

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. We report 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 at the solubility of AgCl despite of the leakage problem. Stability tests have been made in boron and lithium mixture solution at 288 °C. The electrode potential remained stable within ± 10 mV over two weeks period. A thermal cycling to 240 °C and back to 288 °C led to a potential shift not exceeding 15 mV. By using the limiting equivalent conductances and Agar's theory, the thermal liquid junction potential (TLJP) of the electrode has been predicted. Despite of its outstanding stability performance, the agreement between measured and predicted values for the water-filled Ag/AgCl electrode is not satisfactory, apparently due to uncertainty in the predicted electrochemical parameters.

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 ECP reference electrodes for condition monitoring and life management of the secondary system of a 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 appears to increase with the dilution of Cl⁻ ion by more than 100 mV per month. We believed that the main paths of ion leakage were the gap between plug and Teflon[®] tube and through the porous plug body itself. To reduce the leakage through the plug it can be introduced to modify the porosity or use a long plug or double junction. In our reference electrode design, the plug tip was tightened using the machined, threaded and split sleeve and a nut made of stainless steel. Fig. 2 shows the schematic of the modified Ag/AgCl electrode. Fig. 3 shows the comparison test results for the electrode with untightened and tightened plug, respectively. From the results, plug tip tightening retarded the leakage but it is not enough to be qualified as the long-lived reference electrode for use in PWR. Therefore, we report 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. Fig. 4 shows the schematic of experimental system. To protect the penetration seals from the high temperature we turned the autoclave upside down. A refreshed water system was used with a charging/bleeding rate of about 1 L/hr for the loop with an estimated water volume of 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 boron and lithium concentrations.

4. Experimental Results

4.1. Temperature Effect

Fig. 5 shows the experimental results for water-filled Ag/AgCl. A solution of 400 wppm boron and 0.75 wppm Li was used as test solution. Temperature was maintained at 288 °C and then 40 hours later, was brought down to 240 °C. Ag/AgCl potential vs. Cu/Cu₂O/ZrO₂ electrode showed a stable behavior over the entire test period.

4.2. Temperature & pH Effect

Fig. 6 shows test results for water-filled Ag/AgCl vs. temperature and pH. A solution of 200 wppm boron and 3.25 wppm lithium was used for first about 100 hours, then the test solution was changed as 400 wppm boron at 240 °C. Stability tests have been made in 400 wppm boron solution at 288 °C, using Cu/Cu₂O/ZrO₂ electrode as a primary reference. The electrode potential remained stable within ±10 mV over one week period. A thermal cycling to 240 °C and back to 288 °C led to a potential shift not exceeding 15 mV.

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

We have focused our effort to improve the stability of electrode potential by using high purity water as the filling electrolyte in which Cl⁻ ion activity can be established at the solubility of AgCl even with the leakage problem. The potential difference between water-filled Ag/AgCl vs. SHE(T) needs to be calculated. The basic equation for calculation is adopted from the work of Macdonald et al. [6].

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

where $E_{Ag / AgCl}^{\circ}(T)$ was obtained by Greeley et al. [11]. And Greeley's equation is as below.

$$E_{Ag / AgCl}^{\circ}(T) = 0.23735 - 5.3783 \times 10^{-4} T - 2.3728 \times 10^{-6} T^2, \quad T(^{\circ}C) \tag{2}$$

The calculation about $\Delta E^o \int_{298.15}^T$ was conducted using Macdonald's formula [12].

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

The activity coefficient for AgCl was calculated using Debye-Hckel limiting law [13].

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

$$\text{where } I_c = \frac{1}{2} \sum_i c_i z_i^2. \quad (4)$$

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

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

The thermal liquid junction potential (TLJP) of the filling solution was calculated by below equation [14].

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

where F, t, S are Faraday constant, transference number, and entropy of transport, respectively.

5.1. The standard single-ion entropy of transport, S_i^{*o}

The single-ion entropy of transport was calculated using the Agar's hydrodynamic theory [15].

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

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

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

The self-diffusion coefficient has the relationship with the limiting ionic equivalent conductance as below equation [13].

