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Membrane-Coated Electrochemical Sensor for Corrosion Monitoring in Natural Gas Pipelines

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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 previously 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.

In our earlier studies the National Energy Technology Laboratory and the Pennsylvania State University prepared an initial design as part of their collaborative project for performing corrosion measurements in water-contaminated supercritical CO_2 pipelines [1-2]. These probes utilized a thin film of ion conducting polymer deposited across three electrodes, where moisture from the bulk CO_2 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.

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 Fig. 1. In this way, a five-electrode cell can be used to provide both corrosion measurements and accurate conductivity measurements of the membrane. As 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, as 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.

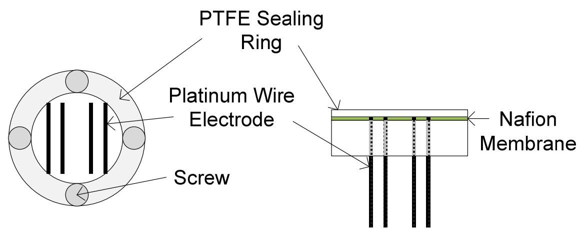

Fig. 1. Four-electrode conductivity probe for high-pressure gas systems [3-4].

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 tranmission lines. Water solubility in natural gas can be calculated according to ASTM D1142 [5].

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.

As an example, Fig. 2 shows the water content, in lb/MMscf, at 1000 psi as a function of dew point temperature calculated from ASTM D1142. It can be seen that the maximum water content, and thus the saturation pressure, increases considerably with the gas temperature.

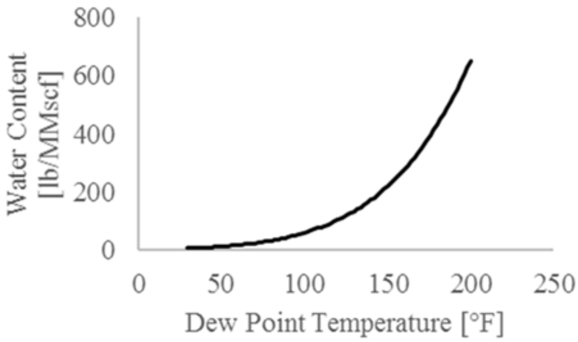

Fig. 2. Water content in 1000 psi (6.9 MPa) natural gas as a function of dew point temperature [3].

In Fig. 3 we see that while water saturation increases with temperature, relative humidity decreases with temperature when the dew point is held constant.

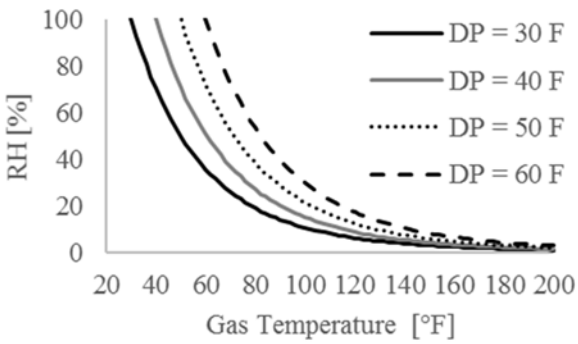

Fig. 3. Relative humidity in 1000 psi (6.9 MPa) natural gas as a function of gas and dew point (DP) temperature [5].

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 Fig. 1, pass a current between them. The inner two electrodes measure the electric 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.

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 used to prevent electrical contact between the electrodes and the steel disk. The sensor is then housed in a stainless steel assembly, as shown in Fig. 4, that is made up of commercial off-the-shelf parts to reduce costs and simplify installation.

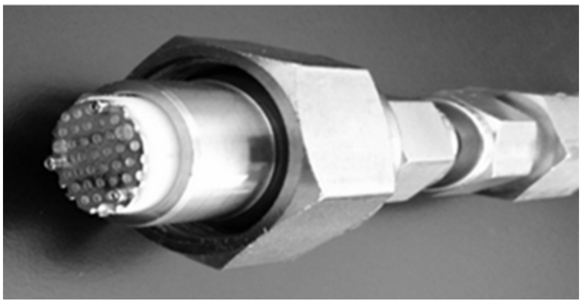

Fig. 4. Assembled high-pressure conductivity sensor.

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), meaning that it should 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 PEM fuel cell development. Fig. 5 presents the low pressure commercial system used.

