should be two linear relationships, with slopes of $-d\eta/d \log j_s = -1/2 d\eta/d \log j_s = 120 \text{ mV/decade}$. The change in slope from 137 to 313 mV/decade of the experimental data does not support this assumption. If the transfer coefficient $\alpha_0$ is a function of overpotential, then $\alpha_0/\eta > 0$ may explain the nonlinear behavior observed in Fig. 2. However, that will give a negative value of $i'_0$ by fitting Eq. 9, proving this assumption is incorrect. Taking into account that the coverage of hydrogen is a function of potential, the I-P-Z model may be used to evaluate the transfer coefficient $\alpha_0$. Using this procedure, different values of $\alpha_0$ were obtained at different potentials.

From Fig. 2, the overpotential became more negative, the cathodic current approached a limiting value, which may be a mass transfer limiting current. Equation 1 uses the assumption that the mass-transfer rate is large enough or the current density is low enough so that the surface concentrations $C(x = 0)$ are close to the bulk concentrations ($C^*$). If the mass-transfer factor is taken into account, then Eq. 1 will become

$$i_e = i'_0 (1 - \theta_s)e^{-\alpha_0 \eta}$$

and according to Ref. 28

$$z_i (x = 0) = \frac{C(x = 0)}{C^*} = 1 - \frac{i_e}{i_i}$$

where $i_i$ is the limiting current density. Inserting Eq. 15 into Eq. 14 and rearranging, one obtains

$$\frac{i_i}{i_e} = (1 - \theta_s)\frac{C(x = 0)}{C^*} e^{-\alpha_0 \eta}$$

and thus

$$\ln \left( \frac{i_i}{i_e} \right) = \ln \left( [i_i (1 - \theta_s)] - a_0 \eta \right)$$

By fitting and extrapolating the experimental curve, $i_s = 29 \text{ mA/cm}^2$. By plotting $\eta$ vs. $\ln \left( [i_i/(i_i - i_s)] \right)$ in Fig. 4 and assuming that $\theta_s$ is close to zero and thereby negligible, the transfer coefficient $\alpha_0$ was computed to be 0.542 from the slope in Fig. 4.

If one includes mass-transfer effects, Eq. 9 becomes

$$\frac{i_i}{i_e} = e^{-\alpha_0 \eta}$$

A plot of $j_s$ vs. $[i_i/(i_i - i_s)] \times e^{b/Fk_i}$ is given in Fig. 5. From the intercept and slope, $i'_0$ and $k^*$ can be evaluated, respectively. These values are $i'_0 = 18 \mu\text{A/cm}^2$ and $k^* = 6.6 \times 10^{-3} \text{ mol/cm}^2$. Assuming Eq. 8 is still applicable, the recombination constant $k_3$ can be obtained from the slope and was found to be $k_3 = 120 \text{ mV/decade, 23'24 assuming a transfer coefficient $a_0 = 0.5$.}

![Fig. 2. The dependence of cathodic current density ($i_s$) and permeation current density ($j_s$) upon cathodic overpotential ($\eta$) in the absence of thallium ions.](image_url)

![Fig. 3. Permeation current density ($j_s$) vs. square root of recombination current density ($\sqrt{n}$) in the absence of thallium ions.](image_url)
have a value of $1.1 \times 10^{-5} \text{ mol/(cm}^2\text{s})$. Using the Eq. 7, the hydrogen surface coverage changes from 0.05 to 0.14 when the overpotential changed from $0.26$ to $-0.43$ V. This range of coverage is found by using the Langmuir isotherm assumption and assuming that it is reasonable to neglect the diffusion layer in Eq. 1.

Hydrogen permeation on cathodically polarized HY-130 steel in the presence of thallium ions.—The permeation experiments, in the presence of thallium were repeated in the same electrolyte (0.5M Na$_2$SO$_4$, 0.5M H$_2$SO$_4$) in which $2 \times 10^{-2}$M of Th$^{++}$ was added (in the form of Th$_2$SO$_4$). In the presence of Th$^{++}$ ions, the experiments were started at a potential of $-0.50$ V followed by an increase in potential in steps of $-50$ mV up to an applied potential of $-0.65$ V. The permeation current densities increase sharply compared with the results in Fig. 1 corresponding to the same applied potentials. In the presence of Th$^{++}$, the permeation current density were increased by 74%. Apparently, the observed increase of the permeation current density is not due to the surface preparation differences.

