

Characterization of Water-Filled Ag/AgCl Reference Electrode

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Abstract. Pressure-balanced external Ag/AgCl electrode has been extensively used for both Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) environments. The use of KCl-based buffer solution often becomes the source of electrode potential drift due to slow leakage through its porous plug, typically made of zirconia. It is reported that results of our effort to improve the stability of electrode potential by using high purity water as the filling solution in which Cl^- ion activity can be established and maintained at the solubility of AgCl even with the sustained leakage for a long period. Stability tests have been made in boron and lithium mixture solution at 288°C. The electrode potential remained stable within 10 mV over one week period. And after a thermal cycle between 288 to 240°C the potential shift of Ag/AgCl electrodes did not exceed 15 mV. By using the limiting equivalent ionic conductances and Agar's hydrodynamic theory, the thermal liquid junction potential (TLJP) of the electrode has been predicted. The calculated values for the water-filled Ag/AgCl electrode potential, in which the chlorine concentration in the filling solution was derived from the measured data at ambient temperature, had a good agreement with the experimental values.

초 록 : 외부 Ag/AgCl 기준 전극은 가압형 및 비등형 경수로 환경에 널리 사용되었다. 전극의 채움 용액 (filling solution)으로 통상 KCl을 사용하는데, 다공성 지르코니아로 만들어 지는 플러그를 통한 Cl^- 이온의 누설이 전극의 전위차 변동을 유발하는 문제가 있다. 누설로 인한 전위차 변동의 문제를 해결하기 위해 채움 용액으로 순수를 사용하였다. 순수를 사용하는 경우 상온에서의 AgCl 용해도에 의해 Cl^- 이온의 농도가 결정된다. 붕산과 수산화리튬 혼합용액으로 288°C에서 전극의 안정성 실험을 실시하였다. 약 일주일간 전위차 변화는 10 mV 이내였으며, 288°C와 240°C에서의 온도 사이클링 시험 전후의 전위차 변화는 15 mV 이내였다. 이온의 limiting equivalent conductances와 Agar의 수역학적 이론을 토대로 하여 전극의 TLJP를 계산하였다. 전극 채움 용액 내의 Cl^- 이온 농도를 상온에서 측정된 값으로 보정하여 이론값을 계산할 경우, 실험값과 비교적 잘 일치하는 것을 알 수 있었다.

Key words : High temperature electrochemistry, Ag/AgCl electrode, Thermal liquid junction potential, Entropy of transport, Agar's hydrodynamic theory

1. Introduction

The corrosion of structural metals in PWR operating water is the primary causes of the degradation and fouling of steam generator (SG), piping, and turbine. As the results of extensive research during the past two decades, it is now possible to predict the corrosion behavior of metals as function of electrochemical corrosion potential (ECP) and pH.¹⁾ For this purpose, it is necessary to develop reference electrodes for condition monitoring and life management of the secondary system of PWR.

The role of a reference electrode is to measure the potential of a particular electrode with stability and reproducibility. A major decision in all high temperature electrochemical studies in an aqueous system is to choose a suitable reference electrode.²⁾ Ag/AgCl reference electrode is well-defined, widely used, and very reliable electrode for high temperature work.³⁻¹⁰⁾ But in a reducing environment at high

temperature, especially when the AgCl surface is not well protected, the decomposition rate of AgCl is very high.⁸⁾ To solve this problem the external reference electrode of which AgCl part was maintained at ambient temperature was developed. Pressure-balanced external Ag/AgCl electrode has been extensively used for both PWR and BWR environments.^{8,9)} The use of KCl-based buffer solution often becomes the source of electrode potential drift due to slow leakage through its porous plug, typically made of zirconia.

2. Rationale and Approach

Fig. 1 shows the schematic of rationale and approach of our Ag/AgCl electrode development. At 288°C, the potential of Ag/AgCl electrode appeared to change with the dilution of Cl^- ion by more than 100 mV per month. It was assumed that the main paths of ion leakage were the gap between a porous plug and Teflon[®] tube and through the porous plug body itself. The leakage through the porous plug may be reduced by modifying the porosity or using a long plug or

