Miniaturized electrochemical gas sensors for monitoring O_2 and CO_2

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Introduction

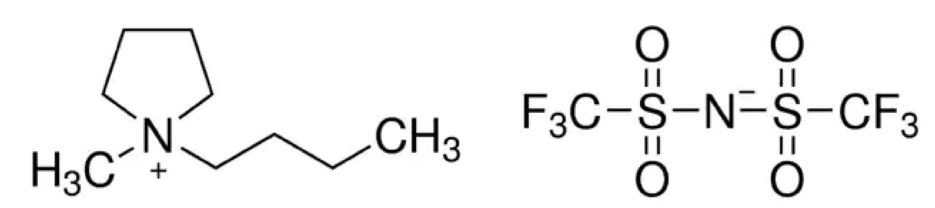
Electrochemical gas sensors have great potential for low-cost, ubiquitous sensing. Commonly, these sensors contain an aqueous electrolyte. The electrolyte of the sensor presented here are ionic-liquid based. **Room Temperature Ionic Liquids (RTILs)** have several favorable properties, such as **low volatility**, **high stability** and sufficient **conductivity**. These properties allow for **miniaturization** of the sensors, which can be optimized for various gasses such as ethylene[1], $\mathbf{O_2}$ **and** $\mathbf{CO_2}$.

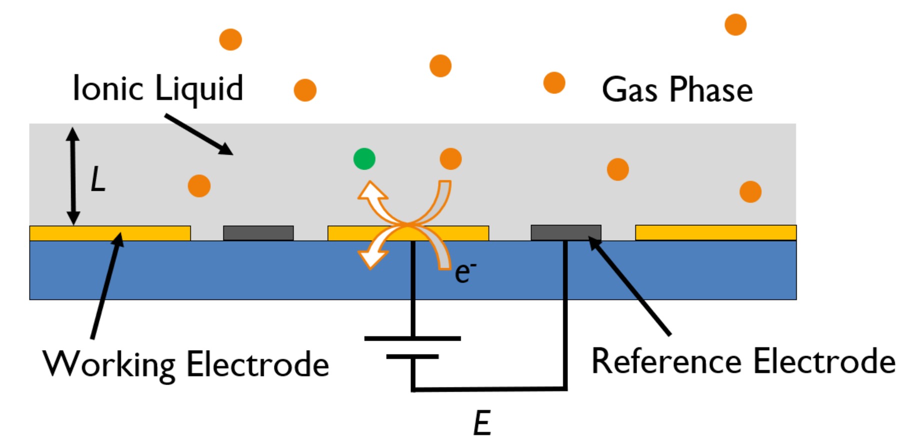
(1) Zevenbergen, M. A. G., et al. (2011). Electrochemical sensing of ethylene employing a thin ionic-liquid layer. Analytical Chemistry, 83(16), 6300–6307.

Room Temperature Ionic-Liquid (RTIL) gas sensors

We have selected the ionic liquid **[Bmpyr][TFSI]**, based on its **high solubility** to CO_2 and O_2, because it is **non-toxic, stable** and has a **large electrochemical window.** The IL is deposited onto planar three- or two-electrode configurations. The sensors are conditioned and operated using a **home-built gas testing system** and **commercial potentiostat** (BioLogic SP 300).

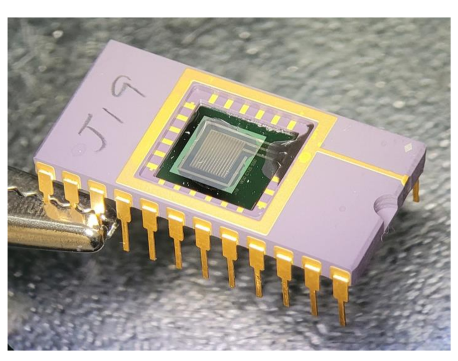
1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide
[Bmpyr][TFSI]



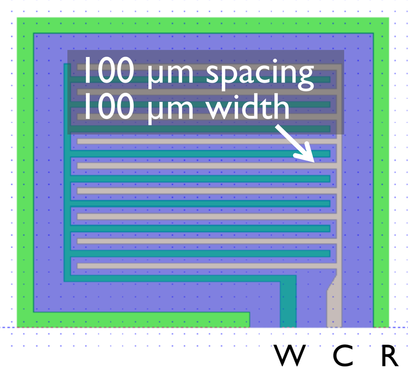


Amperometric O_2 sensor

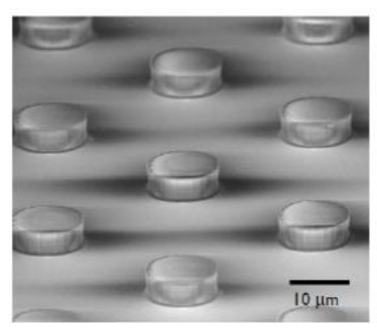
- O_2 sensor based on Si with interdigitated **platinum (Pt) electrodes** on **3D silica (SiO_2) micropillars**
- Micropillars create a **stable, continuous film of ionic liquid** on top of the electrodes[2]



