In this article, a room temperature ammonia sensor on a paper substrate is reported. The electrochemical sensor is constructed using platinum electrodes and ionic liquid electrolyte. The amperometric staircase response shows discernible signal differentiation between each concentration of NH\textsubscript{3} (5–25 ppm). The rise time and fall time for the NH\textsubscript{3} sensor were found to be 8 s and 7 s respectively. The authors believe such a fast responding NH\textsubscript{3} sensor on a paper substrate has never been reported. The detection limit was deduced to be 1 ppm based on the sensitivity versus concentration plot. A 17% decrease in sensor response was observed over 30 days of testing. Implementing an antenna on the paper substrate co-located with the sensor for wireless operation is envisioned in future.

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An Electrochemical Ammonia Sensor on Paper Substrate

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Printing technologies are aiding and revolutionizing the burgeoning field of flexible sensors by providing cost-effective routes for processing diverse electronic materials at temperatures that are compatible with low-cost substrates. Simplified processing steps, reduced materials wastage, low fabrication costs and simple patterning techniques make printing technologies very attractive for cost-effective manufacturing of devices. One of the technologies currently used to print sensors is inkjet printing. Inkjet printing technology offers lot of advantages toward sensor applications. Inkjet printing technology is environmentally friendly technology and cost-effective method. It is because inkjet printing technology does not use any hazardous chemicals to wash away unwanted metals on the substrate surface. It drops nano-sized ink on the desired position so that there are no by-products because it is an additive fabrication method. The advantages of the inkjet printing technology such as fast fabrication and ease of mass production helps to lower the cost of the inkjet-printed devices. Selecting the optimal substrates is one of the major issues in order to effectively realize low-cost and flexible inkjet-printed devices.

Paper-based sensors are alternative technology for fabricating simple, low-cost, portable and disposable analytical devices for many application areas including clinical diagnosis, food quality control, and environmental monitoring. The unique properties of paper which allow passive liquid transport and compatibility with chemicals are the main advantages of using paper as a sensing platform. Depending on the main goal to be achieved in paper-based sensors, the fabrication methods and the analysis techniques can be tuned to fulfill the needs of the end-user. Paper substrate is a conducive platform for inkjet printing to develop functional devices. In particular, the electrochemical modality nicely fits the paper substrate for realizing analytical devices.

Electrochemical paper-based analytical devices (PADs) were first published by Dungchai et al. in 2009. Electrochemical sensing is a good match for PADs because; (a) electrodes can be miniaturized and easily fabricated onto paper, (b) electrochemistry does not require complicated equipment, (c) portable potentiostats are already available for on-site measurements, and (d) a wide range of electrochemical methods are known, extending the application space across many fields of interest. Therefore, PADs have been employed for a variety of applications as discussed in recent articles.

Among the electrochemical PADs, amperometric gas sensors have gained interest with many desirable characteristics, including good sensitivity, selectivity and detection limit for electrochemically oxidizable or reducible toxic gases, and relatively low power requirements. Room temperature ionic liquids (RTILs) have received substantial attention in recent years because of their interesting and often unique chemical and physical properties. RTILs are ionically conductive and can therefore be used as electrolytes in electrochemical systems. In addition to their relevance to electrochemical systems, some RTILs have been reported to impart enhanced capabilities compared to aqueous or non-aqueous media, such as improved gas solubility.

Ammonia is a colorless, flammable gas with a pungent odor. It is commonly present in animal environments that are inadequately ventilated. Ammonia is primarily produced by the decomposition of urea, present in urine, in the presence of the enzyme urease, which is present in feces. A second source of ammonia is from animals that are fed high-protein diets that contain excess nitrogen to ensure that all of their nutritional needs are met. Excess nitrogen that is not metabolized is excreted in the form of urea, ammonia, and organic nitrogen in feces. This can lead to ammonia levels building up in animal facilities that have poor ventilation which can have negative impacts on both the human workers and the livestock. In humans, exposure to high levels of ammonia can cause irritation to the eyes, nose, and respiratory tract. It should also be noted that the human nose, while extremely sensitive to ammonia due to its pungent odor is unable to quantify it. There is a need for a room temperature ammonia sensor which is fast, sensitive, and selective with a detection limit of 5 ppm. There are several investigations of room temperature ammonia sensors. Table I highlights a literature survey of the different modality, electrode materials, and performance comparison of room temperature ammonia sensors from 2012 to 2016. In this article, fabrication and testing of a fast, room temperature amperometric ammonia sensor on paper substrate is reported.