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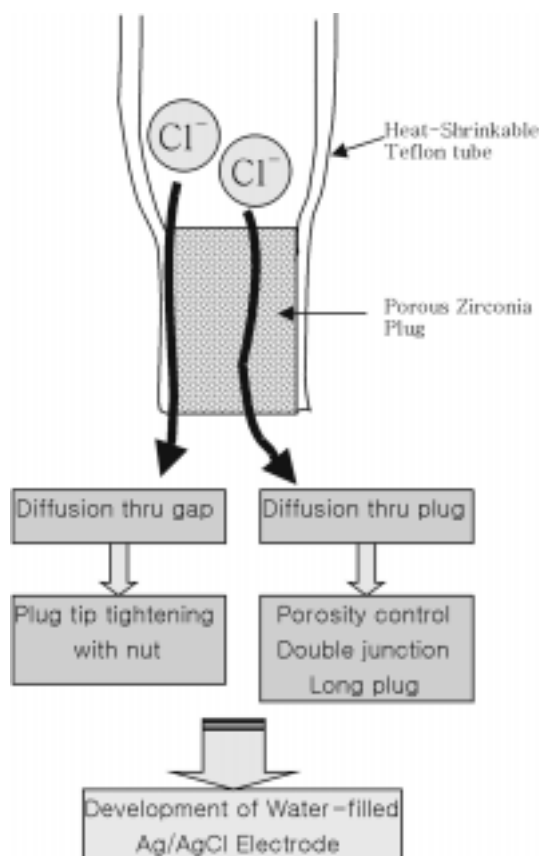


Fig. 1. Schematic of rationale and approach of water-filled Ag/AgCl development.

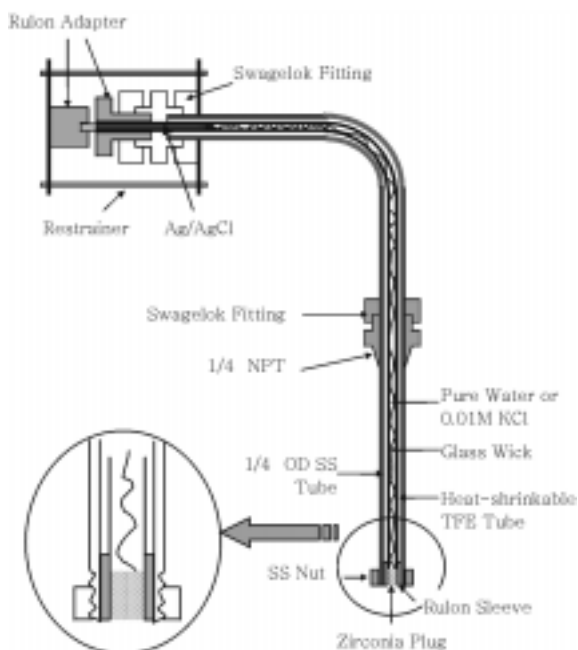


Fig. 2. Schematic of modified Ag/AgCl reference electrode.

double junction. But in this reference electrode design to reduce the leakage through the gap, the plug tip was tightened by means of the machined and threaded stainless steel (SS)

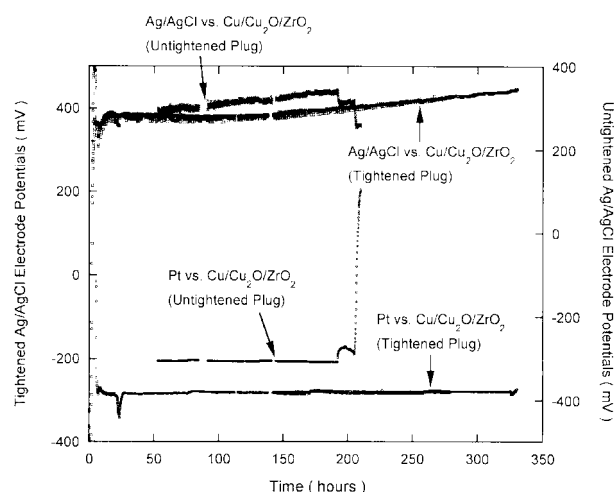


Fig. 3. Plug tip tightened Ag/AgCl electrode potential variation as a function of time in comparison to untightened Ag/AgCl electrode potential.

tube, Rulon[®] sleeve, and a nut. Fig. 2 shows the schematic of the modified Ag/AgCl electrode design, which is based on Danielson's electrode design.⁵⁾ Fig. 3 shows the test results for the plug tip tightened Ag/AgCl electrode potential variation with time in comparison to the untightened one. From the results, plug tip tightening retarded the leakage but it was not enough to be qualified as the long-lived reference electrode for use in PWR. Therefore, it is reported that results of our effort to improve the stability of electrode potential by using high purity water as the filling solution in which Cl⁻ ion activity can be established and maintained at the solubility of AgCl even with the sustained leakage for a long period.

