Ionic Liquid Based Coulometric Trace Humidity Sensors

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***Abstract*—This work presents a first attempt to use ionic liquids as a new coating for planar coulometric sensors. These sensors are used for the measurement of trace humidity in various gases. Usually, the coating of the sensors is tetraphosphorus decaoxide and its hydrolysis products. Instead, a hygroscopic ionic liquid was used as sensor coating in this work. Generated frost point temperatures t_f in the gas ranged from -80 °C to -30 °C, which is equivalent to vapour mole fractions x_v from 0.5 µmol·mol^{-1} to 376 µmol·mol^{-1}. In addition to the coulometric sensors, the generated humidity is determined by a precision dew point hygrometer as reference. First results show that it is possible to measure humidity with ionic liquid based coulometric sensors.**

Keywords-Coulometric sensors; Sensor coating; Trace humidity measurement; Ionic liquids.

I. INTRODUCTION

The accurate value of humidity in gases, which are used in technical and chemical processes, is an important quality factor. Therefore, it is necessary to measure it accurately and continuously. Even trace amounts of water vapour can influence a process negatively and thus its resulting products. Trace humidity of gases is defined by water vapour mole fraction x_v smaller than 2,000 µmol·mol^{-1}, which is equivalent to a frost point temperature t_f below -13 °C. Frost point temperature is the temperature at which the prevailing water vapour pressure is equal to the saturation vapour pressure and at which ice begins to form (constant pressure p) [1].

Coulometric sensors are an effective tool for trace humidity measurement in various technical gases, such as air, helium, argon, chlorine, hydrogen, nitrogen, and nitrous oxide [2][3]. In general, coulometric sensors are coated with tetraphosphorus decaoxide (P_4O_{10}) due to its hygroscopic property. One limitation of coulometric sensors is the measurement in gases which contain ammonia or amines. These substances can react with the P_4O_{10} and thus influence the reaction mechanism of the P_4O_{10}-H_2O-system [4].

In this work, a first attempt is presented to use a hygroscopic ionic liquid as coating for coulometric sensors. Section 2 briefly explains coulometric sensors, ionic liquids, trace humidity generation, and sensor integration. In Section 3, the obtained measurement results are shown and Section 4 presents the conclusion.

II. EXPERIMENTAL SETUP

A. Coulometric Sensors

Coulometric sensors were described first by Keidel as a method to determine water content of gases in 1959 [2][4][5].

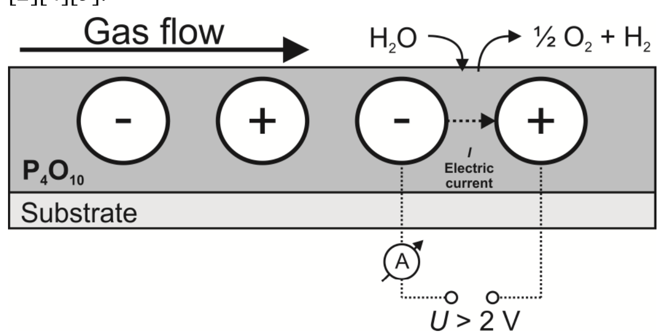

Figure 1. Sensor principle of a coulometric sensor; U: voltage, P_4O_{10}: tetraphosphorus decaoxide, H_2O: water, O_2: oxygen and H_2: hydrogen.

The sensing principle depicted in Figure 1 is based on the electrolysis of absorbed water in which it is decomposed to hydrogen and oxygen at a voltage of at least 2 V. Electrolysis of water can be described by means of Faraday's law, see (1), which states a correlation between the amount of electrical charge Q in C and water substance n_{Water} in mol:

$$Q = n_{\text{Water}} \cdot F \cdot z \tag{1}$$

where F is FARADAY'S constant (F = 96485.3 C·mol^{-1}) and z is the number of transferred electrons per converted molecule of H_2O (z = 2). In equilibrium state, the measured electrical current I is proportional to the mass of water m_{Water} in the gas flow as shown in (2).

$$I \propto m_{\text{Water}} \tag{2}$$

Resulting electrical current is influenced by incomplete water absorption, dependence on the gas flow, given voltage, gas pressure, temperature, and coating thickness.

