High Temperature Reference Electrodes for the Nuclear Industry

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ABSTRACT

Corrosion of steel in elevated temperature aqueous environments is a significant problem in many industries. Therefore, high-temperature/high-pressure reference electrodes are needed for various corrosion measurements such as polarization, galvanic corrosion, electrochemical noise measurement, and electrochemical corrosion potential (ECP) measurement. A high-pressure/high-temperature reference electrode has been developed for applications in the primary system of operating nuclear power plants. The electrode has been designed to operate in high radiation environments and is capable of withstanding rapid temperature and pressure transients. Since previous attempts by others to develop reference electrodes which can operated continuously at 290 C have resulted in electrode failures after less than 3 months of hot operation, the primary focus of the current work has been on the development of a reference electrode which will operate for an entire fuel cycle (2 years of continuous hot operation). As of the writing of this paper, reference electrodes have been continuously operating for one year and have a projected remaining life of 3 years.

INTRODUCTION

Stress corrosion cracking (SCC) of primary system components in the nuclear industry is a serious problem which has resulted in extensive plant outages and costly equipment replacement and repair. The recent discovery of cracks in boiling water reactor (BWR) shrouds has led many utilities to inject hydrogen into the primary system water (hydrogen water chemistry) to lower the electrochemical corrosion potential (ECP) to a level below -230 mV_{SHE}. Correlation between SCC crack growth rates

in stainless steel and ECP [1] have shown that water chemistries which yield large negative potentials result in negligible SCC crack growth rates. Both ECP and crack growth rate can be measured and correlated. These data can be used to set realistic in-service inspection schedules for the core shroud. Since the focus of this paper is on ECP measurement, details concerning the crack growth monitor system will be presented elsewhere.

It is desirable to measure ECP during plant operation to verify that the hydrogen injection has reduced the corrosion potential to an acceptable level. A high-temperature/high-pressure reference electrode has been developed for this purpose. The electrode can operate throughout the two year plant fuel cycle at 290 C and at pressures typical of BWR primary systems (1150 psig). The reference electrode has also been designed to withstand rapid depressurization events as well as thermal ramps of up to 485 C per minute.

This paper presents data obtained in a laboratory flow loop which was designed to simulate BWR water chemistry (including hydrogen water chemistry). The results from rapid pressure/temperature transients and hydrogen injection experiments are presented. The effects of hydrogen injection and flow rate on ECP are presented along with comparisons with literature data.

ELECTRODE DESCRIPTION

The reference electrode constructed for nuclear applications is a pressure balanced external reference electrode. The electrode design incorporates a Ag/AgCl junction exposed to KCl solution. Pressure balanced external reference electrodes induce a thermal liquid junction potential (TLJP) which is created by the temperature gradient that exists between the reference electrode junction and the working electrode environment. The TLJP must be accounted for in the conversion of the measured potential to the standard hydrogen electrode (SHE) scale. The following relation was used to the determine the SHE potentials:

$$E_{\text{Corrected vs. SHE(T°C)}} = E_{\text{measured}} + E_{\text{Ref (25°C)}} + E_{\text{SHE(T°C)}} + E_{\text{TLJP}} \quad (1)$$

where,

$E_{Corrected\ vs.\ SHE(T°C)}$ = potential vs. SHE scale at temperature T [mV],
$E_{measured}$ = measured potential [mV],
$E_{Ref\ (25°C)}$ = reference electrode potential vs. SHE at room temperature [mV],
$E_{SHE(T°C)}$ = SHE potential at temperature T [mV], and
E_{TLJP} = thermal liquid junction potential [mV].

The entire reference electrode is housed inside a high pressure 316 stainless steel (SS) tube. The electrode can be installed in a seismically qualified test frame as shown in Figure 1 or it can be connected directly to the primary system. In cases where it is desirable to make measurements in the plant water cleanup system, a frame as shown in Figure 1 is convenient. For primary system installations, a flow grabber is used to reduce the flow rate past the probe and the probe/flow grabber can be mounted on drain taps or on welding neck flanges. The advantage of installing the electrode directly in the primary system is that, in some cases, a more representative water chemistry is sampled. This is particularly important in high gamma fields where radiolytic decomposition of water leads to high hydrogen peroxide concentrations which decay quickly outside of the radiation field. The ECP is measured by connecting a wire lead to the piping system and acquiring the data continuously. The data acquisition system is shown in Figure 2.

