

# Application Note – Effect of Solution Conductivity on In-Plane Membrane Conductivity Measurement

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## Introduction

The BekkTech BT-110 Conductivity Clamp is a simple and convenient device for characterizing the in-plane conductivity ( $\sigma_{IP}$ ) of solid electrolytes used in electrochemical cells such as fuel cells and redox flow batteries. The BT-110 Conductivity Clamp uses a four-electrode method for true ohmic resistance measurement as illustrated in Figure 1.

Although commonly used for testing membrane resistance and conductivity in humidified gas environments, the measurement can also be performed in bulk solutions, *i.e.*, with the sample fully immersed in liquid. In some instances, testing in solution is preferred because of the ease of measurement and because special equipment such as an environmental chamber or other environmental control system are not required: One simply needs a suitable container (*e.g.*, a clean glass beaker), test solution, BT-110 Conductivity Clamp, membrane sample, and potentiostat or other DC source meter capable of performing four-terminal measurements.

When performing measurements in a solution, as opposed to gaseous environments, it is important to recognize that charge transport can take place in the bulk solution as well as the membrane as shown in Figure 1. The test solution surrounding the membrane can be considered an alternative, parallel pathway for ion transport. The assumption when evaluating sample resistance is that all of the current is carried by the membrane. This assumption is valid only if the resistance to charge transport in the solution is significantly greater than the resistance to charge transport in the membrane, *i.e.*,  $R_{solution} \gg R_{membrane}$ .

In this application note, we examine the effect of bulk solution conductivity on the in-plane membrane resistance measurement using the BT-110 Conductivity Clamp, and determine the solution conductivity at which measurement of the membrane resistance is compromised.

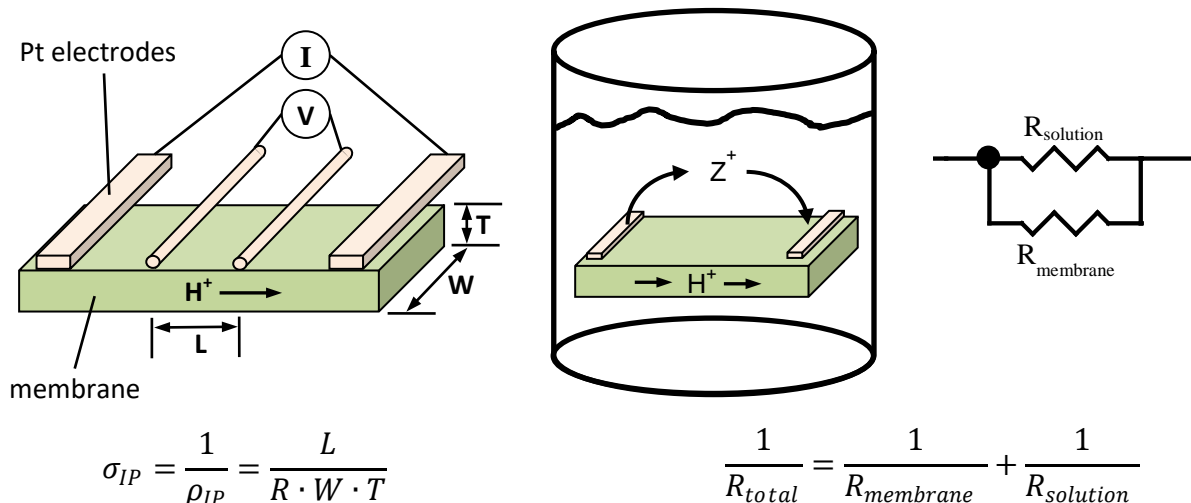


Figure 1. Four electrode in-plane membrane conductivity ( $\sigma_{IP}$ , S/cm) configuration, where  $\rho_{IP}$  = resistivity ( $\Omega$ -cm),  $L$  = distance between the inner V-sense electrodes (cm),  $W$  and  $T$  are sample width and thickness (cm), and  $R$  = resistance ( $\Omega$ ). When testing in bulk solutions, multiple current paths exist (*i.e.*, in the solution and membrane) which can lead to errors in measuring the membrane resistance. The measured resistance  $R_{total}$  is the sum of the parallel membrane resistance  $R_{membrane}$  and bulk solution resistance  $R_{solution}$ .

## Experimental

All experiments were carried out at ambient temperature in solutions of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) of varying concentration and conductivity. Solutions were prepared by dilution of analytic grade  $\text{H}_2\text{SO}_4$  with high purity water ( $> 17 \text{ M}\Omega\text{-cm}$ ). Solution conductivity was measured with a calibrated conductivity meter (AR50 Accumet<sup>®</sup>).

Experiments were conducted using as-received Nafion<sup>®</sup> NR-212 (nominal dry thickness = 51  $\mu\text{m}$ ) and Nafion<sup>®</sup> 117 (178  $\mu\text{m}$ ) (DuPont) and BT-110 Conductivity Clamp (Scribner Associates). Membranes were immersed for 24 hours in high purity water (HPW) prior to resistance measurement. Resistance was first measured in the HPW and then in successively more concentrated  $\text{H}_2\text{SO}_4$  solutions.

