

Effect of Halide Ions on Hydrogen Entry Efficiency into Steel Sheet

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In this study, hydrogen permeation currents were investigated in hydrogen permeation tests for NaCl solutions at different concentrations to clarify the effect of chloride ion on hydrogen entry into the steel sheet. Hydrogen permeation currents for bromide and iodide ions were also investigated in the same test to determine the effect of halide ion species on hydrogen entry. The amount of hydrogen entry increased with increasing chloride ion concentration in hydrogen permeation tests due to an increase in the amount of chloride ions adsorbed on the steel sheet surface, which prevented hydrogen atoms from bonding with each other. It was also found that hydrogen entry was higher in bromide and iodide ion environments than in the chloride ion environment. According to the HSAB rule, bromide and iodide ions are considered to have stronger adsorption with the steel sheet surface than chloride ions, preventing bonding between hydrogen atoms more than chloride ions.

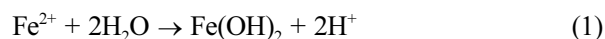
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1. Introduction

In line with the Japanese government's declaration of carbon neutrality in 2050, the automobile industry has set a target of reducing CO₂ emissions by 35% by 2030 (compared to 2013) [1]. One of the efforts to achieve this goal is to reduce the weight of the vehicle body, and one of the issues with steel materials is to achieve both weight reduction (thinner wall) and collision safety performance. To achieve these goals, we are currently working on the development of high-strength steel sheets (high-tensile steel). However, it is generally known that the higher the strength of the steel sheet, the higher the risk of hydrogen embrittlement cracking with a smaller amount of hydrogen penetration [2]. One of the factors that cause hydrogen embrittlement cracking is hydrogen generated on the cut end surface (exposed base iron) of parts when the automobile is running in a real environment. This hydrogen is generated by the corrosion (oxidation) of the bare iron exposed portion of the cut end face and the reduction of H⁺ produced by the hydrolysis reaction of the eluted iron ions. Then, after being adsorbed onto the bare steel substrate, part of it penetrates the steel, leading to

hydrogen embrittlement cracking. Therefore, suppressing the penetration of hydrogen into steel during corrosion is one of the issues for promoting high strength.

For example, it is known that high concentrations of chloride ions in the environment promote hydrogen penetration into steel sheets. This phenomenon can be attributed to two phenomena: Hypothesis (1): The amount of hydrogen atoms generated increases due to the promotion of the cathode reaction, and Hypothesis (2): The hydrogen entry efficiency increases due to the presence of ion species. Hypothesis (1) has been examined in the past. For example, according to Ref. [3] when the amount of hydrogen permeation into the steel sheet was evaluated at different temperatures and relative humidity in corrosive environment (during repeated dry-wet tests), the hydrogen permeation current increased at a medium humidity of 60% relative humidity [3]. This is because chloride ions in the water film present on the test piece are relatively concentrated when the humidity is lowered from high to medium humidity, so that the hydrolysis reaction of ferrous ions in (1) below proceeds.



As a result, pH drops. So, it is considered that the

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hydrogen permeation current increases because the amount of hydrogen atoms generated increases.

On the other hand, regarding the increase in the hydrogen entry efficiency of hypothesis (2), it is possible that ions adsorb to the steel sheet surface and suppress gasification due to surface diffusion of hydrogen atoms. There is also a literature that increases the hydrogen entry efficiency due to this hypothesis (2) [4]. In Ref. [4], iodide ion, one of the halide ions, is used as the efficiency promoters. However, there has been no investigation of this phenomenon for ion species such as chloride ions that exist in corrosive environments.

To study the suppression of hydrogen penetration during corrosion, it is necessary to clarify the effects of corrosive environmental factors (temperature, humidity, ion species, etc.) on hydrogen penetration. Therefore, in this study, first, the effect of chloride ions, which are typical ion species present in corrosive environments, on the hydrogen entry efficiency was investigated by hydrogen permeation tests using constant current electrolysis. Furthermore, in order to systematically organize the effects of chloride

ions on the hydrogen entry efficiency, similar tests were carried out on halide ions such as bromide ions and iodide ions, and comparative studies were conducted.