During the electrode design phase, experiments were performed to verify that the electrode can withstand rapid pressure and temperature transients. The electrode was installed in the flow loop and rapid depressurization experiments were performed. The electrode can withstand depressurization from 1300 psig to one atmosphere over a few seconds. In addition, rapid thermal transients were introduced in the flow loop. The electrode was exposed to rapid cooling water introduction after steady state operation at 290 C. The reference electrode can withstand thermal ramps of up to 485 C per minute. The reference electrode was shown to operate properly after the combined thermal and pressure transients described above.

HYDROGEN INJECTION

Hydrogen injection into the primary system of BWRs lowers the open circuit potential as a result of recombination of hydrogen and oxygen. As mentioned earlier, it is desirable to reduce the ECP of stainless steel components below about -230 mV_{SHE} to reduce SCC crack growth rates to a negligible level. Verification of the efficacy and accuracy of the high temperature reference electrode has been performed by testing in a simulated BWR flow loop. The flow loop consists of a high pressure pump, a heat exchanger, an electric heater, a water cleanup system, hydrogen injection capability, and an ion feeder for conductivity control. The water chemistry is characterized using an oxygen sensor, a pH sensor, and 2 conductivity meters. The flow loop is capable of simulating both normal water chemistry (NWC) and hydrogen water chemistry (HWC).

During operation of the flow loop over the past year, several specialized experiments have been performed to test the performance of the high temperature reference electrode design. One of the more important experiments performed involves hydrogen injection after NWC conditions have been established. The water chemistry of a nuclear power plant shortly after startup is characterized as having high conductivity and a dissolved oxygen concentration in the ppm range. The flow loop experiment was designed to simulate a BWR plant startup after a refueling outage. The goal in the case of a nuclear power plant is to introduce HWC as soon as possible after startup. Typical data from a hydrogen injection experiment are presented in Figure 3. These data show that that the ECP decreases below -230 mV_{SHE} when the oxygen level is decreased below about 35 ppb. Figure 3 compares MPM data with data obtained by Macdonald [2] and with data obtained by Kim at GE [3]. As shown in the figure, the ECP data are in good agreement. This is because the flow rates and conductivity levels were comparable for the three experiments reported in Figure 3. The MPM experimental parameters were adjusted to match the literature data so that a meaningful comparison could be made.

SENSITIZED VS. NON-SENSITIZED 304 SS

Most ECP measurements which have been made in power plants are obtained with the piping as the working electrode. As a result, the measured potential does not sample a significant amount of sensitized material. Similarly, laboratory flow loop data are also obtained using the loop tubing as the working electrode. In order to examine the differences between sensitized and non-sensitized materials, an experiment was performed using two working electrodes. The first working electrode, in accordance with conventional practice, consisted of the flow loop tubing, which in this case, is 316 SS. The second electrode was an electrically isolated 304 SS electrode (see Figure 1) which was thermally sensitized. The entire electrode was sensitized by thermal soaking at 621 C for 4 hours followed by furnace cooling. Both single loop and double loop Electrochemical Potentiokinetic Reactivation (EPR) measurements confirmed that the heat treated material yielded an average single loop EPR level of 15 C/cm^2.

The results of the loop exposure of the working electrodes are shown in Figure 4. The data show

close agreement at oxygen levels below about 25 ppb. This result is expected because the rate of SCC attack at potentials below-230 mV_{SHE} is very low. At higher oxygen levels, the sensitized material exhibits a higher ECP as expected. The largest difference observed was about 80 mV and this difference occurred at an oxygen concentration of 100 ppb.