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

Therefore, the single-ion heat of transport and entropy of transport can be expressed by the ionic conductance, as follows;

$$Q_i^{*o} = -\frac{6\pi e^2 z_i^2 \eta}{4k\epsilon^2} \frac{RT\lambda_i^o}{F^2 z_i^2} \frac{\partial \epsilon}{\partial T}$$

$$= -\frac{3\pi e^2 \eta RT\lambda_i^o}{2kF^2 \epsilon^2} \frac{\partial \epsilon}{\partial T}$$
(8)

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

where η = viscosity of water (9)

ϵ = dielectric constant of water

λ_i^o = the limiting ionic equivalent conductance

5.2. The viscosity of water, η

The following equation was used calculating the viscosity of water [16]. This equation was derived by fitting the original data in Ref. [16].

$$\eta(T) = -0.051099 + 149.92/T - 1.8686 \times 10^5 / T^2 + 1.2841 \times 10^8 / T^3$$

$$- 5.2562 \times 10^{10} / T^4 + 1.2827 \times 10^{13} / T^5 - 1.7302 \times 10^{15} / T^6 + 9.976 \times 10^{16} / T^7, T(K)$$
(10)

5.3. Dielectric constant of water

The following equation was used to calculate the dielectric constant of water [17].

$$\epsilon_r = 5321/T + 233.76 - 0.9297T + 0.001417T^2 - 8.292 \times 10^{-7} T^3, \quad T(K)$$

$$\epsilon_o = 8.854 \times 10^{-12} C/V \cdot m$$

$$\epsilon = \epsilon_o \epsilon_r$$
(11)

5.4. The limiting equivalent ionic conductance, $\lambda_i^o [S \cdot m^2 / mol]$

The data of limiting equivalent ionic conductance was adopted from the work of Quist et al. [18]. Fig. 7 shows the Quist's data and the fitted equations. And the coefficients of the polynomial fitted equations like Eq. (12) were tabulated at Table 1.

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

5.5. Calculation of S_i^{*o}

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

As like the above equation, the entropy of transport can be expressed by the viscosity of water, dielectric constant, and the limiting ionic equivalent conductance.

5.6. Transference numbers, t_i

$$t_i = \frac{|z_i| \lambda_i^o c_i}{\sum_i |z_i| \lambda_i^o c_i} \tag{14}$$

where z_i = ionic valence

λ_i^o = limiting equivalent ionic conductance

c_i = ionic concentration

The transference number was calculated by using the above equation [14]. The concentration of each ion, c_i was calculated in molal unit. The dissociation constant of water was introduced to calculate the concentration of H^+ and OH^- . Eq. (15) is the fitted equation from the original data in Ref. [20]. It assumes that other ions such as Ag^+ , Cl^- , and K^+ , have the constant molal concentration with temperature variation.

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

6. Calculation Results & Discussion

Fig. 8 was reproduced from Lvov's data on the entropy of transport [14]. Fig. 9 shows the comparison between the calculated values and Lvov's data. The calculated values show a large difference with the referenced values, and have larger values than the reference case. Also, the calculated results show that the ion-to-ion variation is much larger than the reference case. The equation used in this calculation is dependent on the limiting equivalent conductance of each ion. Furthermore the ion-to-ion variation of

S_i^{*0} is only dependent on the limiting equivalent conductance. But the referenced data was extrapolated from the low temperature data [14]. This feature seems to make such difference.

Fig. 10 shows the results of the calculated TLJP for two cases: water-filled Ag/AgCl and 5×10^{-5} N KCl Ag/AgCl. Fig. 11 shows the experimental and calculated results on the potential of Ag/AgCl vs. SHE(T). In Fig. 11, 5×10^{-5} N KCl case was referenced from EPRI's data [21]. From the experimental results, water-filled Ag/AgCl and 5×10^{-5} N KCl Ag/AgCl show the similar behavior with temperature. But we can find the large difference between the calculated results and experimental results. The causes of the difference seem to come from the discrepancy between the actual value and the calculated value of the entropy of transport. The more detailed review on Lvov's method for calculating the entropy of transport appears to be needed. Finally, the calculation about the concentration and composition of the filling electrolyte at high temperature is also needed to verify the assumption used in this calculation.

