

Electrochemical Sensors for Gas Pipelines Using Ion Conducting Membranes

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ABSTRACT

Electrochemical sensors can be used for a wide range of online in-situ process monitoring applications. However, the lack of a consistent electrolyte layer has limited electrochemical monitoring in gas and supercritical fluid streams. A solid state sensor is being designed that uses an ion conducting membrane to perform conductivity and corrosion measurements in natural gas pipelines up to 1000 psi. Initial results show that membrane conductivity measurements can be correlated directly to water content down to dew points of 1 °C with good linearity. Corrosion monitoring can also be performed using methods such as linear polarization resistance and electrochemical impedance spectroscopy (EIS), though care must be taken in the electrode design to minimize deviation between sensors.

Keywords: sensor, corrosion, conductivity, electrochemical impedance spectroscopy, natural gas, high-pressure, moisture, carbon dioxide

1 INTRODUCTION

Electrochemical sensors are regularly used for the detection of chemical species in many industrial operations. The most common example is potentiometric measurement of pH. In addition to pH, dissolved oxygen sensors (e.g. the Clark electrode) and corrosion sensors are good examples of electrochemical sensors used in industrial operations. Systems using bulk aqueous streams provide a suitable electrolyte for most electrochemical measurements. However, operation is currently limited in environments where water is distributed within a compressed gas or supercritical fluid. In such environments, the dispersed water does not provide adequate ion conductivity for conventional electrochemical sensors. Furthermore, many sensor designs are not suitable for high-pressure operation. The development of solid state electrochemical sensors for

non-aqueous environments will allow for improved monitoring of such streams for impurities and corrosion.

The National Energy Technology Laboratory (NETL) and Pennsylvania State University prepared an initial design as part of their collaborative project for performing corrosion measurements in water-contaminated supercritical CO₂ pipelines [1,2]. These probes utilized a thin film of ion conducting polymer deposited across three electrodes where moisture from the bulk CO₂ phase allowed the polymer film to serve as the electrolyte. The study found that electrochemical corrosion measurements could be accomplished, although the quality of the deposited polymer film and its contact with the electrodes affected the measurements.

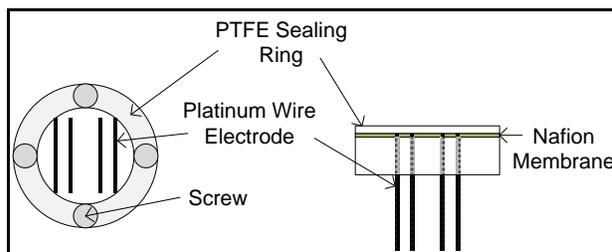


Figure 1: Four-electrode conductivity probe for high-pressure gas systems.

The current project has improved upon this design and focused on its application to natural gas transmission pipelines. Commercial Nafion® membranes are used as the electrolyte to reduce the variability and contact issues with the polymer film. Electrode geometries have been adapted from test cells used for determining conductivity of polymer electrolyte membrane (PEM) fuel cells to provide reliable and repeatable contact. An example is shown in Figure 1. In this way, a five-electrode cell can be used to provide both corrosion measurements and accurate conductivity measurements of the membrane. Because the conductivity of the membrane depends on the concentration

of water in the gas stream, the results can be used to determine the water content of the stream. This is the determining factor for the corrosion risk of a natural gas pipeline, because corrosion generally does not occur without condensed water. While the conductivity of commercial membranes has been studied extensively for PEM fuel cells, almost all data are at ambient pressure. High-pressure conductivity measurements may be required to calibrate the sensor for more aggressive environments.

2 WATER IN NATURAL GAS PIPELINES

Corrosion risk in natural gas pipelines is tied to the risk of condensation in the line. Saturation of water is a function of both the temperature and pressure of the gas, the latter of which can be as high as 1000 psi (6.9 MPa) in transmission lines. Water solubility in natural gas can be calculated according to ASTM D1142 [3].