FLOW VELOCITY EFFECTS

Macdonald et. al. [2] have reported flow velocity effects for 304 SS and alloy 182 in simulated BWR water chemistry environments. Macdonald noted that the corrosion potentials are sensitive to flow velocity in the range of oxygen concentration from 10 to about 500 ppb. At oxygen concentrations in the 10 to 500 ppb range, the arrival of oxygen at the pipe surface depends on the transport from the bulk flow. Therefore, the ECP is observed to increase with increasing flow velocity in this oxygen concentration range. The data from Figure 3 are plotted in Figure 5 along with Lin's equation [4] for comparison. This equation was developed by fitting data obtained from rotating cylinder electrode experiments conducted at 288 C. Lin's equation has 90% confidence bounds of ± 50 mV. The experimental data shown in Figure 5 are in good agreement with Lin's equation up to about 500 ppb oxygen. The Lin model predictions plotted in Figure 5 are for flow velocities up to 20 cm/s.

HYDROGEN EFFECTS ON THE REFERENCE ELECTRODE

There has been confusion in the literature concerning the use of Ag/AgCl reference electrodes in HWC environments. For example, in a paper by R.L. Cowan, et al., it was incorrectly stated that, "the Ag/AgCl type electrode has also been used successfully in BWR service, but since it is only reliable under non hydrogen addition conditions its use has been limited" [5]. The effect of hydrogen on silver/silver chloride (Ag/AgCl) reference electrodes was also incorrectly portrayed by Ives and Janz in 1961 [6]. These authors state: "in a one compartment cell, the hydrogen reaching silver-silver chloride electrodes was found to have considerable effect on the potential. It was suggested that the diminution by hydrogen of the potential of the Ag/AgCl electrode toward that of a hydrogen electrode may be due to the co-existence of simultaneous hydrogen and AgCl electrodes at the hydrogenated AgCl reference electrode". This book was also referenced in a paper by R. N. Roychoudhury and C. F. Bonilla [7]. In this paper, it was reported that the presence of hydrogen shifted the potential by 2.3 mV to 7.6 mV at room temperature. Reference 4 reported a potential shift of 30 – 35 mV at 225 C.

A key problem with the experiments reported in the references cited is the fact that the reference electrode junction was constructed using platinum gauze which was first silver-plated and then chloridized in HCl. Further, the reference solution used in References 7 and 8 to establish the reference potential was dilute HCl (0.01689 N). Any pinholes or other breaches in the silver coating would result in platinum exposure to a hydrogen rich solution. These electrodes therefore exhibit a mixed potential which manifests itself as an apparent potential shift. The MPM reference electrode does not use silver plated platinum because of this problem. Properly constructed reference electrodes are not sensitive to the presence of hydrogen in solution.

In order to prove the efficacy of the Ag/AgCl reference electrode in HWC, a definitive experiment was conducted. A solution of saturated KCl and a three-electrode cell was prepared as shown in Figure 6 with platinum as the working electrode. A potential of -900 mV_{SHE} was applied and hydrogen was allowed to evolve. A Ag/AgCl reference junction was placed in the cell and its potential was monitored against a separate saturated calomel reference electrode. The potential of the Ag/AgCl was monitored while the generated hydrogen was allowed to contact the Ag/AgCl junction. In fact, hydrogen bubbles

were observed on the surface of the Ag/AgCl junction. During this period, no drift was observed in the potential of the Ag/AgCl junction.

SUMMARY AND CONCLUSIONS

This work has produced a high-temperature and high-pressure reference electrode which can be used in the high radiation environments of the primary system of operating nuclear power plants. The reference electrodes are capable of continuous hot operation for an entire 2 year fuel cycle. Comparison of ECP measurements with literature data have shown excellent agreement for various oxygen concentrations and flow rates. It has been definitively established that Ag/AgCl junctions are not sensitive to the presence of hydrogen. An explanation has been provided for literature reports of hydrogen effects on Ag/AgCl junctions which were constructed by plating Ag on platinum. This approach to construction of the reference electrode junction is not recommended because any pinholes or other breaches in the sliver coating would result in platinum exposure to a hydrogen rich solution. Electrodes constructed by Ag plating therefore exhibit a mixed potential which manifests itself as an apparent potential shift.

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8. M. H. Lietzke, *Atomic Energy Commission Report, ORNL 1741* (July 14, 1954) from Oak Ridge National Laboratory; Paper # 223. American Chemical Society paper before the Engineers' Joint Council Nuclear Engineering Congress, December 1955.