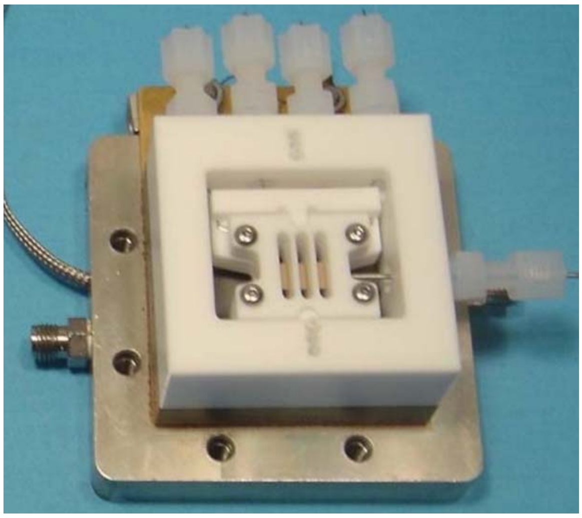

Fig. 5. Low pressure conductivity test cell.

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 Fig. 6, where the dew point was translated into water content at 100 psi (0.69 MPa).

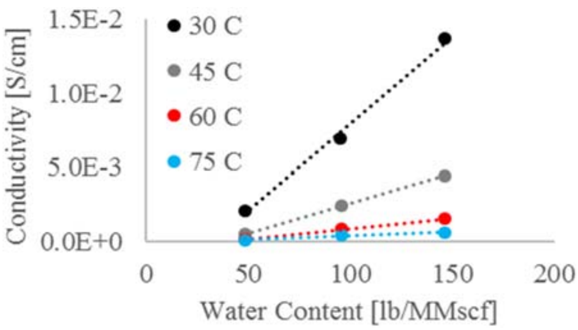

Fig. 6. Conductivity of Nafion 117 with water content in 100 psi (0.69 MPa) nitrogen using the commercial conductivity system [4].

Conductivity of the membrane increased linearly with water content. The decrease in conductivity with gas temperature follows the trend of decreasing relative humidity shown previously in Fig. 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.

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 Fig. 7. There was generally good agreement between the measuremets 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.

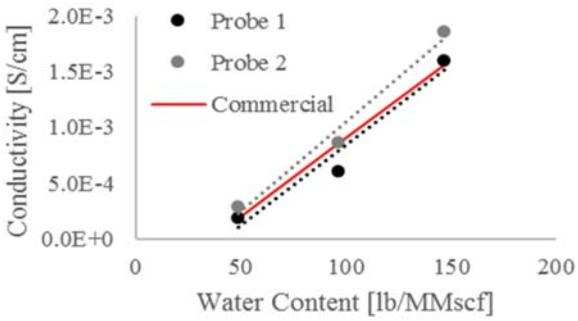

Fig. 7. Conductivity of Nafion 117 with water content in 100 psi (0.69 MPa) nitrogen using the homemade (Probs 1 and 2) and commercial probes.

The high-pressure probes were then tested in 1000 psi (6.9 MPa) nitrogen at 140°F (60°C). The flow-through system used with the commercial cell was modified to allow high-pressure operation. A gas booster was added that compressed the test gas from 100 psi to the test pressure of 1000 psi. The use of the booster allowed more efficient use of the test gas cylinders. The commercial conductivity cell was replaced with a custom high-pressure test cell, which consisted of a 1 in. diameter stainless steel cross and tee. A picture of the cell is shown in Fig. 8.

Fig. 8. High-pressure flow-through test cell with attached conductivity/corrosion sensors (right side of cell) and thermocouple/pressure transducer (left side of cell).

Flow was from top to bottom through the cell to allow any trapped water to be flushed through the system. Early tests had the flow horizontal, and over time water was found to collect in the dead legs which affected humidity control of the system. The new test cell was pressure tested up to 1000 psi and 75 °C. The high-pressure conductivity sensors attached to the system using 1 in. compression tubing fittings. A thermocouple and pressure transducer were connected opposite one of the sensors to monitor the temperature and pressure of the test cell.

The conductivity results are shown in Fig. 9. 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.