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, we developed the water-filled Ag/AgCl reference electrode.
- 2) The water-filled Ag/AgCl electrode potential remained stable within ± 10 mV over two weeks period. A thermal cycling to 240 °C and back to 288 °C led to a potential shift not exceeding 15 mV.
- 3) By using the limiting equivalent conductances and Agar's theory, TLJP of the water-filled Ag/AgCl electrode has been predicted.
- 4) The agreement between measured and predicted values for the water-filled Ag/AgCl electrode is not satisfactory, apparently due to uncertainty in the predicted electrochemical parameters.

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Table 1. The limiting equivalent conductances of each ion. (Ref. [18])

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) Referenced from [19].

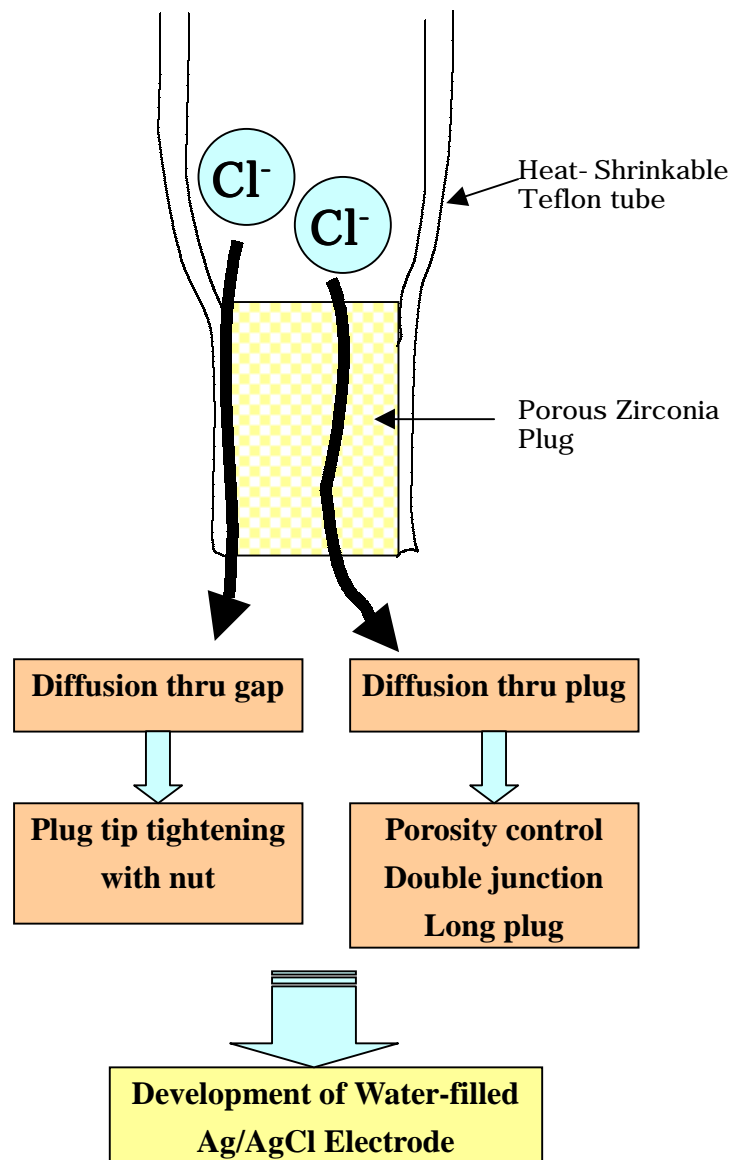


Fig. 1. Schematic of rationale and approach of water-filled Ag/AgCl development.