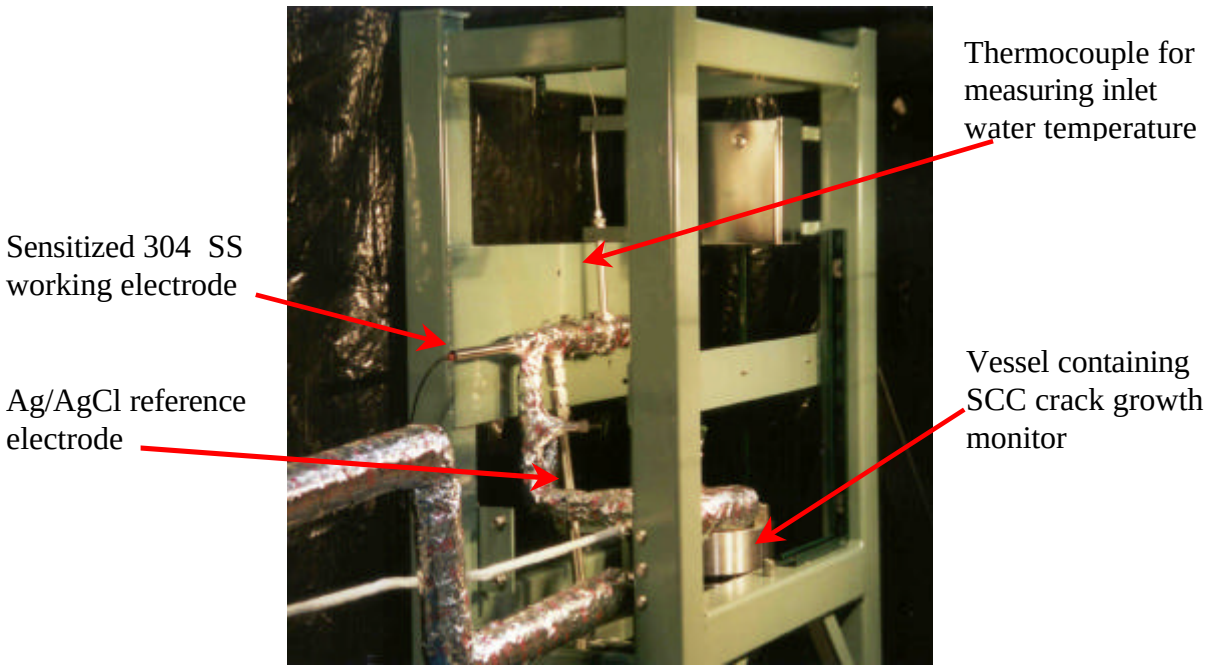

FIGURE 1 - Seismically qualified frame showing high-temperature/high-pressure reference electrode, sensitized 304 SS working electrode, and pressure vessel containing SCC crack growth rate monitor.