2. Experiments

2.1 Specimen preparation

In the hydrogen permeation test, 0.225 mm Al-killed steel was used as the test piece. After shear cutting to 125 mm (L) × 100 mm (C), Ni electroplating with current density of 4 A/dm², plating area of 36 cm², target Ni coating weight: 0.89 g/m² (0.1 μm thickness) in the plating bath shown in Table 1 was applied to one side as the test piece.

2.2 Hydrogen permeation test

The set-up, represented in Fig. 1, consisted of two double cells with the sample that the area in contact with the electrolyte was 19.63 cm² per side clamped in between. The non-plated surface is hydrogen-charged side, and the Ni-plated surface is hydrogen-extracted side. On the hydrogen-charged side, electrolytic solution is 1M, 5M-NaCl, 1M-NaBr and NaI aqueous solution, counter electrode is platinum wire, reference electrode is Ag/AgCl electrode (saturated KCl solution). Electrolysis was performed at a constant current of 0.1 mA/cm² on the hydrogen charge side, and then changed to 1.0 mA/cm² after the current on the hydrogen extraction side stabilized. In this case, the current was applied so that the steel surface was the cathode and the hydrogen atom

Table 1. The composition of Ni plating bath

NiSO ₄ ·6H ₂ O (g/L)	250
NiCl ₂ ·6H ₂ O (g/L)	45
B(OH) ₃ (g/L)	30
pH	4
Bath temperature (°C)	50

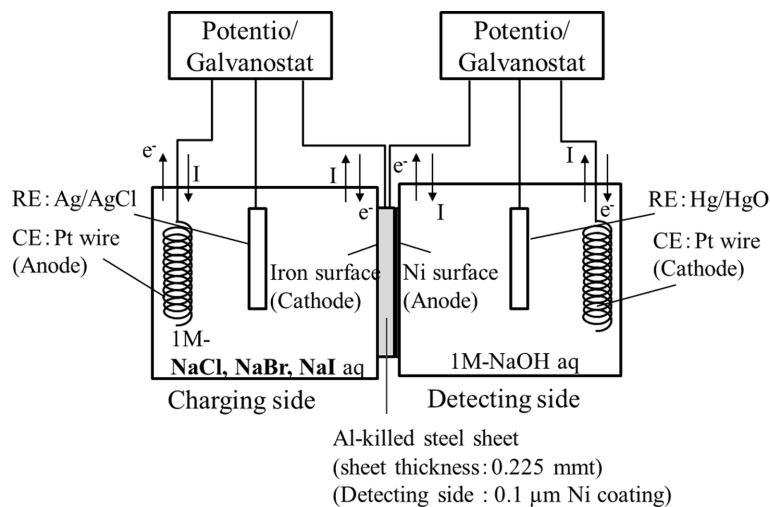


Fig. 1. Schematic diagram of hydrogen permeation test

generation reaction proceeded on the steel surface. The direction of charge current and electron is shown in Fig. 1. This charge current increase/decrease operation was repeated three times, and the hydrogen permeation current density obtained during the third increase operation was evaluated. The operation of repeating the increase and decrease of the charge current in the hydrogen permeation test is to fill the hydrogen trap sites that originally existed in the steel sheet [5]. The reason why the charging was continued at a low current (0.1 mA/cm^2) is that the corrosion reaction of iron is suppressed by using the steel sheet surface as a cathode, and the surface condition is kept as low as possible. On the hydrogen extraction side, a 1M-NaOH aqueous solution was used as the electrolyte, a platinum electrode was used as the counter electrode, and a Hg/HgO electrode (electrode for alkali) was used as the reference electrode. The hydrogen extraction side was subjected to constant potential electrolysis at 0.1 V vs. Hg/

HgO. In this case, the potential was applied so that the Ni coating surface was the anode and the reaction of hydrogen ion generation proceeded on the Ni coating surface.