Resistance was determined with a Solartron 1286 Potentiostat (Ametek) and CorrWare software (Scribner Associates) by performing a potentiodynamic scan from 0 V  $\rightarrow$  -0.1 V  $\rightarrow$  +0.1  $\rightarrow$  0 V vs. open circuit potential (OCP) at 10 mV/s. The resistance was taken as the slope of the voltage vs. current (V-I) curve per Ohm's Law:  $V = I \times R$ .

## Results and Observations

Example V-I curves for various test conditions – with vs. without membrane sample, HPW vs.  $\text{H}_2\text{SO}_4$  solution - are shown in Figure 2. Very linear response was generally observed which facilitated determination of the resistance from the V-I data.

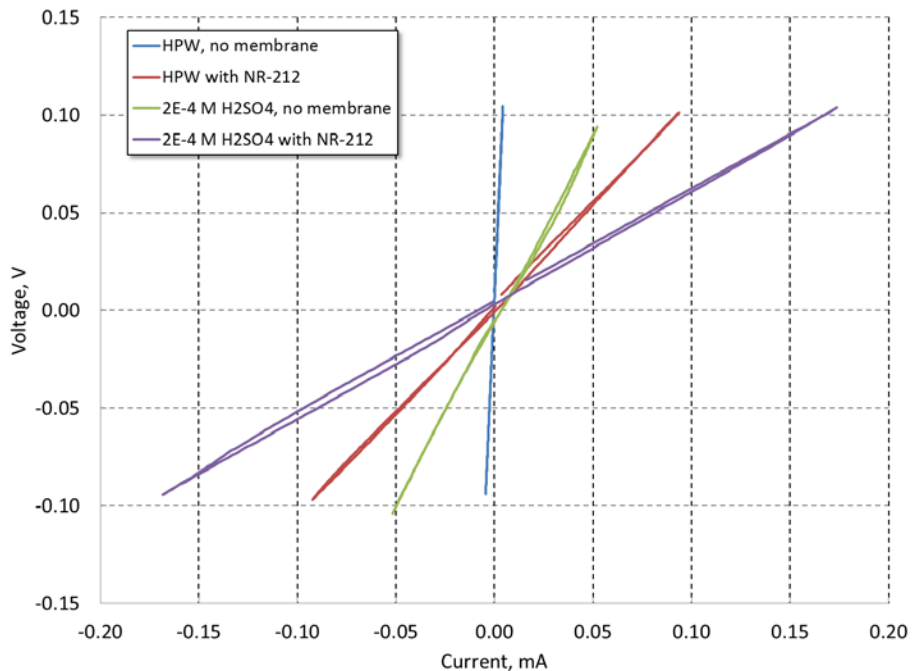


Figure 2. Voltage-current response for various test conditions. HPW = high purity water ( $\sigma_{\text{HPW}} \sim 6 \times 10^{-5} \text{ mS/cm}$ ).

Results of the solution conductivity and resistance tests are summarized in Table 1 and Figure 3. As the aqueous solution concentration increased, and its conductivity increased, the measured resistance decreased. These results clearly demonstrate that when making measurements in bulk solutions, it is important that the solution be fairly resistive, *i.e.*, low ion concentration.

The true membrane resistance in aqueous solution can be taken as the resistance measured when exposed to high purity water. In this case, the bulk solution resistance (22.5 k $\Omega$ ) was much greater than the membrane resistance (1.1 k $\Omega$  and 680  $\Omega$  for NR-212 and N117, respectively) and therefore current transport occurred predominately in the polymer membrane.

At low solution concentration, the membrane resistance was much less than the solution resistance, and therefore the membrane properties dominated the measurement and the measurement accurately reflected the membrane resistance. However, as the concentration and conductivity of the bulk solution increased, the measured resistance with the membrane approached the resistance of the solution and thus was not reflective of the actual membrane resistance.

The resistance measured with a membrane sample was independent of solution concentration for solution concentration less than  $\sim 2 \times 10^{-5}$  M H<sub>2</sub>SO<sub>4</sub> or, more generally, solution conductivity less than  $\sim 0.01$  mS/cm (resistivity greater than  $\sim 7.7 \times 10^4$   $\Omega$ -cm). Because the in-plane resistance varies inversely with membrane thickness, thicker membranes are less susceptible to erroneous measurement as a result of bulk solution conductance. That is, bulk solution conductivity  $\sim 0.1$  mS/cm can be tolerated for a thick membrane such as Nafion® 117, whereas the solution conductivity should be lower than  $\sim 0.01$  mS/cm for a thin membrane such as Nafion® NR-212.

Table 1. Solution conductivity and resistance with and without membrane samples as a function of solution H<sub>2</sub>SO<sub>4</sub> concentration.