3. Experimental

The performance and life tests for the water-filled Ag/AgCl electrode have been conducted. To protect the penetration seals from high temperature, the autoclave was turned upside down. A refreshed water system was used with a charging/bleeding rate of about 1 L/hr for the loop of which an estimated water volume was about 4 L. Overall flow diagram for the test loop is shown in Fig. 4. Two water-filled Ag/AgCl electrodes and two platinized Pt electrodes were installed with a Cu/Cu₂O/ZrO₂ electrode. To maintain a reducing environment, the solution supply tank was pressurized by 5% hydrogen gas (95% nitrogen) at 2.0 atm. The pH of test solution was controlled by adjusting boric acid (H₃BO₃) and lithium hydroxide (LiOH) or potassium hydroxide (KOH) concentrations.

4. Experimental Results

Fig. 5 shows the experimental results for the effect of temperature on water-filled Ag/AgCl electrode potential. A solution composed of 0.01 M boric acid and 0.001 M potassium hydroxide was used as test solution. Solution temperature maintained as sequence 200, 225, and 250°C. Ag/AgCl elec-

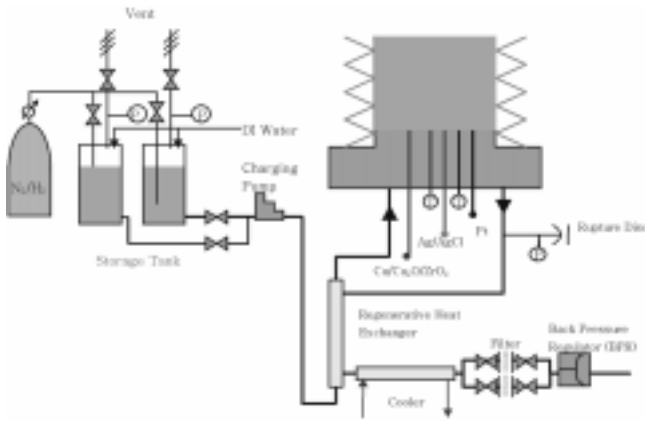


Fig. 4. Schematic of electrode life and performance test loop.

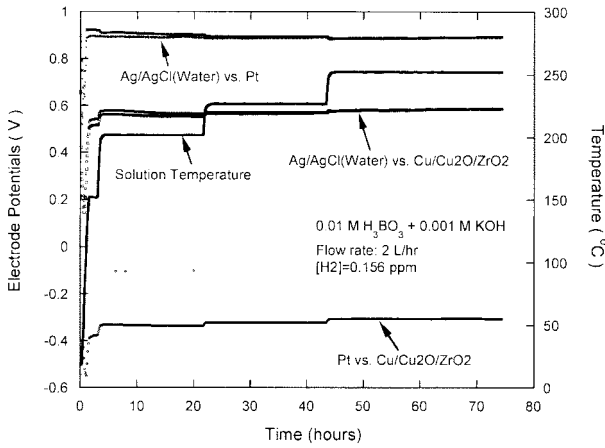


Fig. 5. Test results for the effect of temperature on water-filled Ag/AgCl electrode potential.

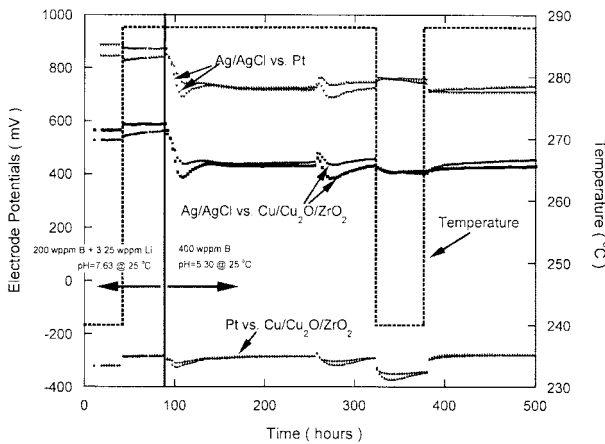


Fig. 6. Test results for the long-term stability of water-filled Ag/AgCl electrode potential.

trode potentials versus platinum and Cu/Cu₂O/ZrO₂ electrodes were measured with temperature variation. Based on these results, it is possible to calculate the potential of Ag/AgCl electrode vs. SHE(T) as a function of temperature. The derived equation can be used as the calibration results of a water-filled Ag/AgCl electrode.