**Experimental**

The printing system used is the Dimatix 2831 Materials Printer from Fujifilm. The main advantage of this printer is it uses a low cost user fillable piezoelectric MEMS ink jet cartridge capable of printing a wide range of fluids. The drop formation and the overall printing settings for the fluid were tailored using the drop watcher mode. The electrode ink used for this project is a platinum ink from Gwent Electronic Materials. The ink was degassed and stored in a bottle under slight vacuum to reduce gas bubbles trapped in the ink. Ink performance is visually and qualitatively observed to decline over the life of a single disposable cartridge. For this reason the print cycles are planned in advanced and each cartridge is printed to exhaustion in a short time frame to avoid ink settling and jet clogging. The ink is vacuum treated and stored in 20 mL quantities and drawn with a fine needle syringe in 1.5 mL quantities with care taken to not introduce air bubbles into the ink. The cartridge is then left to settle in the printer for 30 minutes before initiating printing. In between print cycles the printer is left on with a cleaning cycle setup to run every 3 minutes to avoid jet clogging and ink settling as much possible.
The electrolyte used in this sensor is an RTIL from Sigma Aldrich, 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide (BmpyrNTf₂). This electrolyte was chosen for its chemical stability, low vapor and chemical safety. The RTIL ink is a clear liquid. The substrate used here is Kodak photo paper. The electrochemical gas sensor was fabricated using the inkjet printing method. First the RTIL was deposited on the paper substrate, and (B) SEM micrograph of the electrode and the RTIL is shown. The AC impedance measurement was performed using the potentiostat/galvanostat. The electrodes are bathed in the electrolyte. Figure 1A shows the photograph of the sensor. Figure 1B shows the scanning electron micrograph of the electrode and the electrolyte.

The enclosed sensor set-up was connected a Princeton Applied Research PARSTAT 4000 potentiostat/galvanostat. The sensors were biased at +250 mV vs. Pt reference. NH₃ was used as the analyte whereas NO, NO₂, C₃H₆, H₂, H₂S, C₂H₅OH, and CO were used for interference testing.

Air was used as the base gas. In the current study, the flow rate of the various gas mixtures was controlled using an automated Trace Vapor Generator (TVG). TVG was also used to generate varying concentrations of CH₄ and other interfering species. The flow rate was fixed at 200 sccm. The concentration of NH₃ was varied from 5 ppm to 25 ppm using the dilution system automated by the TVG. The AC impedance measurement was performed using the potentiostat instrument in the impedance mode with a frequency sweep from 13 MHz down to 10 mHz and a perturbation of 10 mV. In addition, an I-V plot was generated by a voltage sweep spanning −0.5 V to 0.5 V.

### Results and Discussion

Based on preliminary investigations, the authors found that the best electrode and electrolyte material for a sensitive, fast, and selective ammonia sensor to be Pt and BmpyrNTf₂ respectively. Figure 2A shows a plot of the response time of the sensor as a function of concentration of NH₃. The baseline response is 0 A. The staircase response shows discernible signal differentiation between each concentration of NH₃. Response time of the sensor was extracted from the time varying amperometric response. The rise time (tᵣᵣᵣ) is defined as the time required for the sensor output to reach 90% of the full-scale value (maximum current). Similarly, fall time (tᵣᵣᵣᵣ) is defined as the time required for the sensor output to diminish to 10% of the full-scale value. The rise time and fall time of the NH₃ sensor were found to be 8 s and 7 s respectively. The authors believe such a fast responding NH₃ sensor on a paper substrate has never been reported. The device sensitivity is defined as the difference in current generated upon exposure to the test and base gas respectively.

Figure 3 shows the sensitivity plot as a function of concentration with added error bars. The error bars are based on three trials of NH₃ exposure. An initial assessment of the data points indicate a nonlinear response. Upon curve fitting, it was found that an ‘Exponential Rise’ model fitted the data points with an R² value of 0.99 and a low chi-square value. The equation of the fit was found to be:

\[
y = m_1 + m_2(1 - e^{-x^{m_3^{m_4}}})
\]
Figure 2. Staircase NH₃ amperometric response. Concentration of NH₃ varying from 5 ppm to 25 ppm. Flow rate was maintained at 200 sccm. The letter ‘μ’ stands for the symbol ‘μ’. The current is in microamps. The baseline response is 0 A. The rise time and fall time for the NH₃ sensor were found to be 8 s and 7 s respectively.