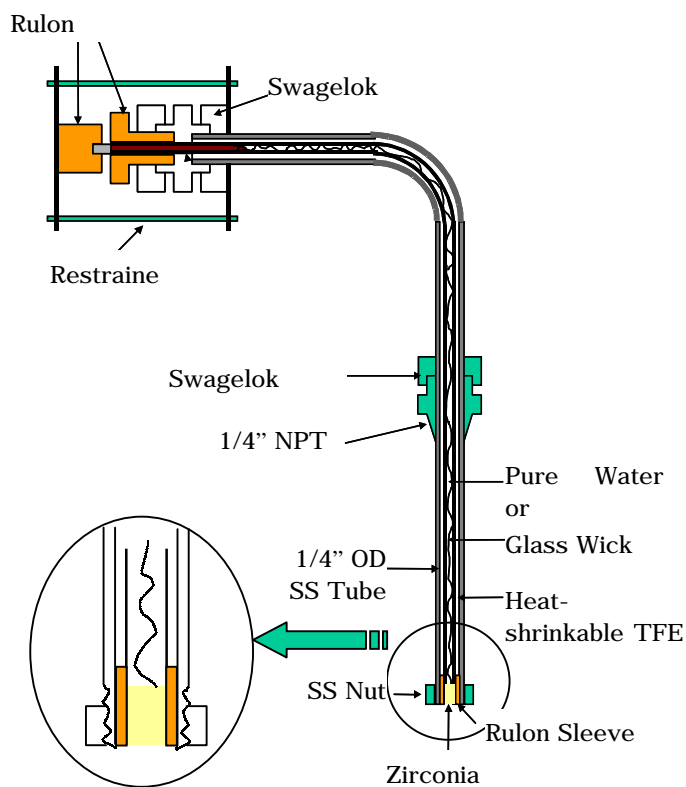


Fig. 2. Schematic of modified Ag/AgCl reference electrode.

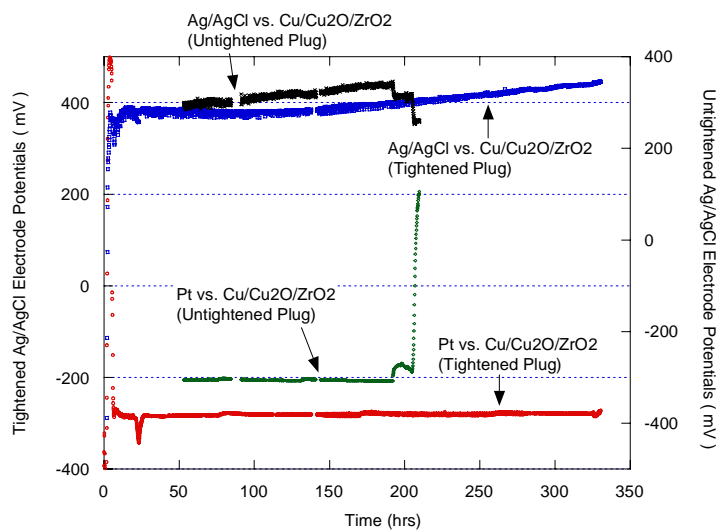


Fig. 3. Comparison between untightened and tightened plug Ag/AgCl electrode at 288 °C for a filling solution of 0.01 M KCl.