Fig. 6 shows test results for the long-term stability of water-filled Ag/AgCl electrode potential. A solution composed of 200 wppm boron and 3.25 wppm lithium was used until 90 hours elapsed. At that test period, solution temperature increased from 240 to 288 °C. Then the test solution was changed as 400 wppm boron to observe the dependency of Ag/AgCl electrode potential on solution pH. In 400 wppm boron solution, long-term stability test has been conducted at 288 °C. As shown in Fig. 6 the Ag/AgCl electrode potential remained stable within 10 mV over one week period. After a thermal cycle between 288 to 240 °C the potential shift of Ag/AgCl electrodes did not exceed 15 mV. It was found that the potential of the water-filled Ag/AgCl electrode showed a very stable behavior as was expected.

5. Calculation of Potential Difference Between Water-Filled Ag/AgCl vs. SHE(T)

Main focus in the development of the electrode was to improve the stability of electrode potential by using high purity water as the filling electrolyte in which Cl⁻ ion activity could be established by the solubility of AgCl even with the leakage problem. But to understand the fundamentals of electrode reaction and high temperature electrochemistry the potential difference between water-filled Ag/AgCl and SHE(T) needs to be calculated. The basic equation for calculation is adopted from the work of Macdonald et al..⁶⁾

$$\begin{aligned}
 E_{\text{water Ag/AgCl vs. SHE}(T)}(T) &= \Delta E_{\text{Ag/AgCl}}(T) - \Delta E_{Th} \\
 &= E_{\text{vs. SHE}}^{\text{Internal, Ag/AgCl}}(T) - \{ \Delta E \}_{298.15}^T + \Delta \phi_{TLJP, \text{AgCl}} \} \\
 &= E_{\text{Ag/AgCl}}^o(T) - 2.303 \frac{RT}{F} \log [\gamma_{\pm}(T) s(T)]_{\text{AgCl}} \\
 &\quad - \left\{ \Delta E^o \right\}_{298.15}^T - 2.303 \frac{RT}{F} \log [\gamma_{\pm}(T) s(T)]_{\text{AgCl}} \\
 &\quad + 2.303 \frac{R \cdot 298.15}{F} \log [\gamma_{\pm} s]_{298.15, \text{AgCl}} + \Delta \phi_{TLJP, \text{AgCl}} \} \\
 &= E_{\text{Ag/AgCl}}^o(T) - \left\{ \Delta E^o \right\}_{298.15}^T \\
 &\quad + 2.303 \frac{R \cdot 298.15}{F} \log [\gamma_{\pm} s]_{298.15, \text{AgCl}} + \Delta \phi_{TLJP, \text{AgCl}} \}
 \end{aligned} \quad (1)$$

In Eq. (1), $E_{\text{Ag/AgCl}}^o(T)$ is the standard potential of Ag/AgCl electrode with temperature, which is experimentally obtained by Greeley et al..¹¹⁾ And Greeley's equation is as below.

$$\begin{aligned}
 E_{\text{Ag/AgCl}}^o(T) &= 0.23735 - 5.3783 \times 10^{-4} T \\
 &\quad - 2.3728 \times 10^{-6} T^2, T(^{\circ}\text{C})
 \end{aligned} \quad (2)$$

$\Delta E^o \right\}_{298.15}^T$ is the difference between Ag/AgCl electrode vs. SHE at the temperature of T and Ag/AgCl electrode vs. SHE at 25 °C, and it can be calculated by using Macdonald's formula as described in Eq. (3).¹²⁾

$$\Delta E^o_{298.15} = -0.5879 + 0.005468T + 6.6351/T - 4.2452 \times 10^{-4} T \ln T - 3.8643 \times 10^{-6} T^2 \quad (3)$$

In Eq. (1), s denotes the solubility of AgCl and γ_{\pm} is the mean ionic activity coefficient of AgCl which can be calculated by using Debye-Hückel limiting law.¹³⁾

$$\log \gamma_{\pm} = (0.5092 L^{1/2} / \text{mol}^{1/2}) z_+ z_- I_c^{1/2} \text{ at } 25^\circ\text{C}$$

where $I_c = \frac{1}{2} \sum_i c_i z_i^2$.