3. Result

Fig. 2 shows the measurement results of hydrogen permeation current density in NaCl baths with different concentrations. Furthermore, the hydrogen entry efficiency is shown beside each caption. The hydrogen entry efficiency was calculated by the method shown in the following formula (2) with respect to the hydrogen permeation current density obtained during the third increasing operation for each solution.

$$\begin{aligned} &\text{Hydrogen entry efficient [\%]} \\ &= \frac{\text{Hydrogen permeation current density } [\mu\text{A}/\text{cm}^2]}{\text{Charge current density } [\mu\text{A}/\text{cm}^2]} \quad (2) \end{aligned}$$

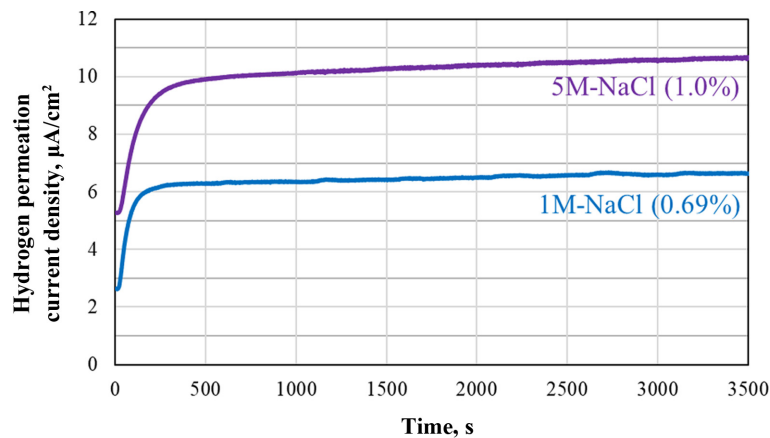


Fig. 2. Hydrogen permeation current density of NaCl

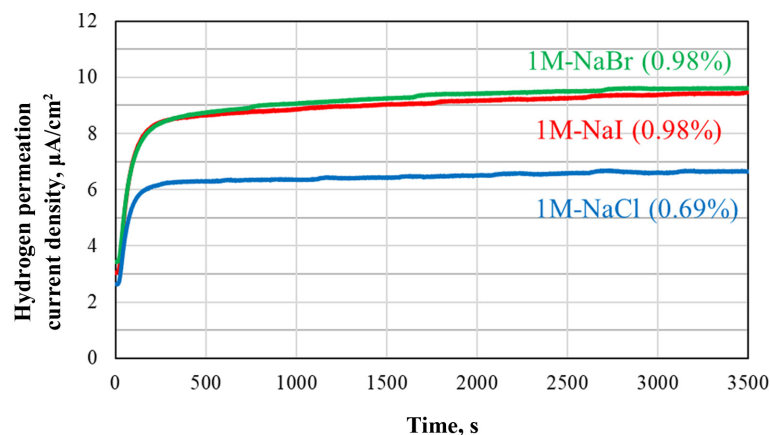


Fig. 3. Hydrogen permeation current density of NaCl, NaBr, NaI

This value indicates the ratio of how much hydrogen permeation current (the amount of hydrogen permeation) was detected to the charge current (the amount of hydrogen entry). The higher the chloride ion concentration, the greater the hydrogen permeation current density and the hydrogen entry efficiency.

Fig. 3 shows the measurement results of hydrogen permeation current in NaCl, NaBr, and NaI baths of the same concentration. Similarly, the hydrogen entry efficiency is shown beside each caption. The hydrogen permeation current density and the hydrogen entry efficiency of NaBr, NaI baths were greater than NaCl bath.

4. Discussion

4.1 Effects of chloride ion concentration on hydrogen entry efficiency

First, the effect of chloride ion concentration on hydrogen permeation current density and hydrogen entry efficiency is discussed.