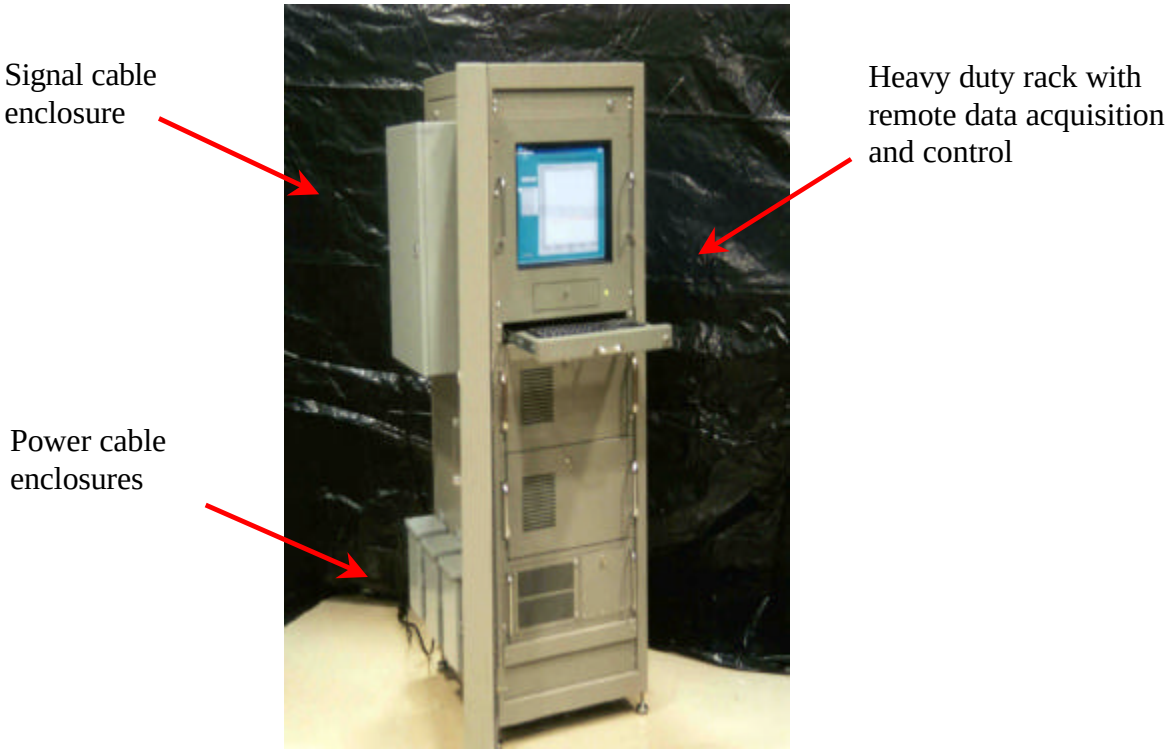

FIGURE 2 – Seismically qualified data acquisition and control cabinet.

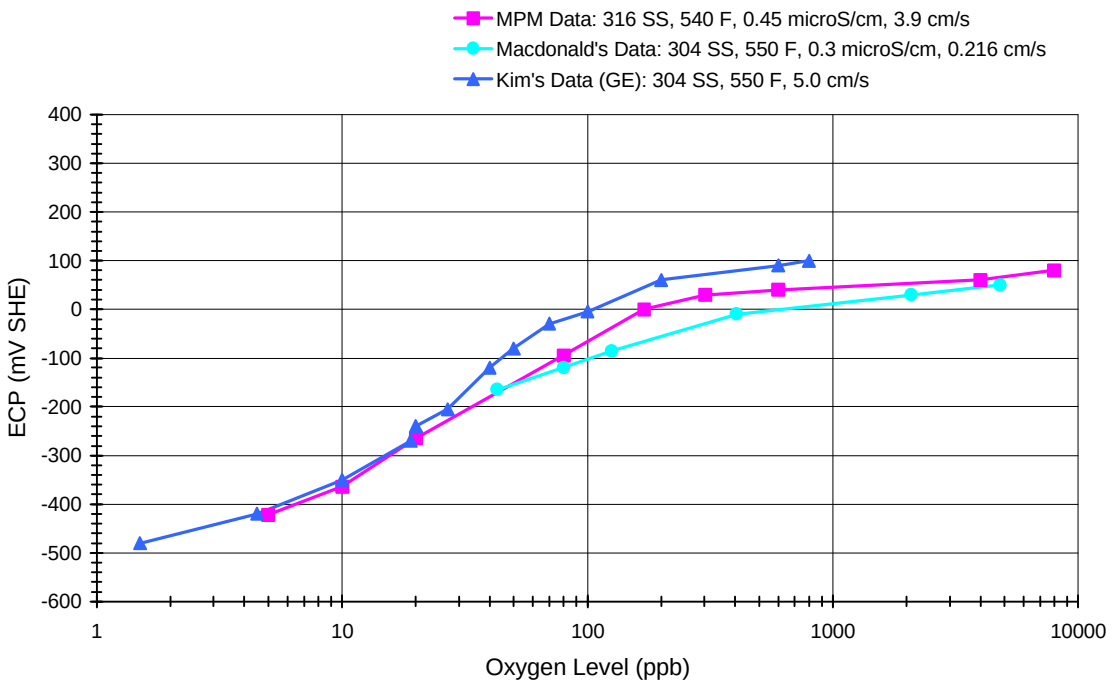

FIGURE 3 – Effect of hydrogen injection on ECP. MPM data is compared with similar measurements reported by Macdonald [2] and Kim [3]. Kim's flow velocity was estimated from the reported volumetric flow rate of 200 cm^3/minute.