There are many ways the water content can be reported. In the natural gas industry it is often reported in terms of pounds-water per million standard cubic feet of gas (lb/MMscf), where the gas is assumed to be 60 °F (15.6 °C) and 14.7 psi (0.1 MPa). Absolute water content can also be reported in mole/mass/volume fraction and partial pressure of water in the gas stream. Another common measure is the dew point temperature, which is the temperature at which water will condense in a gas of known pressure. The dew point is directly related to the saturation pressure, which is the pressure at which water will condense in a gas of known temperature. Finally, relative humidity is the ratio of the current water content to the saturated content at the gas temperature and pressure. This is often calculated using the partial pressure and saturation pressure of water.

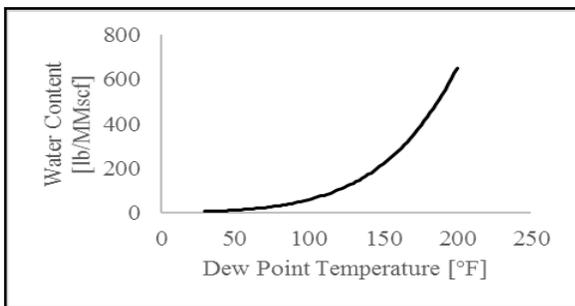


Figure 2: Water content in 1000 psi (6.9 MPa) natural gas as a function of dew point temperature [3].

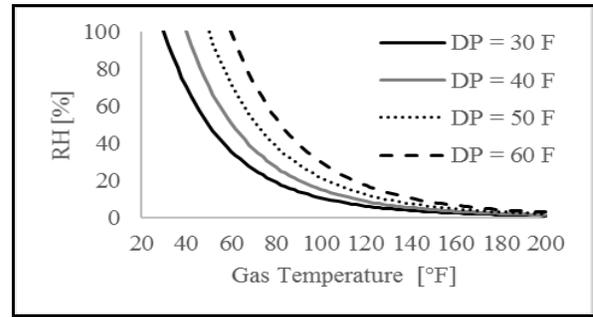


Figure 3: Relative humidity in 1000 psi (6.9 MPa) natural gas as a function of gas and dew point (DP) temperature [3].

For example, Figure 2 shows the water content, in lb/MMscf, at 1000 psi as a function of dew point temperature calculated from ASTM D1142. The maximum water content, and thus the saturation pressure, increases considerably with the gas temperature. Figure 3 shows that while water saturation increases with temperature, relative humidity decreases with temperature when the dew point is held constant. Calculations have found that, for constant gas and dew point temperature, relative humidity is largely independent of the total gas pressure. However, the total water content at saturation decreases almost linearly with total pressure. For example, at a constant dew point and gas temperature, increasing the gas pressure from 100 to 1000 psi would decrease the saturated water content by a factor of 10.

3 NEW SENSOR DESIGN

Nafion 117 was selected as the membrane material due to its commercial availability and the considerable body of literature available on its properties. The sensor design is taking place in two stages. The first is the assembly of the high-pressure four-electrode conductivity probe. In a four-electrode cell, the outer two electrodes, shown as platinum wires in Figure 1, pass a current between them. The inner two electrodes measure the potential change across the membrane caused by the ohmic drop. While a two-electrode cell allows a more simple design, the use of four electrodes increases measurement accuracy as errors due to electrochemical reactions on the electrodes are mitigated.

The second stage is the addition of a fifth carbon steel electrode between the inner two platinum electrodes. Combining the steel electrode with two of the conductivity electrodes allows a three-electrode cell for making corrosion measurements. The Nafion membrane will provide a consistent electrolyte for electrochemical measurements, such as linear polarization resistance and EIS, to monitor corrosion behavior over time. The assembly could eventually allow the inclusion of further electrodes for additional real-time electrochemical measurements of gas-phase and corrosion properties.