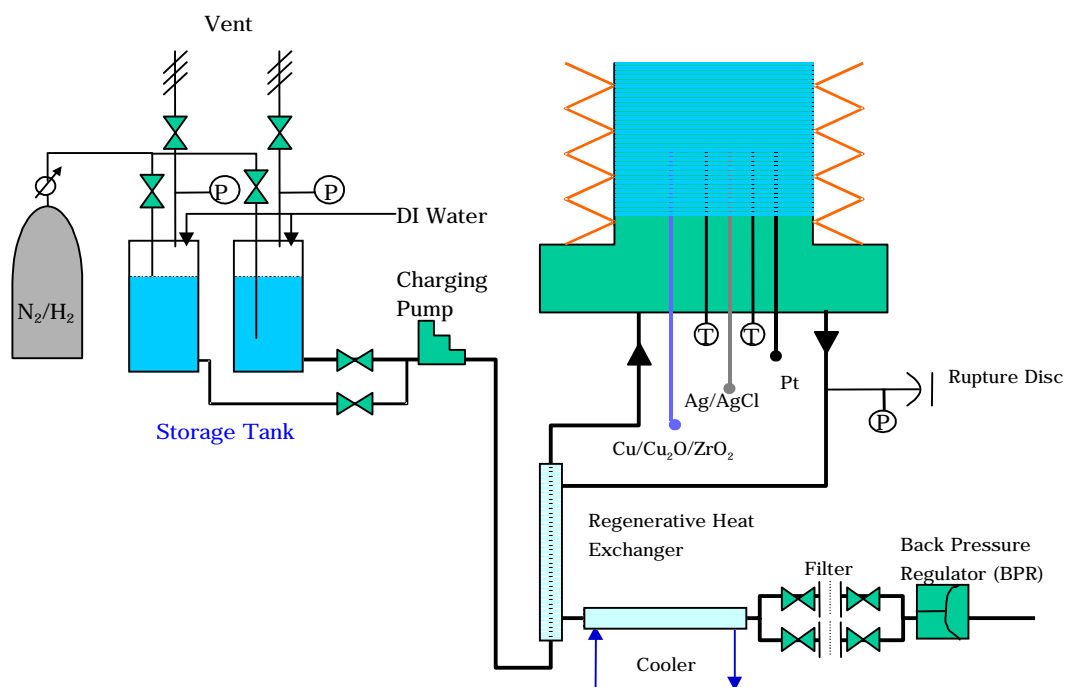


Fig. 4. Schematic of electrode life and performance test loop.

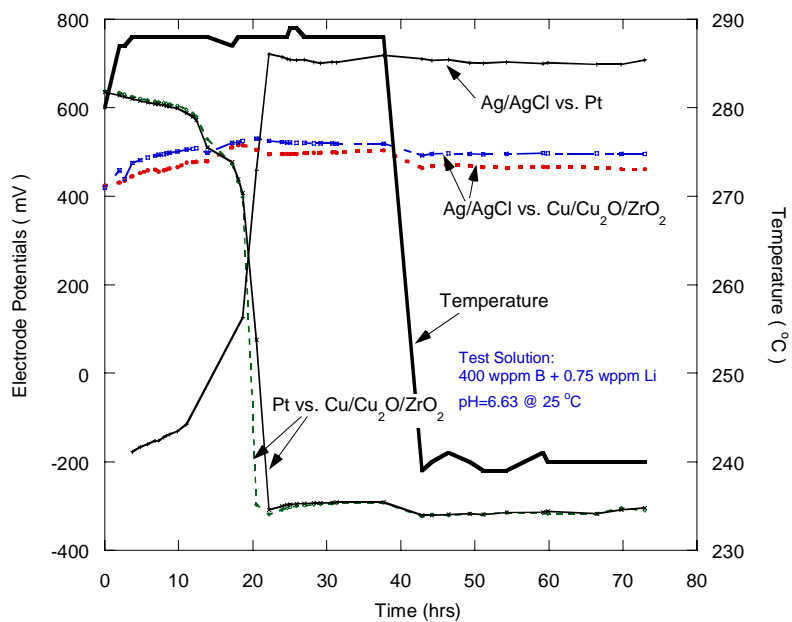


Fig. 5. Test results on temperature effect for water-filled Ag/AgCl electrode.