[H <sub>2</sub> SO <sub>4</sub> ], M	$\sigma_{\text{solution}}$ , mS/cm	Resistance without membrane, $\Omega$	Resistance with NR-212, $\Omega$	Resistance with N117, $\Omega$
HPW <sup>a</sup>	$5.9 \times 10^{-5}$	22,536	1,068	680
$2.33 \times 10^{-5}$	0.0133	18,096	1,069	660
$2.33 \times 10^{-4}$	0.135	1,881	577	665
$2.33 \times 10^{-3}$	1.37	253	146	298
$2.33 \times 10^{-2}$	11.4	39	34	31

<sup>a</sup> HPW = high purity water

Figure 1 summarizes the resistance measured with the conductivity clamp with and without the N117 or NR-212 membrane sample as a function of bulk solution concentration. At low solution concentration, the membrane resistance was significantly less than the solution resistance. However, as the concentration of the solution increases, the measured resistance of the membrane begins to resemble the resistance of the solution much more than the resistance of the membrane. The resistance measured with a membrane sample was independent of solution concentration for solution concentration less than  $2 \times 10^{-5}$  mol/L H<sub>2</sub>SO<sub>4</sub>.

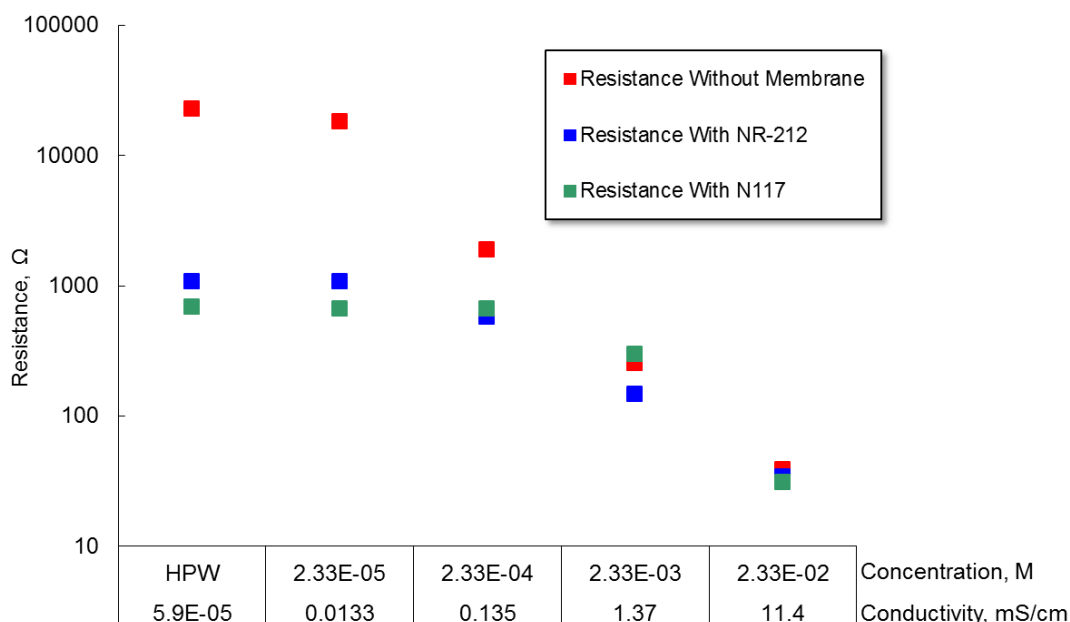


Figure 3. Measured resistance with and without membrane as a function of solution  $H_2SO_4$  concentration and conductivity. Measured “membrane” resistance was independent of bulk solution concentration only for solutions with conductivity less than  $\sim 0.01$  mS/cm.

As shown in Table 3, for solutions with conductivity less than  $\sim 0.013$  mS/cm, the error was negligible for both NR-212 and N117. However, for NR-212, any higher concentration would result in an error exceeding 40%. For the thicker N117 material, the error in membrane resistance would be less than 5% for solution conductivities less than  $\sim 0.13$  mS/cm, but exceeded 50% for higher concentration solutions.

**Table 3.** Error in membrane resistance measurements as a function of bulk solution concentration / conductivity.

$[H_2SO_4]$ , M	$\sigma_{\text{solution}}$ , mS/cm	Error for NR-212, %	Error for N117, %
HPW <sup>a</sup>	$5.9 \times 10^{-5}$	--	--
$2.33 \times 10^{-5}$	0.0133	< 1	< 1
$2.33 \times 10^{-4}$	0.135	46	2
$2.33 \times 10^{-3}$	1.37	86	56
$2.33 \times 10^{-2}$	11.4	97	96

## Conclusion

Solution conductivity can impact the accuracy of in-plane membrane resistance measurements because the bulk solution provides a current path parallel to the solid membrane electrolyte. In order for the solution to negligibly influence the membrane resistance measurement,  $R_{\text{solution}} \gg R_{\text{membrane}}$ , a general guideline would be  $R_{\text{solution}} / R_{\text{membrane}} \sim 10^2$ - $10^3$ . Higher solution resistance (lower conductivity) is required when testing samples of high in-plane resistance, for example, samples with small cross-sectional area (*i.e.*, thin and narrow) or of high intrinsic charge transport resistivity (low conductivity).