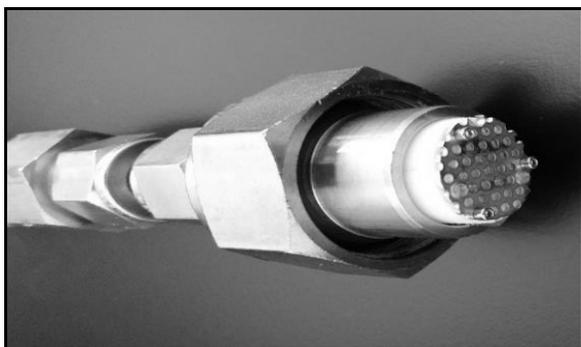


Figure 4: Assembled high-pressure conductivity sensor.

The electrodes are set into a polytetrafluoroethylene (PTFE) base, which is chemically stable over a wide range of temperature and chemical environments. A PTFE, or perforated stainless steel disk, is screwed against the base to ensure adequate contact between the electrodes and the membrane with a porous insulator to prevent electrical contact between the electrodes and the steel disk. The sensor is then housed in a stainless steel assembly, as shown in Figure 4, that is made up of commercial off-the-shelf parts to reduce costs and simplify installation. The design and materials of construction are compatible in a wide range of environments with temperatures and pressures above 300 °F (149 °C) and 1000 psi (6.9 MPa), indicating that it could be applicable to many processes beyond natural gas transmission.

4 CONDUCTIVITY RESULTS

Initial conductivity measurements were performed using a commercial membrane conductivity system designed for fuel cell development. The system was chosen to provide a comparison point for later tests using the high-pressure probe. Measurements were made using EIS in 100 psi nitrogen for gas temperatures between 86 and 167 °F (30 and 75 °C) and dew points between 34 and 64 °F (1 and 18 °C). The results are given in Figure 5, where the dew point was translated into water content at 100 psi (0.69 MPa). Conductivity of the membrane increased linearly with water content. The decrease in conductivity with gas temperature follows the trend of decreasing relative humidity shown in Figure 3. Measurements were repeated in 100 psi (0.69 MPa) methane and a 90/10 % mixture of methane/carbon dioxide. The conductivity of the membrane was found to be largely independent of the gas composition, even with the presence of an acid gas such as carbon dioxide.

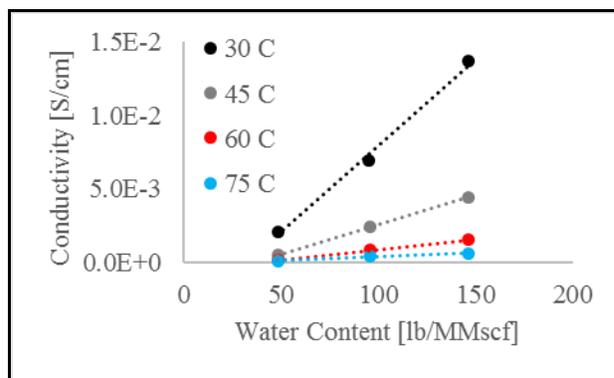


Figure 5: Conductivity of Nafion 117 with water content in 100 psi (0.69 MPa) nitrogen using the commercial conductivity system.

Two high-pressure conductivity probes were assembled and tested simultaneously in 100 psi ((0.69 MPa) nitrogen at 140 °F (60 °C) for comparison with the commercial cell. The results are shown in Figure 6. There was generally good agreement between the measurements using the homemade and commercial cells. The decrease in linearity was attributed to instability in the dew point control, as the trend was observed in both probes.

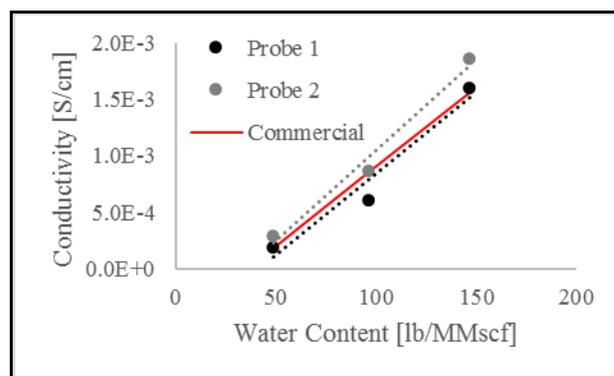


Figure 6: Conductivity of Nafion 117 with water content in 100 psi (0.69 MPa) nitrogen using the homemade (Probs 1 and 2) and commercial probes.