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B. Ionic Liquids

Ionic liquids have a huge potential for nanoparticle synthesis, electrochemistry, batteries, fuel cells, and for sensor applications [6]. In general, ionic liquid is a salt in the liquid state at room temperature and consists usually of an organic cation and an inorganic anion. Further interesting properties are electrochemical stability against oxidation and reduction, electrical conductivity, and non-acid character.

C. Trace Humidity Generation

Trace humidity generation consists of a gas supply, dryer, humidifier, pressure controllers, mass flow controllers and a reference hygrometer. Test gas is generated by mixing two gas flows: a dry and a wet one. One flow is dried with a molecular sieve and the other flow is humidified by passing it through a bubbler filled with pure water. After this, the rate of both flows is controlled by mass flow controllers and mixed together resulting in a test gas. Next the generated test gas is split into four single gas flows: whereby three flows pass over coulometric sensors and one passes a calibrated dew point hygrometer (S4000 TRS, Michell Instruments).

D. Sensor Integration

During the measurements, the coated planar sensor elements (dr. Wernecke Feuchtemesstechnik GmbH) were protected by a porous polymer membrane to diminish the influence of a fluctuating gas flow rate [7]. Furthermore, the protected elements were embedded in stainless steel cells with gas inlet and outlet. A multiplexer allowed the simultaneous reading of the electrical current via a digital multimeter (3458A, Agilent) and provided the connection to the voltage supply, which was modified by adding a polarity reversal [8].

III. Results

Figure 2 shows the results of a performed measurement with three coulometric sensors that are dip-coated with an ionic liquid. The generated humidity in the gas expressed as frost point temperature ranged from -80 °C to -30 °C.

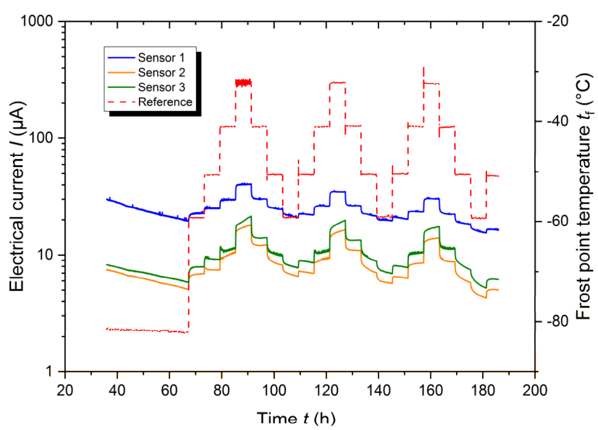

Figure 2. Electrical current I in µA of six coulometric sensors (left y-axis) and the reference humidity t_f in °C (right y-axis) over measuring time t in h.

Electrical current I (sensor signal) of the sensors (one to three) and reference value of humidity t_f (red-dotted line) are represented on the left and right y-axis, respectively. It is proved that electrical currents increase with a raise of humidity in the gas. Converse behavior is shown by a reduction of the humidity in the gas. However, the results show obvious deviations of the sensor signals. In total, sensor one measures higher signals in comparison to sensors two and three. A feasible explanation for the different signal intensity could be the unknown thickness of the sensor coating. Additionally, a distinct drift was observed for all three sensors.

IV. Conclusion

In this work, a first attempt is presented to use ionic liquids as coating for coulometric trace humidity sensors. First results show that sensors coated with ionic liquids response to humidity changes in the gas. However, the sensor intensities were different and an obvious sensor drift was observed. Further measurements are required to understand the reaction mechanism of water vapour and ionic liquid.

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