$$\text{Then, } \log \gamma_{\pm, \text{AgCl}} = -0.5092 \sqrt{s_{\text{AgCl}}}$$

$$\text{where } s_{\text{AgCl}} = 1.25 \times 10^{-5} \text{ mol/kg at } 25^\circ\text{C}$$

In Eq. (4), z_+ and z_- denotes the charge number of cation and anion, respectively. I_c , c_i , and z_i are the ionic strength, the concentration and the charge number of the i th ion, respectively.

In Eq. (1), the final term, the thermal liquid junction potential (TLJP) of the water-filled Ag/AgCl electrode can be calculated by below equation.¹⁴⁾

$$\begin{aligned} \Delta \phi_{\text{TLJP, AgCl}} &= -\frac{1}{F} \int_{T_o}^T \sum_i \frac{t_i S_i^*}{z_i} dT \\ &= -\frac{1}{F} \int_{T_o}^T [t_{\text{Ag}^+} S_{\text{Ag}^+}^* + t_{\text{H}^+} S_{\text{H}^+}^* - t_{\text{Cl}^-} S_{\text{Cl}^-}^* - t_{\text{OH}^-} S_{\text{OH}^-}^*] dT \end{aligned} \quad (5)$$

where F , t_i , and S_i^* are Faraday constant, the transference number of ionic specie i , and the entropy of transport of ionic specie i , respectively. In an electrolyte solution that is homogeneous in concentration but with a temperature gradient, an internal electric field occurs almost instantaneously through the migration of ions due to the Soret effect. Corresponding to this electrostatic field there occurs an electric potential that is designated as the thermal diffusion potential.¹⁵⁾ After a time, concentration gradients also arise in the solution, which, in turn, leads to the diffusion potential.¹⁵⁾ In this paper, it is assumed to designate the sum of the thermal diffusion potential and the diffusion potential as the “thermal liquid junction potential”. When calculating TLJP it is supposed that the filling solution is composed of only four ionic species: Ag^+ , Cl^- , H^+ , and OH^- .

To calculate TLJP by using Eq (5), the entropy of transport must be known as a function of temperature. And the standard entropy of transport, which is valid only in the case of infinitely dilute solution, can be introduced from the Agar’s hydrodynamic theory to calculate the entropy of transport.¹⁶⁾

$$Q_i^{*o} = -T(e^2 z_i^2 / \epsilon^2) (\partial \epsilon / \partial T) 4 R_i \quad (\text{stick boundary condition}) \quad (6-1)$$

$$\text{where } R_i = kT / 6\pi\eta D_i \quad (\text{stick boundary condition}) \quad (6-2)$$

$$\text{Then, } Q_i^{*o} = -\frac{6\pi e^2 z_i^2 \eta D_i}{4k\epsilon^2} \frac{\partial \epsilon}{\partial T} \quad (6-3)$$

In Eq. (6-1), Q_i^{*o} denotes the standard heat of transport and T is temperature. e is the charge of electron and z_i is the charge number of ionic specie i . ϵ is the permittivity of water and R_i is the ionic radius. In the Agar’s hydrodynamic theory there are stick and slip boundary conditions for the hydrodynamic boundary conditions. The two boundary conditions yield values differed by 10%. Because it is impossible to know which one is more appropriate for this study from the two conditions and the main focus is to compare the calculated results with the experimental results, in this study stick boundary condition is employed arbitrarily. k is the Boltzmann constant and η is the viscosity of water. The self-diffusion coefficient D_i has the relationship with the limiting equivalent ionic conductance λ_i^o as below equation.¹³⁾

$$D_i = \frac{RT\lambda_i^o}{F^2 z_i^2} \quad (7)$$

Therefore, the standard heat of transport and entropy of transport can be expressed by the ionic conductance, the permittivity and viscosity of water, when Eq. (7) is inserted into Eq. (6-3).