The high-pressure probes were then tested in 1000 psi (6.9 MPa) nitrogen at 140 °F (60 °C), and the conductivity results are shown in Figure 7. The membrane conductivity was largely unchanged with the increase in total pressure, following the correlation with relative humidity discussed in Section 2. The offset between the probes is attributed to small variations in the electrode spacing between the two assemblies. These results show that calibration and confirmation of conductivity probe data can be completed below the operating pressure to decrease both cost and calibration time without major effects on the accuracy. One issue of note is that the response time decreased considerably in the high-pressure environment. Use of a

thinner membrane is being investigated to improve the response.

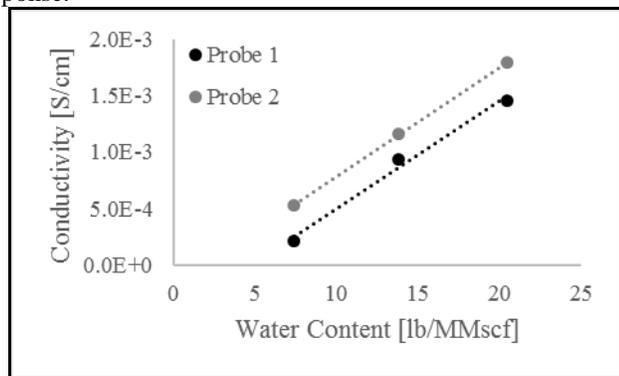


Figure 7: Conductivity of Nafion 117 with water content in 1000 psi (6.9 MPa) nitrogen using the high-pressure conductivity probes.

5 CORROSION RESULTS

Proof-of-concept corrosion measurements were performed using a carbon steel electrode in the commercial conductivity cell in 100 psi (0.69 MPa) nitrogen at 140 °F (60 °C) with a dew point of 52 °F (11 °C). The measured corrosion rate ranged between 4×10^{-4} and 8×10^{-3} mpy (10^{-5} and 2×10^{-4} mm y⁻¹). It was found that small variations in the contact surface between assemblies caused significant variation in the measured corrosion rate. This issue will be addressed as the high-pressure conductivity probes are modified to include a corrosion electrode.

6 SUMMARY AND ONGOING WORK

A solid state high-pressure conductivity sensor utilizing an ion conducting membrane was designed and tested for use in natural gas transmission pipelines. Testing found good agreement with results from a commercial membrane conductivity system in 100 psi (0.69 MPa) nitrogen from 86 to 167 °F (23 to 75 °C) and a linear relation between water content and conductivity. Membrane conductivity was largely independent of gas composition and system pressure up to 1000 psi (6.9 MPa). Preliminary corrosion measurements of carbon steel in 100 psi (0.69 MPa) (nitrogen using a modified commercial conductivity system found corrosion rates on the order of 10^{-4} to 10^{-3} mpy (10^{-5} to 10^{-4} mm y⁻¹), though variations in contact area between assemblies caused deviation in measurements between the tested assemblies. Modification of the high-pressure conductivity sensor is underway to include a carbon steel electrode for in-situ corrosion measurements. Corrosion testing will follow to determine the sensitivity of corrosion rate to changes in the water content. While membrane conductivity has been shown to be largely independent of total pressure and gas composition, it must still be

determined whether corrosion behavior shares this independence.

Initial results show promise that the current design can allow for low-cost solid state electrochemical sensors that can provide in-situ and real-time measurements of the water content and corrosivity in a natural gas pipeline. A second generation of the sensor could further improve reliability and decrease costs by depositing the electrodes and membrane onto a ceramic wafer. Once the platform for electrochemical measurements is established, it may be possible to incorporate additional electrodes, such as reference electrodes and ion selective electrodes, to increase the capabilities of the sensor. Such a sensor could be employed in a variety of gas and supercritical environments where the moisture content allows adequate conductivity of the membrane.

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