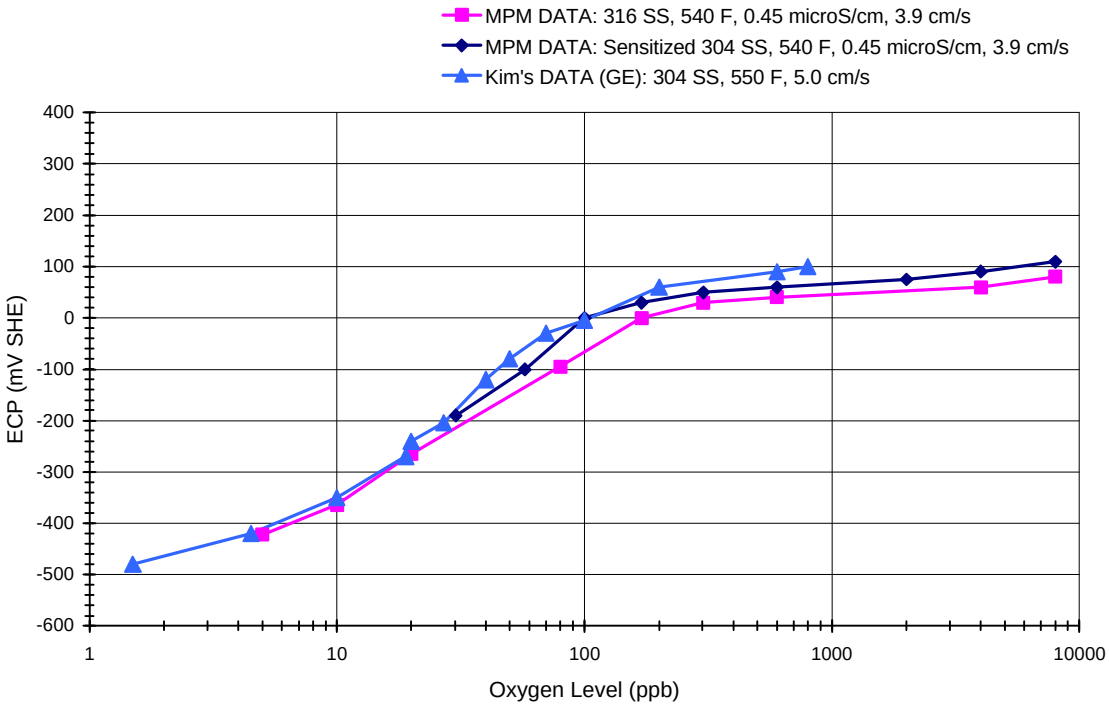

FIGURE 4 – Comparison of sensitized 304 SS with 316 SS data (non-sensitized). MPM data is compared with similar measurements reported by Kim [3]. Kim's flow velocity was estimated from the reported volumetric flow rate of 200 cm^3/minute.