$$\begin{aligned} Q_i^{*o} &= -\frac{6\pi e^2 z_i^2 \eta RT\lambda_i^o}{4k\epsilon^2} \frac{\partial \epsilon}{F^2 z_i^2 \partial T} \\ &= -\frac{3\pi e^2 z_i^2 \eta RT\lambda_i^o}{2kF^2 \epsilon^2} \frac{\partial \epsilon}{\partial T} \end{aligned} \quad (8)$$

$$S_i^{*o} = \frac{Q_i^{*o}}{T} = -\frac{3\pi e^2 R \eta \lambda_i^o}{2kF^2 \epsilon^2} \frac{\partial \epsilon}{\partial T} \quad (9)$$

Eq. (10) was used as the viscosity of water as a function of temperature. This equation was obtained by fitting the original data.¹⁷⁾

$$\begin{aligned} \eta(T) &= -0.051099 + 149.92/T - 1.8686 \times 10^5/T^2 \\ &\quad + 1.2841 \times 10^8/T^3 - 5.2562 \times 10^{10}/T^4 \\ &\quad + 1.2827 \times 10^{13}/T^5 - 1.7302 \times 10^{15}/T^6 \\ &\quad + 9.976 \times 10^{16}/T^7, \quad T(K) \end{aligned} \quad (10)$$

Eq. (11) was used to calculate the dielectric constant of water as a function of temperature.¹⁸⁾

$$\begin{aligned} \epsilon_r &= 5321/T + 233.76 - 0.9297T + 0.001417T^2 \\ &\quad - 8.292 \times 10^{-7} T^3, \quad T(K) \\ \epsilon_o &= 8.854 \times 10^{-12} \text{ C/V} \cdot \text{m} \\ \epsilon &= \epsilon_o \epsilon_r \end{aligned} \quad (11)$$

The data of the limiting equivalent ionic conductance was adopted from the work of Quist et al..¹⁹⁾ Fig. 7 shows the Quist’s original data and the fitted curves. And the coefficients of the polynomial fitted equations like Eq. (12) were tabulated at Table 1.

$$\lambda_i^o(T) = A + BT + CT^2 + DT^3, \quad T(K) \quad (12)$$

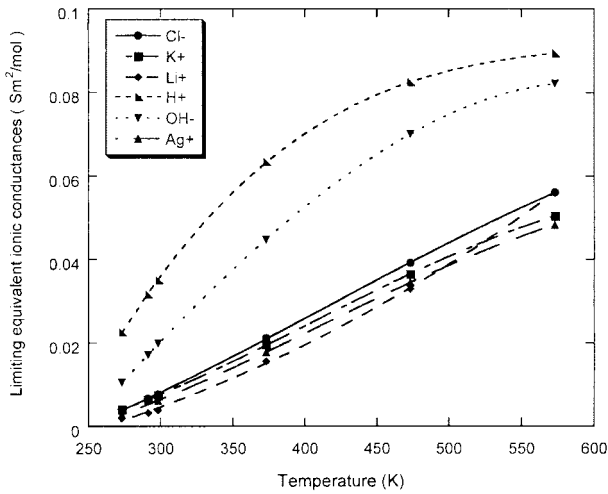


Fig. 7. Limiting equivalent ionic conductances of important ions as a function of temperature.¹⁹⁾

Table 1. The limiting equivalent ionic conductances of each ion¹⁹⁾

Ionic species	A	B × 10 ⁵	C × 10 ⁷	D × 10 ¹⁰
Cl ⁻	-0.015067	-4.9382	5.5471	-4.3961
K ⁺	0.006945	-21.033	9.4067	-7.702
Li ⁺	-0.020571	5.1822	0.6934	1.2878
Ag ⁺ 1)	0.0055	-20.007	8.9473	-7.2516
H ⁺	-0.27596	175.15	-28.435	15.698
OH ⁻	-0.092911	33.085	3.7546	-7.3268

1) From other work.²⁰⁾

As like Eq. (13), the standard entropy of transport can be expressed by the viscosity of water, dielectric constant of water, and the limiting equivalent ionic conductances of ionic species.