Fig. 4. ln ($i/|i - i|$) vs. overpotential ($\eta$) in the absence of thallium ions.

In order to check whether the permeation current density increased due to possible surface preparation differences, the permeation experiments were repeated at potential $-0.50$ V in the absence of thallium ions in the electrolyte. After the permeation transient stabilized, the thallium ions in the form of Th$_2$SO$_4$ were directly added to the solution to make $2 \times 10^{-2}$M of Th$^{++}$. The permeation transients and cathodic current density are shown in Fig. 8 and 9, respectively. In the presence of Th$^{++}$, the permeation current density increased by 74%. Apparently, the observed increase of the permeation current density is not due to the surface preparation. The permeation curves in Fig. 8 gave reproducible results compared with the corresponding results in Fig. 1 and 6. Figure 9 illustrates the significant suppression of the h.e.r. brought about by the addition of thallium. Initially, the sulfate electrolyte (0.5M Na$_2$SO$_4$ + 0.5M H$_2$SO$_4$) containing no thallium. At an applied constant potential of $-0.50$ V, the current density increased to a value of 3800 $\mu$A/cm$^2$. When thallium was added in the electrolyte, the cathodic current was reduced by 93%. The sharp reduction in h.e.r. was due to the kinetic limitations of the hydrogen discharge reaction on the deposited thallium monolayers.

Fig. 5. In ($i/|i - i|$) e$^{+\eta}$ vs. permeation current density ($i$) in the absence of thallium ions.

Fig. 6. Hydrogen permeation transients through HY-130 steel membrane at different applied potentials ($-0.50$ to $-0.65$ V vs. SCE) in the presence of $2 \times 10^{-2}$M of Th$^{++}$ in the electrolyte containing 0.5M Na$_2$SO$_4$, 0.5M H$_2$SO$_4$, the thickness of the membrane = 0.15 mm.

Fig. 7. Hydrogen permeation transients through HY-130 steel membrane at different applied potentials ($-0.50$ to $-0.80$ V vs. SCE) in the presence of $2 \times 10^{-2}$M of Th$^{++}$ in the electrolyte containing 0.5M Na$_2$SO$_4$, 0.5M H$_2$SO$_4$, the thickness of the membrane = 0.15 mm.
Fig. 8. Hydrogen permeation transients through HY-130 steel membrane at applied potentials of -0.50 V vs. SCE in the absence and presence of $2 \times 10^{-2}$ M of TI$^+$ in the electrolyte containing 0.5M Na$_2$SO$_4$, 0.5M H$_2$SO$_4$, the thickness of the membrane = 0.15 mm.

The relation between the hydrogen recombination current density ($i_\text{r}$) and the permeation current density ($j_\text{p}$) is given in Fig. 10, showing that a linear relation exists between $i_\text{r}$ and $j_\text{p}$. Obviously, the hydrogen evolution and permeation mechanism in the presence of thallium ions is different from the mechanism observed in the absence of thallium. Also the data do not fit either the modified I-P-Z model, in which a linear relation should exist between $i_\text{r}$ and $j_\text{p}$, or the equations derived by McBreen and Genshaw for activated desorption, in which $j_\text{p}$ is proportional to the square of $i_\text{r}$. According to Gileadi and Conway, the effect of the pre-exponential terms in $\theta$, in these equations dominate the effect. Thus, Eq. 10 and 11 can be simplified

$$i_\text{r} = i_0^\prime e^{-C_\text{ads} \alpha_i \theta}$$  \hspace{1cm} [19]$$i_\text{r} = Fk_\theta e^{2C_\text{ads} \theta}$$  \hspace{1cm} [20]

under the Temkin isotherm assumption, Eq. 4 becomes

$$j_\text{p} = F(k_{\text{ads}}e^{C_\text{ads} \theta} - k_{\text{ads}}e^{-C_\text{ads} \theta})$$  \hspace{1cm} [21]