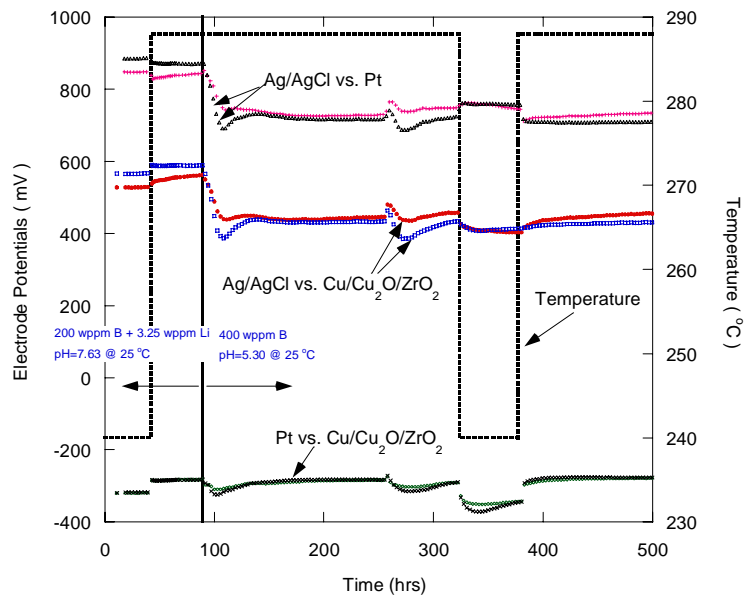


Fig. 6. Test results on temperature and pH effects for water-filled Ag/AgCl electrode.

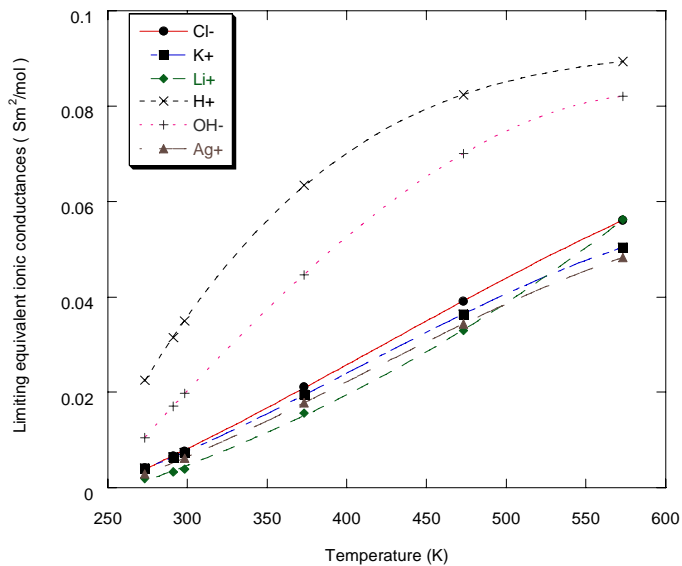


Fig. 7. Limiting equivalent ionic conductance of important ions as a function of temperature (Ref. [18]).

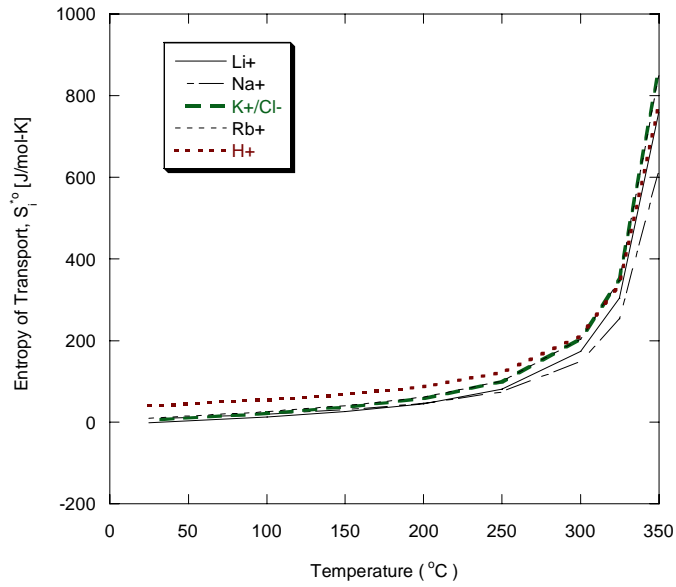


Fig. 8. Entropy of transport for important ions as a function of temperature (Reproduced from Ref. [14]).