$$\begin{aligned}
 S_i^{*o} &= -\frac{3\pi e^2 R \eta \lambda_i^o}{2kF^2} \frac{\partial \epsilon}{\partial T} \\
 &= -\frac{3\pi e^2 R \eta \lambda_i^o}{2kF^2 \epsilon_o} \frac{\partial \epsilon_r}{\partial T} \quad [J/K] \\
 &= -\frac{3\pi e^2 N_A^2}{2F^2 \epsilon_o} \frac{\eta \lambda_i^o}{\epsilon_r^2} \frac{\partial \epsilon_r}{\partial T} \quad [J/mol \cdot K] \\
 &= -\frac{3\pi (1.602 \times 10^{-19} C)^2 (6.02 \times 10^{23}/mol)^2}{2(96485 C/mol)^2 (8.854 \times 10^{-12} C/V \cdot m)} \frac{\eta \lambda_i^o}{\epsilon_r^2} \frac{\partial \epsilon_r}{\partial T} \\
 &= -5.3174 \times 10^{11} \frac{\eta \lambda_i^o}{\epsilon_r^2} \frac{\partial \epsilon_r}{\partial T} \quad [J/mol \cdot K]
 \end{aligned} \quad (13)$$

As well as the entropy of transport, to calculate the TLJP from Eq. (5), the transference number of ionic species must be also known. And it can be calculated by using the below equation.¹⁴⁾

$$t_i = \frac{|z_i| \lambda_i^o c_i}{\sum_i |z_i| \lambda_i^o c_i} \quad (14)$$

The concentration of each ion c_i was calculated in molal

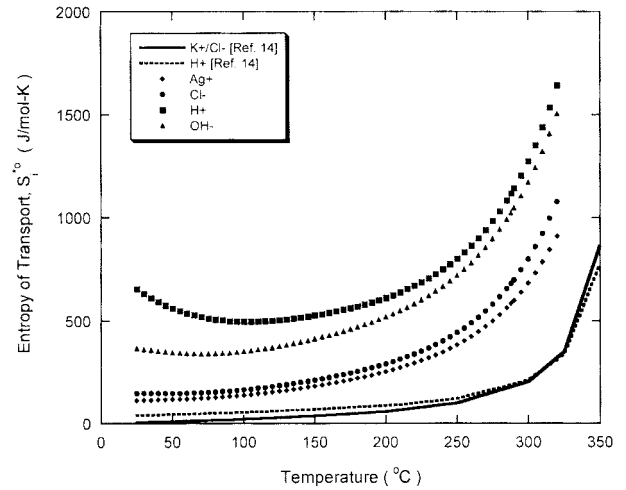


Fig. 8. Calculated values of the standard entropies of transport for important ions in comparison to the referenced values.

unit. The dissociation constant of water was introduced to calculate the concentration of H⁺ and OH⁻ as a function of temperature. Eq. (15) is the fitted equation from the original data.²¹⁾ It is assumed that except H⁺ and OH⁻ other ions such as Ag⁺, Cl⁻, and K⁺ have the constant molal concentration even if the solution temperature varies.

$$\begin{aligned}
 \log K_w &= -52.023 + 0.28552T - 0.00078946T^2 \\
 &\quad + 1.0284 \times 10^{-6}T^3 - 5.302 \times 10^{-10}T^4, \quad T(K)
 \end{aligned} \quad (15)$$

6. Calculation Results & Discussion

Fig. 8 shows the calculation results of the standard entropies of transport for considered ions as a function of temperature in comparison to Lvov's data.¹⁴⁾ The calculated values are larger than the Lvov's data. Also, the calculation results show that the ion-to-ion variation is much larger than the results of reference case. The equation used to calculate the standard entropies of transport is dependent on the limiting equivalent ionic conductance of each ion. Furthermore the ion-to-ion variation of S_i^{*o} is only dependent on the limiting equivalent ionic conductance. But in the case of the reference values, by combing the measured initial and stationary state thermoelectric powers of the cells incorporating Ag/AgCl electrodes and aqueous NaCl, KCl solutions, the standard entropies of transport have been derived and extrapolated by employing Agar's hydrodynamic theory.²²⁾ This feature seems to make such difference.

Fig. 9 shows the results of the calculated TLJP with variation of compositions and concentrations of the filling solution. In the case of AgCl, TLJP increases with the increase of the solution concentration. In Fig. 9, '1.25 × 10⁻⁵ m AgCl' corresponds to the solubility of AgCl at the ambient temperature. To be compared with an experimental result, the case of '5 × 10⁻⁵ m KCl' is also calculated. Fig. 10 shows the calculation results based on Eq. (1) for the potential of Ag/AgCl vs. SHE(T) in comparison to the experimental results.