When the Cl^- concentration is low (Fig. 4, left), the hydrogen ions in the solution react with the electrons on the steel surface (cathode) and the hydrogen atoms are generated, which are then adsorbed on the steel surface. It is thought that this is an environment in which the hydrogen atoms are likely to bond (gasification) due to surface diffusion. In other words, it is considered that the

hydrogen permeation current density is low, and the hydrogen entry efficiency is also low because a large proportion of the hydrogen atoms produced by the reduction are gasified and the amount of hydrogen that enters the steel is small. On the other hand, when the Cl^- concentration is high (Fig. 4, right), a large amount of Cl^- is adsorbed on the steel surface. This is an environment where the hydrogen atoms generated by the reduction are physically inhibited from diffusing to each other by the chloride ions adsorbed on the steel surface, making it more difficult for them to bond than in the case of low Cl^- concentrations. The hydrogen permeation current density is higher because the gasification ratio of the hydrogen atoms generated by reduction is lower and more hydrogen atoms enter the steel. In other words, it is thought that the effect of suppressing gasification of hydrogen such as iodide ion and thiocyanate ion (I^- , SCN^-) in the past knowledge can occur even in environment where Cl^- are present [4,6].

4.2 Effects of halide ion concentration on hydrogen entry efficiency

Next, a comparison of hydrogen permeation currents with halide ions is considered.

The hydrogen permeation current of NaBr, NaI is greater than that of NaCl, and it can be said that the Cl^- environment is the most likely to gasify. Following the

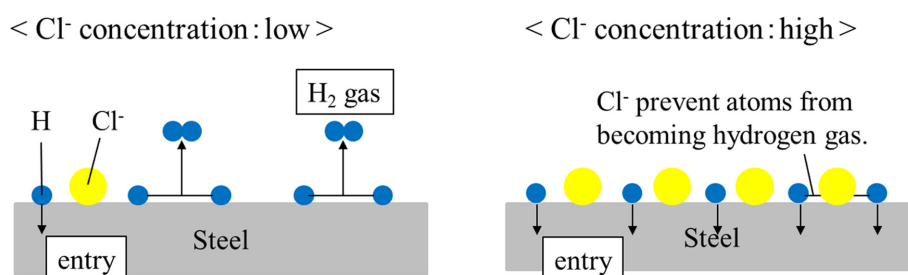


Fig. 4. Schematic diagram of reduced hydrogen entry in NaCl of different concentrations

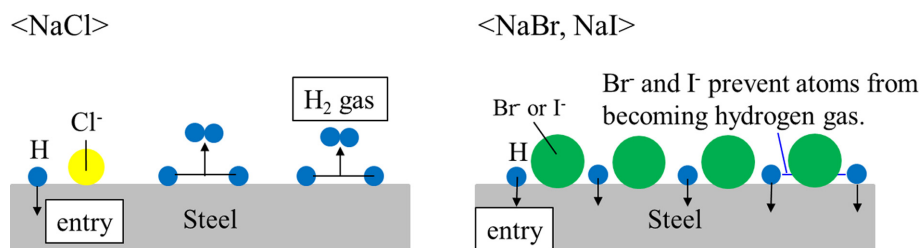


Fig. 5. Schematic diagram of reduced hydrogen entry due to different halide ions

same approach as in Fig. 4 for this result, a model like that shown in Fig. 5 can be considered. First, in the NaCl bath (Fig. 5, left), the coverage of the steel surface by Cl⁻ is low and the hydrogen atoms are considered to be likely to bond (gasify) by surface diffusion. In other words, it is considered that the hydrogen permeation current density is low, and the hydrogen entry efficiency is also low because a large proportion of the hydrogen atoms produced by the reduction are gasified and the amount of hydrogen that enters the steel is small. On the other hand, in the NaBr and NaI baths (Fig. 5, right), the coverage of Br⁻ and I⁻ is high. This is considered to be an environment where the hydrogen atoms on the steel surface are difficult to bond according to the same model as in Fig. 4, right. In other words, compared to Cl⁻, the hydrogen permeation current density was high because the gasification ratio of the hydrogen atoms generated by reduction was low, and more hydrogen enter the steel.