Combining Eq. 3 and 21 and rearranging

$$C_\text{ads} = \frac{k_{\text{ads}}e^{C_\text{ads} \theta}}{D} e^{C_\text{ads} \theta} + k_{\text{ads}}$$  \hspace{1cm} [22]

Equation 24 shows that $j_\text{p}$ is linearly related to $i_\text{r}$, which is consistent with present experimental results in the presence of thallium ions. Since $i_\text{r} = i_0 + j_\text{p}$

$$\frac{\partial i_\text{r}}{\partial \log i_\text{r}} = \frac{\partial i_\text{r}}{\partial \log j_\text{p}} = \frac{\partial j_\text{p}}{\partial \log j_\text{p}}$$  \hspace{1cm} [25]

Figure 11 shows that $\partial i_\text{r}/\partial \log j_\text{p} = \partial i_\text{r}/\partial \log j_\text{p}$, which agrees with the Eq. 25. The first two points of $i_\text{r}$ in Fig. 11 give a slope of 126 mV/decade, which can be used to evaluate the value of $i_0$ under Langmuir isotherm. The calculated $i_0^\prime$ is 1.7 $\mu$A/cm². However, the slope also are a function of over-potential. Again, it has been assumed that this variation is due to a mass-transfer limit. Introducing the mass-transfer term into Eq. 19 shows that

$$i_\text{r} = \left(1 - \frac{1}{\tilde{i}_\text{p}}\right) i_0^\prime e^{-C_\text{ads} \theta}$$  \hspace{1cm} [26]

and combining Eq. 26 with Eq. 20, yields

$$\tilde{i}_\text{p} = \frac{k_\text{ads}/D}{\theta} e^{2\theta}$$

where $k_\text{ads}/D/L \equiv \theta_{\text{ads}}$. Note that in the modified I-P-Z model, Eq. 5, obtained under Langmuir assumption, was used instead of using the Temkin isotherm assumption. Substituting Eq. 22 into Eq. 3, the permeation current is obtained as

$$j_\text{p} = \frac{k_\text{ads}/D}{\theta} e^{2\theta}$$  \hspace{1cm} [23]

Combining Eq. 20 and 23, one obtains

$$j_\text{p} = \frac{k_\text{ads}/D}{\theta} e^{2\theta}$$  \hspace{1cm} [24]

Figure 10. Permeation current density ($j_\text{p}$) vs. the recombination current density ($j_\text{r}$) in the presence of $2 \times 10^{-2}$ M of thallium ions.
Fig. 12. $\frac{\log(\frac{i_i}{i}}{\log(\eta)}$ vs. overpotential ($\eta$) in the presence of thallium ions.

$$\log \left( \frac{i_i}{i} \right) = \log \left( \frac{i}{\sqrt{RT}} \right) - \frac{a \alpha_n \eta}{2.303} \quad [27]$$

A limiting current density $i_l$ of 1850 $\mu$A/cm$^2$ was estimated by extrapolating the experimental data given in Fig. 12. Then, using Eq. 27, the constants $a$, $k_3$ were calculated from the intercept and slope in Fig. 12 to be $2.6 \times 10^{-10}$ mol/cm$^2$s, respectively. From the slope in Fig. 10, $k$ was calculated to be $2.6 \times 10^{-6}$ mol/cm$^3$. The kinetic parameters $a$, $i_l$, $k_3$, and $k$ (in the presence and absence of thallium) are listed in Table 1 for comparison. According to Table 1, the exchange current density, the recombination constant, and the absorption-adsorption constant decrease in the presence of thallium. Note that hydrogen recombination constant decreased by a factor 10$^5$. Consequently, the permeation current density according to Eq. 24 should increase, a phenomena observed in our experiments. The hydrogen entry efficiency, defined as $j_i/i_l$, was plotted vs. overpotential in Fig. 13. The hydrogen entry efficiency was increased by a factor of 10 in the presence of thallium.