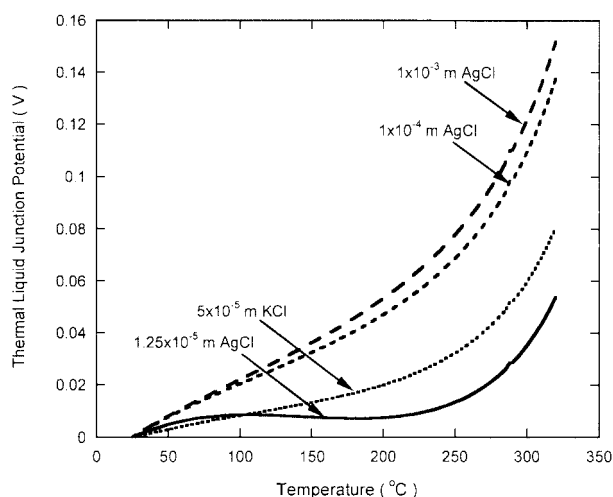


Fig. 9. The calculated values of the thermal liquid junction potential with variation of the compositions and concentrations of the filling solution.

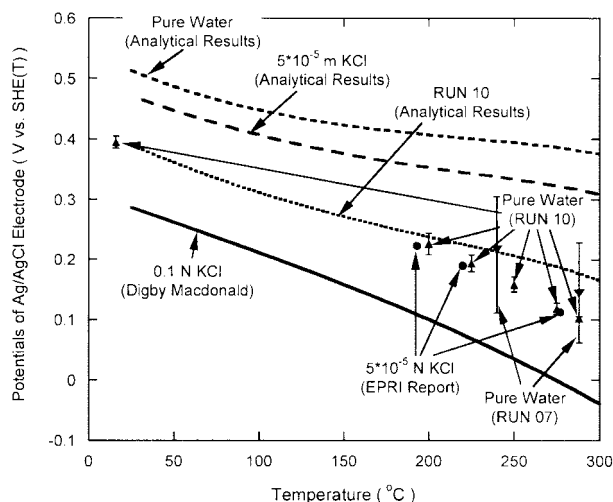


Fig. 10. The calculated potential of Ag/AgCl reference electrode vs. SHE(T) as a function of temperature in comparison to the experimental results.

In Fig. 10, the three points denoted as ' 5×10^{-5} N KCl' were referenced from EPRI's experimental data.²³⁾ And the points denoted as 'Pure Water(RUN 10)' and 'Pure Water(RUN 07)' mean the two experimental results for the water-filled Ag/AgCl electrodes. As shown in Fig. 10, there is the large difference between the experimental results 'Pure Water (RUN 10)' and the analytical results denoted as 'Pure Water' and ' 5×10^{-5} m KCl'. The analytical result denoted as 'RUN 10' shows a similar behavior, but some different temperature dependency to the experimental results in comparison to other analytical results. The potentials of the water-filled Ag/AgCl electrodes used in 'RUN 10' experiment were measured versus the saturated calomel electrode (SCE) at 16°C and the value was $+140 \pm 10$ mV. The concentration of chlorine ion corresponding to the measured value was derived. And using the measured concentration the analytical result 'RUN 10' was calculated. The cause of the difference between the mea-

sured chlorine concentration and the theoretical one seems to be the chlorine contamination during the build-up of the electrode or the high solubility of the chloridized AgCl caused by a certain surface condition. In this calculation, it is supposed that the positive ion corresponding to the contaminated chlorine ion is silver ion. It can be verified by the analysis for the compositions of the positive ions in the filling solution. And the assumption that the concentrations of Ag^+ , Cl^- , and K^+ in the filling solution except H^+ and OH^- have the constant molal concentration, even if the solution temperature varies, needs to be verified by other methods.

7. Summary and Conclusions

From the experiment and analysis for water-filled Ag/AgCl reference electrode, following conclusions are made.

- 1) To improve the stability of a reference electrode, the water-filled Ag/AgCl reference electrode has been developed.
- 2) The water-filled Ag/AgCl electrode potential remained stable within 10 mV over one week period. And after a thermal cycle between 288 to 240°C the potential shift of Ag/AgCl electrodes did not exceed 15 mV.
- 3) By using the limiting equivalent ionic conductances and Agar's hydrodynamic theory, the thermal liquid junction potential of the water-filled Ag/AgCl electrode has been calculated.
- 4) The calculated values for the water-filled Ag/AgCl electrode potential, in which the chlorine concentration in the filling solution was derived from the measured data at ambient temperature, showed a similar behavior to the experimental values.

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