One hypothesis for why this difference in adsorption state of NaBr, NaI and NaCl occurs can be considered using the HSAB theory (hard and soft, acids and bases theory).

The HSAB theory is a rule that categorizes acids and bases into “hard” and “soft” according to the ease of deformation and derives the adsorption stability of acids and bases empirically [7]. Halide ions and iron (metal) in this study are classified as shown in Table 2. In this test, when the steel surface is a metallic iron, the adsorption force of Br⁻ and I⁻ to the steel surface is stronger than that of Cl⁻.

Fig. 6 shows the charge potential and pH of this test. It changes at about 1.2 V in any bath. The state of iron can be estimated by comparing the potential and pH during hydrogen charging to the pourbaix diagram of iron.

Fig. 7 shows the pourbaix diagram of iron and the potential (red line), pH (yellow area) of each bath after the test. The vertical axis was converted to Ag/AgCl electrode in order to match Fig. 6. This indicates that the steel surface during the hydrogen permeation test may have been in the Fe region. therefore, it can be said that the hypothesis of the adsorption force using the HSAB theory agrees with respect to the differences between Br⁻, I⁻ and Cl⁻.

In this study, the cause of the increased hydrogen entry was estimated by the hypothesis using HSAB theory.

Table 2. Table of HSAB theory

	Hard Bases Cl ⁻	Medium Bases Br ⁻	Soft Bases I ⁻
Soft Acids Fe	Weak adsorption	Medium adsorption	Strong adsorption

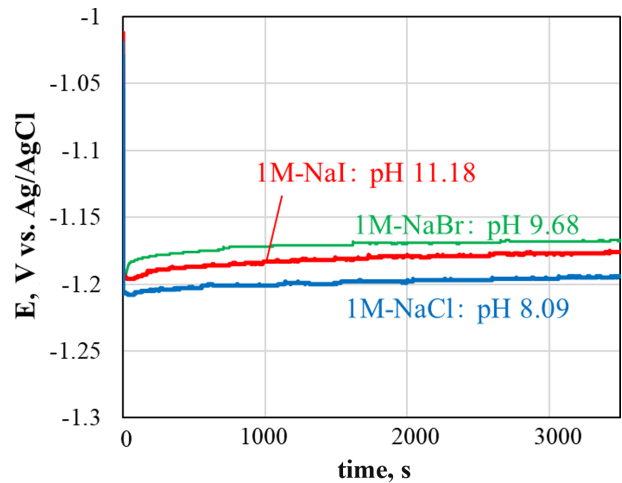


Fig. 6. Potential and pH of each bath during the test

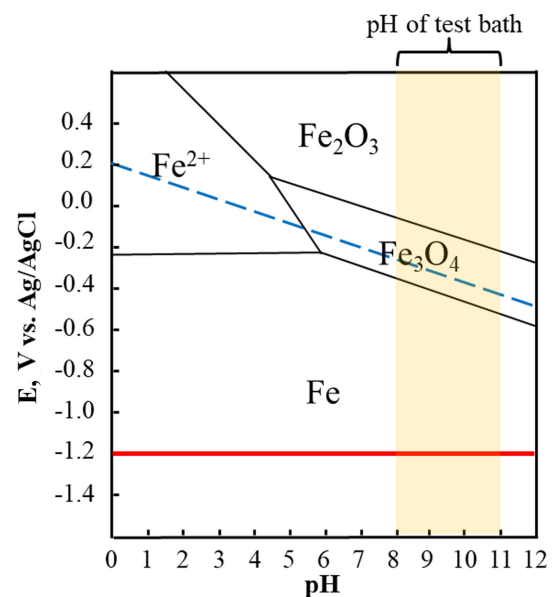


Fig. 7. Pourbaix diagram of iron in aqueous solutions

However, another hypothesis, for example, such as the effect of ionic radius, is also possible. The radius of halide ions is Cl⁻:1.81 Å, Br⁻:1.96 Å, I⁻:2.20 Å [8]. The radius of Br⁻ and I⁻ is larger than that of Cl⁻. It is also possible that the surface diffusion of hydrogen atoms is inhibited by the larger ionic radius when these ions are adsorbed at