The hydrogen coverages can be evaluated from Eq. 2 and 20, and the results, together with the values obtained in the absence of thallium are given in Fig. 14 as a function of overpotential. The surface coverage also increased in the presence of thallium.

Although Smialowski et al. postulate that the active form of a hydrogen entry promoter is the form of hydrides, no thallium hydride formed on the steel surface under our experimental conditions as explained next. The equilibrium potential for the system Ti/TiH is $E_{eq} = -2.107 - 0.0591 \pH - 0.0591 \log [\text{TiH}]$ vs. SCE.$^3$ Thus, the experimental potentials used here were more positive than the equilibrium potential. Therefore, the atomic thallium rather than its hydride has a significant effect on the hydrogen entry, as claimed by McCright and Staehle$^4$ for As.

**Conclusion**

The absorption of thallium on steel enhances hydrogen entry. The active form of thallium acted as a hydrogen entry promoter. The observed increase in the hydrogen entry rate is due to a decrease of the hydrogen recombination rate constant. This constant was decreased by five orders of magnitude in the presence of adsorbed thallium. A mass-transfer term was introduced into the I-P-Z model to interpret the experimental results presented here. Also $j_i/i_l$ relationships for coupled discharge-recombination mechanism under Temkin isotherm were derived.

**Table I. Kinetic parameters in the absence and presence of Ti$^+$.**

<table>
<thead>
<tr>
<th>Condition</th>
<th>$a$, $i_l$/μA/cm$^2$</th>
<th>$k_3$ (mol/cm$^2$s)</th>
<th>$k$ (mol/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of Ti$^+$</td>
<td>0.54</td>
<td>18</td>
<td>$6.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>In the presence of Ti$^+$</td>
<td>0.58</td>
<td>1.7</td>
<td>$2.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

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**LIST OF SYMBOLS**

- $a$: $F/RT$, a constant, V$^{-1}$
- $b$: $L/(FD)$, a constant, equiv A cm$^{-1}$
- $c_0$: surface hydrogen concentration, mol cm$^{-3}$
- $D$: hydrogen diffusion coefficient, cm$^2$s$^{-1}$
- $E_{ap}$: applied potential, V
- $E_c$: cathodic potential, V
- $E_{eq}$: equilibrium potential for the h.e.r., V
- $f$: $\sqrt{RT}$, variable, dimensionless
- $F$: Faraday constant, 96,487 C/equiv
- $L$: membrane thickness, cm
- $i_e$: exchange current density, A/cm$^2$
- $i_i$: mass-transfer limiting current density, A/cm$^2$
- $i_i$: cathodic current density, A/cm$^2$
- $i_r$: recombination current density, A/cm$^2$
- $i_o$: initial hydrogen permeation current density, A/cm$^2$
- $i_o$: steady-state hydrogen permeation current density, A/cm$^2$
- $k_{ads}$: absorption rate constant, mol (cm$^2$s)$^{-1}$
- $k_{ads}$: adsorption rate constant, cm$^{-1}$
- $k_r$: recombination rate constant, mol (cm$^3$s)$^{-1}$
- $\eta$: thickness dependent absorption-adsorption con-
\[ \frac{\text{constant}, k^*}{\text{mol cm}^{-2} \text{s}} = \frac{k_{\text{ads}}}{k_{\text{ads}}} + \frac{D/L}{R} \text{for Langmuir isotherm, mol cm}^{-2} \]

\[ k^* = k_{\text{ads}}e^{-\theta_h} + \frac{D/L}{R} \text{thickness dependent absorption-adsorption constant for Temkin isotherm, mol cm}^{-2} \]

\[ R \] gas constant, \(8.3143 \text{ J (g-mol K)}^{-1}\)

\[ T \] temperature, K

Greek

\[ \alpha \] transfer coefficient, dimensionless

\[ \theta_e \] hydrogen surface coverage at equilibrium, dimensionless

\[ \theta \] the hydrogen surface coverage, dimensionless

\[ \eta \] overvoltage, \([E_{\text{app}} - E_{\text{eq}}]\), V

\[ \gamma \] gradient of the apparent standard free energy of adsorption with hydrogen coverage, \([\text{g-mol}]^{-1}\)

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