Where, ‘y’ represents the sensitivity and ‘x’ represents the concentration of NH₃ in ppm. The response of these gas sensors to analyte is complex and directly dependent on several factors, including the nature of the interaction of the electrolyte with the dense working electrode structure, and the kinetics of electron transfer at the dense electrode. It is speculated that the possible cause for non-linearity may be caused by printing a dense electrode over the RTIL such that the amount of active Pt surface area is limited, which limits the current that can be supported. The sensing mechanism is based on the oxidation of ammonia. NH₃ is oxidized at the Pt working electrode according to:

\[
4 \text{NH}_3 \rightarrow 3\text{NH}_4^+ + \frac{1}{2}\text{N}_2 + 3\text{e}^-
\]

The direct oxidation of ammonia in RTILs/Pt is an electrochemical process, where three ammonium ions are formed for every four ammonia molecules, in an overall three-electron process. Ammonia is initially oxidized, to produce nitrogen gas and protons, which readily protonate or are solvated by the RTIL. The protonated anion then reacts further with ammonia, to set up equilibrium with ammonium and solvent ions. A detailed reaction pathway can be found in an article by Roger et.al. The oxidation of NH₃ can be accomplished at 0 V versus the reference electrode which is optimal for commercial implementation, or the reaction can be driven by application of positive bias as presented here. Based on the inference from supplementary Figure 1, the detection limit of this device was found to be 1 ppm.

Figure 4 shows the Nyquist plot of the device when exposed to 15 ppm of NH₃ and air (base gas). In an impedance spectrum obtained from an electrochemical device, the contributions of the bulk electrolyte and the electrode/electrolyte interface are identified by the frequency dispersions. In general, the low frequency region represents the electrode polarization/charge transfer phenomenon while the high frequency component represents the bulk conductivity of the sample. It is to be noted that the bulk conductivity of the sample is an additive effect of the ionic conductivity of the electrolyte, electronic conductivity of the electrodes, and electronic conductivity of the leads. As the ionic conduction in the electrolyte forms a major representation of the high frequency portion of the Nyquist plot, in further sections, the bulk conductivity of the sample will be approximated to the ionic conductivity of the electrolyte. A subtle difference is seen in the low frequency region indicating a possible change in interfacial (Electrode/Electrolyte) resistance upon exposure to NH₃ in comparison to air.

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electrolyte resistance $R_E$ and capacitance $C_E$ were found to be 72.56 kΩ and 67.85 pF. The interface resistance and capacitance upon exposure to NH$_3$ was found to be 256.2 kΩ and 9.91 μF. The difference between the interfacial resistance upon exposure to air and NH$_3$ was found to be 26.6 kΩ. Chi-square ($\chi^2$) value of all the fits were found to be $1 \times 10^{-5}$.

Figure 5 shows the cross-sensitivity plot. The concentration of all the analytes were fixed at 15 ppm. The sensor was insensitive to NO, NO$_2$, C$_2$H$_5$OH, and CO. The sensor signal to NH$_3$ was six fold higher when compared to C$_3$H$_6$ and H$_2$ and three fold higher when compared to H$_2$S. Selectivity to NH$_3$ can be further increased by incorporating a hydrocarbon filter on top of the sensor. The authors then tested the long-term stability of sensor. The NH$_3$ response was recorded every 5 days for a 1 month period. The sensor was kept at room temperature and was biased only during testing. Figure 6 shows the amperometric response of the sensor over a 30 day period. A slight decrease in the sensor response was observed from the 10th day. Overall, a 17% decrease in sensor response was observed on the 30th day when compared to the start date. The error bars indicate three trials of NH$_3$ exposure. It is speculated that the sensor response decrease is attributed to the electrolyte aging and microstructural changes in platinum. After 30 days of testing, the authors measured the I-V response of the sensor upon exposure to 15 ppm of NH$_3$ with an applied voltage from $-0.5$ V to 0.5 V. Figure 7 shows the I-V plot indicating a linear relationship between the applied voltage and the measured current. The slope of the curve matches with the total resistance of the device calculated from the impedance curve.

In comparison to the different electrode materials and devices listed in Table I, the current device seems to be superior in terms of the response and recovery times and selectivity. However, the sensor reported is non-linear, an impediment to practical applications. Future investigations are necessary to bring in a linear trend in the sensor response to various concentrations of ammonia. The authors envision the following tasks as future activities: (a) construct an electrical equivalent model from the Nyquist plot and extract the resistance and capacitance parameters; (b) study the microstructural changes in platinum to improve long-term stability and linearity; (c) introduce hydrocarbon and H$_2$S filter; and (d) implement antennas on the paper substrate co-located with the sensor for wireless transmission of data.

Summary

The article reported on a room temperature amperometric ammonia sensor on paper substrate. The sensor was fabricated using Pt electrodes and RTIL electrolyte. The sensor responded to varying concentration of NH$_3$ from 5 ppm to 25 ppm. The rise time and fall time for the NH$_3$ sensor were found to be 8 s and 7 s respectively. The Nyquist plot indicating a possible change in interfacial resistance upon exposure to NH$_3$ in comparison to the base gas. The sensor is selective to NH$_3$ with six fold increase in the signal in comparison to
C₃H₆ and H₂. A 17% decrease in sensor response was observed over 30 days of testing.

Acknowledgments

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