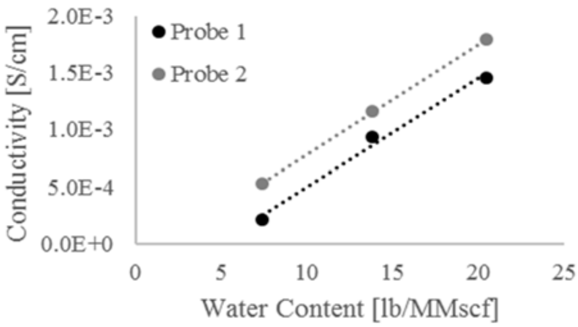

Fig. 9. Conductivity of Nafion 117 with water content in 1000 psi (6.9 MPa) nitrogen using the high-pressure conductivity probes [4].

5. Corrosion Results

Proof-of-concept corrosion measurements were performed using a carbon steel electrode in the commercial conductivity cell at 100 psi (0.69 MPa) nitrogen for 140 °F (60 °C) with a dew point of 52 °F (11 °C). The measured corrosion rate ranged between $4 \cdot 10^{-4}$ and $8 \cdot 10^{-3}$ mpy (10^{-5} and $2 \cdot 10^{-4}$ mm·y^{-1}). Linear polarization resistance (LPR) measurements were used to evaluate the corrosion rate of carbon steel. The system was held at a steady state for three days. Fig. 10 presents the corrsion rate over a 5 hour period for day 3 of the exposure test.

It was found that small variations in the contact surface between assemblies caused significant variation in the measured corrosion rate. This issue was addressed by using amn X-65 carbon steel plate in place of a wire when constructing the high-pressure corrosion probes. Furthermore, the low response time was reduced by replacing the 0.0178 cm thick Nafion membrane with the 0.0022 cm thick Nafion HP membrane.

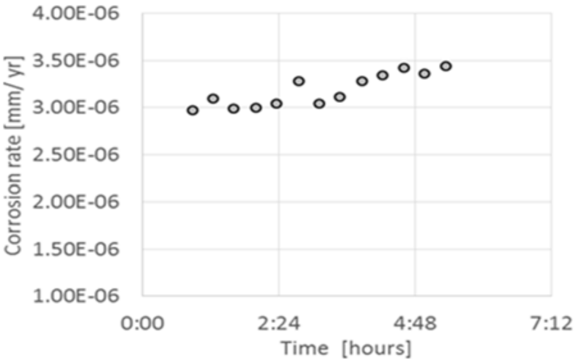

Fig. 10. Corrosion rate of a carbon steel wire overtime via LPR on day 3 at 60°C using the modified commercial cell.

Using the Nafion HP probe, the corrosion rate was quantified for a number of different water contents governed by dew point at 100 and 1000 psi. All tests were perfromed at 60 °C with N_2 as the background gas. Fig. 11 presents the LPR corrosion rate values obtained.

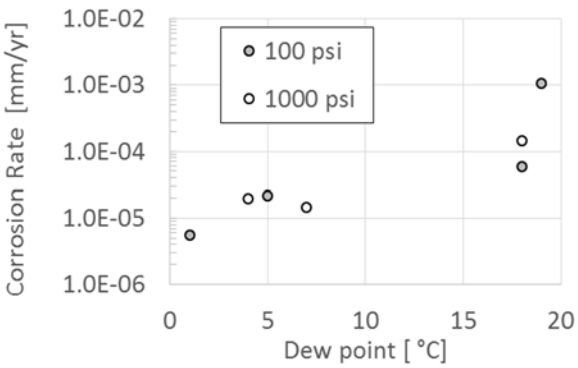

Fig. 11. Corrosion rate data for acell temperautre of 60 °C as a function of the dew point for the inlet humidifier.

As can be seen from Fig. 11, The corrosion rate did not depend strongly on the cell pressure. Little difference was found between results obtained for 100 and 1000 psi. Additionally, the humidifier dew point weakly influenced the corrosion rate at low dew points. However at higher dew points, the corrosion rate appeared to increase significantly with increases in dew point.

6. Summary and Ongoing Work

A solid state high-pressure conductivity sensor utilizing an ion conducting membrane has been designed and tested for use in natural gas transmission pipelines. Testing has 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 contents 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^{-3} mm·y^{-1}).

The high-pressure sensor solved the contact issue by using a rigid plate for the corrosion electrode and a perforated steel face plate to ensure good contact with the membrane. Corrosion rates for X-65 carbon steel measured with the high-pressure sensor increased from 0.01 to 0.1 μm·y^{-1} in N_2 at 60 °C as the dew point increased from 1 to 18 °C (7 to 21 lb/MMscf at 1000 psi). The corrosion rate was largely independent of system pressure.

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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