the same concentration on the steel surface. Therefore, the previously mentioned the steel surface during hydrogen permeation test and the adsorption force of halide ions, as well as other possible interactions with hydrogen ions, will continue to be examined in the future.

5. Conclusion

In this study, the effects of environmental Cl^- on the hydrogen entry efficiency into steel sheet were investigated by hydrogen permeation tests using constant current electrolysis, and the following findings were obtained.

1) The higher the Cl^- concentration, the higher the hydrogen permeation current density and the hydrogen penetration efficiency.

From this result, it was found that the higher the Cl^- concentration, the more hydrogen permeated into the steel sheet by the ions themselves, regardless of the exposure of the steel sheet to the corrosive environment. The mechanism is presumed to be that when the Cl^- concentration is high, the amount of Cl^- adsorbed on the steel sheet surface increases, inhibiting the surface diffusion of H atoms, thereby suppressing the gasification of H atoms (promoting their penetration).

Furthermore, in order to systematically organize the effects of chloride ions on the hydrogen entry efficiency, similar tests were conducted on halide ions such as bromide ions and iodide ions, and the following findings were obtained.

2) In the halide ion bath, the hydrogen permeation current density and the hydrogen entry efficiency were NaBr bath, NaI bath $>$ NaCl bath.

From this result, it is estimated that the surface coverage of the steel sheet by halide ions is Br^- , $\text{I}^- >$ Cl^- . According to the HSAB theory, when the steel surface is a metallic

iron, the adsorption force of Br^- and I^- to the steel surface is stronger than that of Cl^- . Comparison of the pourbaix diagram of iron and the potential, pH of each bath after the test suggests that the steel surface during the hydrogen permeation test may have been in the Fe region. Therefore, it can be said that the hypothesis of the adsorption force using the HSAB theory agrees with respect to the differences between Br^- , I^- and Cl^- .

References

1. Nippon Steel Corporation, Nippon Steel Quarterly, Vol.12, pp.4-7 (2022).
2. S. Matsuyama, Delayed Destruction (1989)
3. T. Omura, Title, *Surface Technology*, **71**, 336 (2020).
4. E. G. Dafft, K. Bohnenkamp and H. J. Engell, Investigations of the hydrogen evolution kinetics and hydrogen absorption by iron electrodes during cathodic polarization, *Corrosion Science*, **19**, 591 (1979). Doi: [https://doi.org/10.1016/S0010-938X\(79\)80130-4](https://doi.org/10.1016/S0010-938X(79)80130-4)
5. H. Ieguchi, N. Fujiwara, T. Iwata, Evaluation on the effect of hydrogen in metals on material characteristics, *Copernicus*, **42**, 1 (2014). https://www.kobelcokaken.co.jp/tech_library/2014/20141201.html
6. J. O'M Bockris, J. McBreen, and L. Manis, The Hydrogen Evolution Kinetics and Hydrogen Entry into α -Iron, *Journal of The Electrochemical Society*, **112**, 1025 (1965). Doi: <https://doi.org/10.1149/1.2423335>
7. K. Aramaki, Action of Metallic Corrosion Inhibitors and the Hard and Soft Acids and Bases Principle, *Zairyo-to-Kankyo*, **45**, 674 (1996). Doi: <https://doi.org/10.3323/jcorr.1991.45.674>
8. R. D. Shannon and C. T. Prewitt, Effective ionic radii in oxides and fluorides, *Acta Crystallographica Section*, **B25**, 925 (1969). Doi: <https://doi.org/10.1107/S0567740869003220>