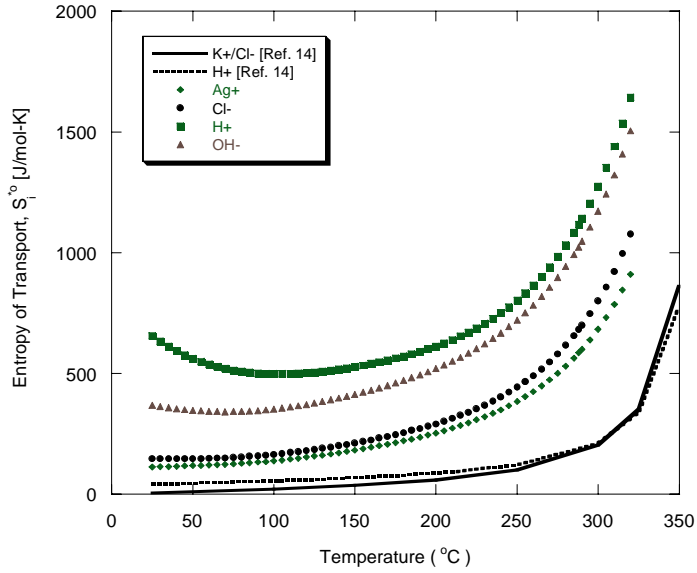


Fig. 9. Comparison between calculated values and referenced values of the entropy of transport for important ions.

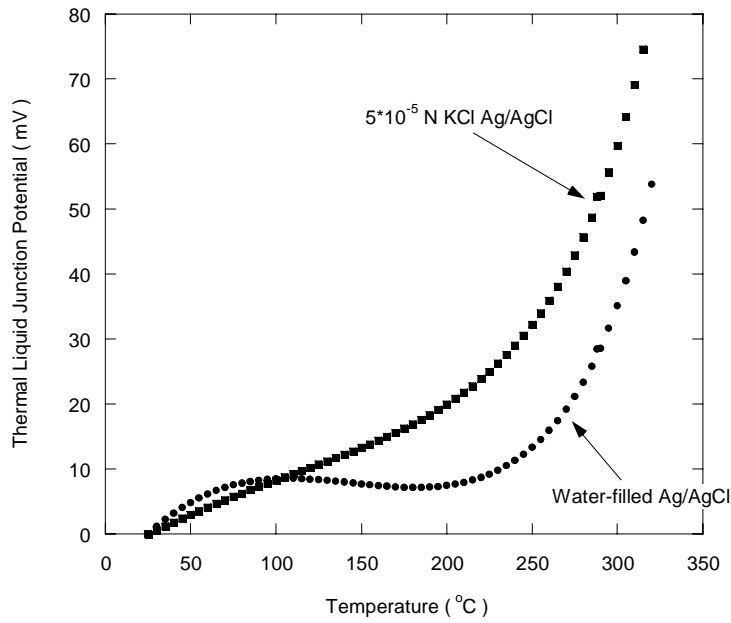


Fig. 10. The calculated values of thermal liquid junction potential for the modified water-filled Ag/AgCl electrode.

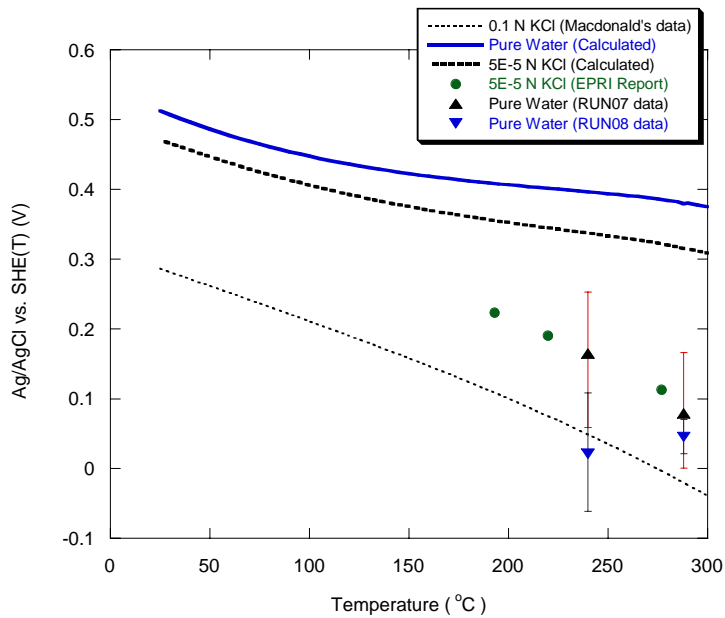


Fig. 11. The evaluated and measured potential of Ag/AgCl reference electrode vs. SHE(T).