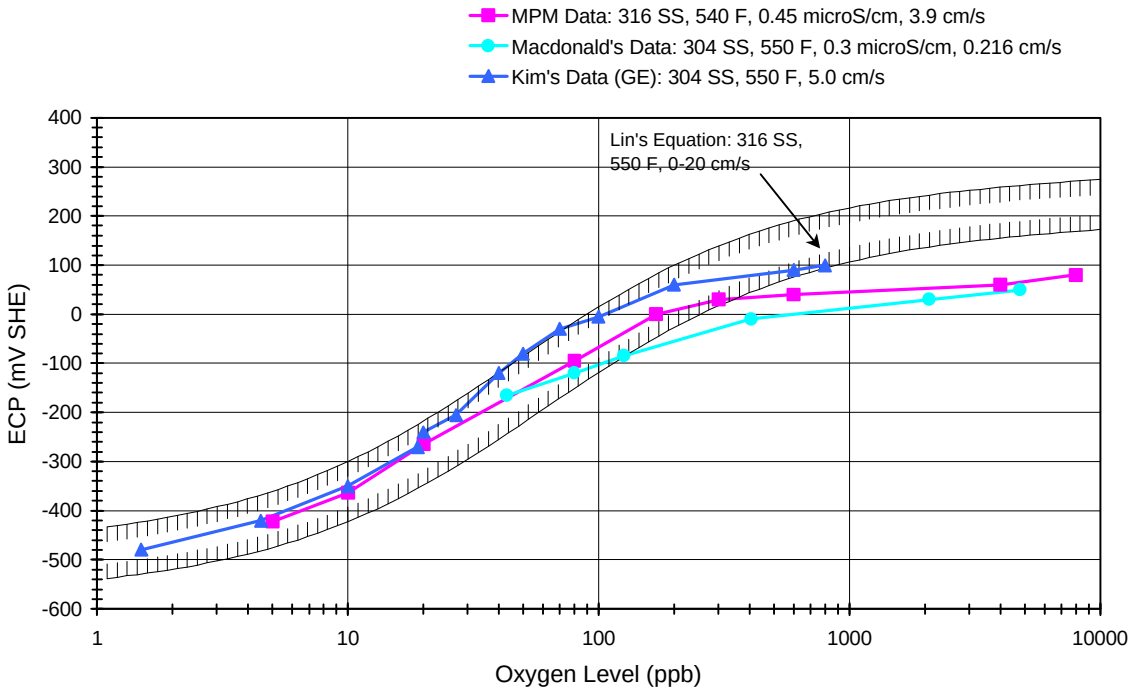

FIGURE 5 – Comparison of ECP data obtained at various flow rates with a theoretical calculation published by Lin [4]. MPM data is compared with similar measurements reported by Macdonald [2] and Kim [3]. Kim's flow velocity was estimated from the reported volumetric flow rate of 200 cm^3/minute.

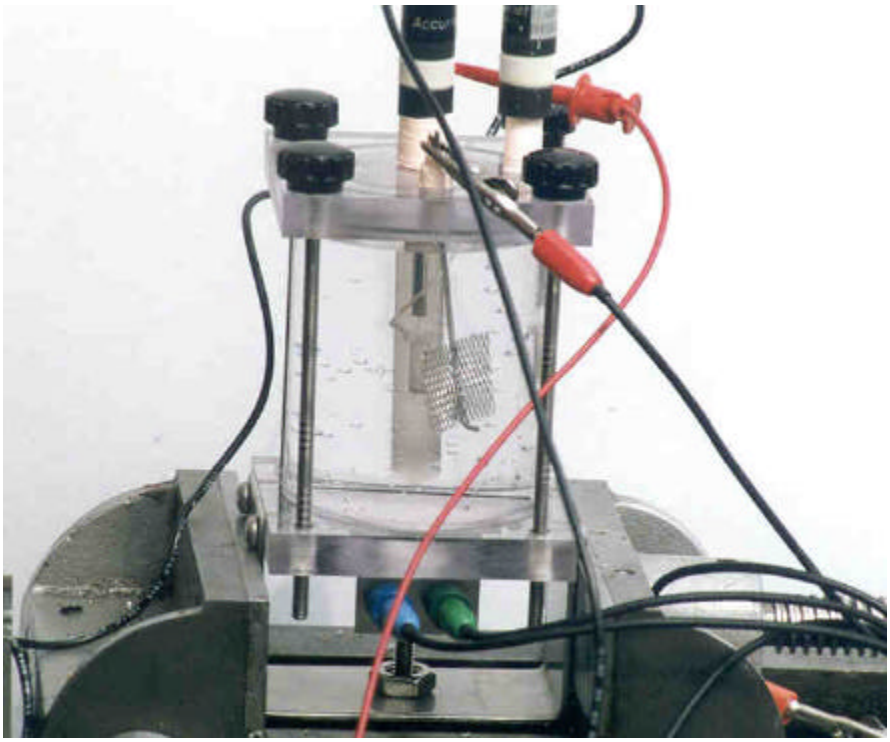

FIGURE 6 – Test cell used to prove that hydrogen does not affect the Ag/AgCl reference electrode.