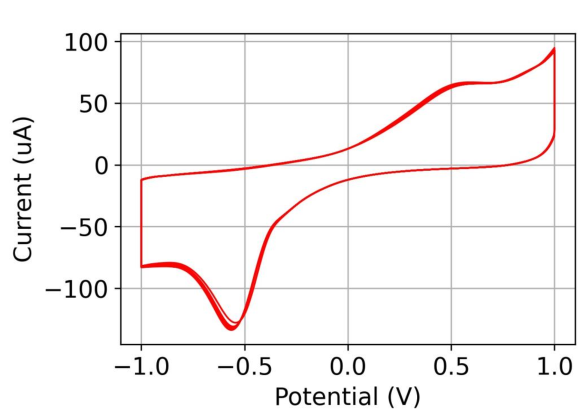
Sensor-die attached in ceramic DIL package



W = Working electrode
C = Counter electrode
R = (pseudo) Reference electrode



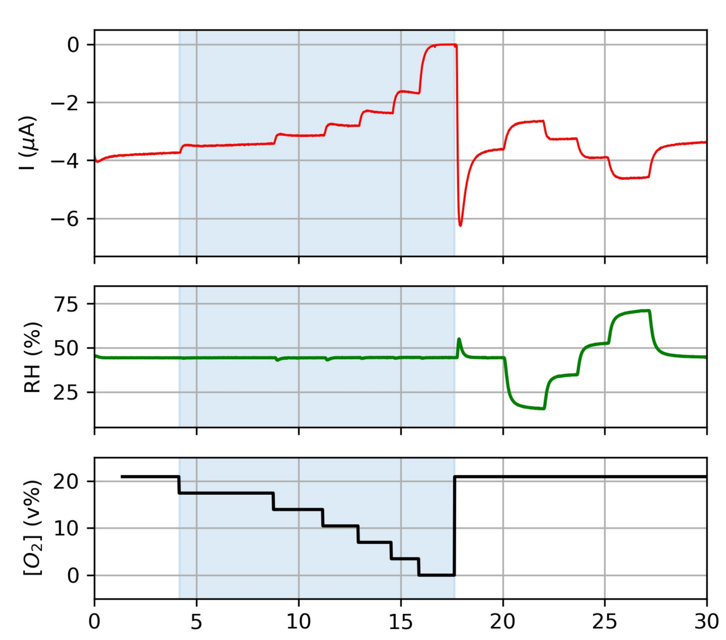
3D SiO_2 micropillar surface[2]



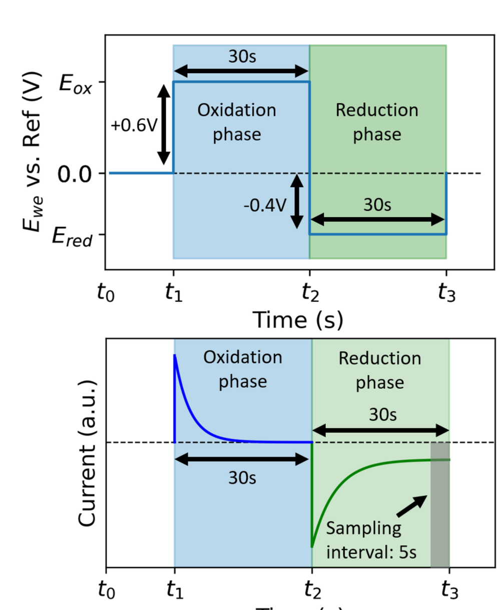
Cyclic voltammogram (with 10s hold step at the vertices) shows a clear O_2 reduction peak around -0.6V vs. Pt ref

$$i_s = \frac{nFADc_B}{L}$$

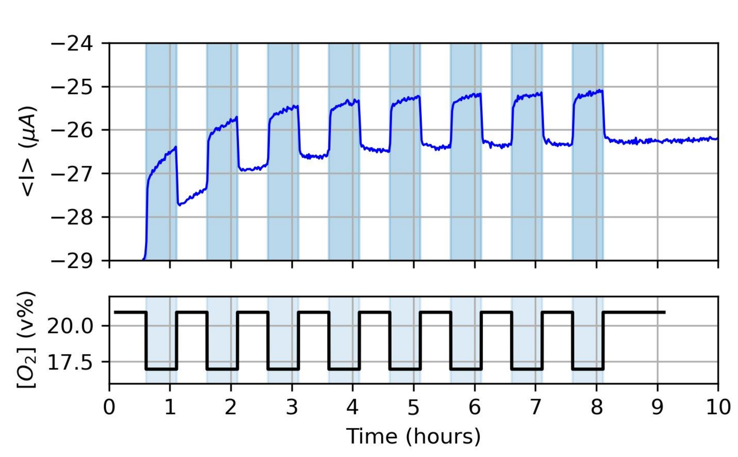
Diffusion-limited steady-state current i_s depends on:
- Electrode area A
- IL layer thickness L
- Diffusion coefficient D
- Analyte concentration c_B



Chrono-Amperometric response at -0.6V shows the sensitivity towards O_2 and RH



Double Step Chrono-Amperometric (DSCA) readout to improve sensor baseline stability

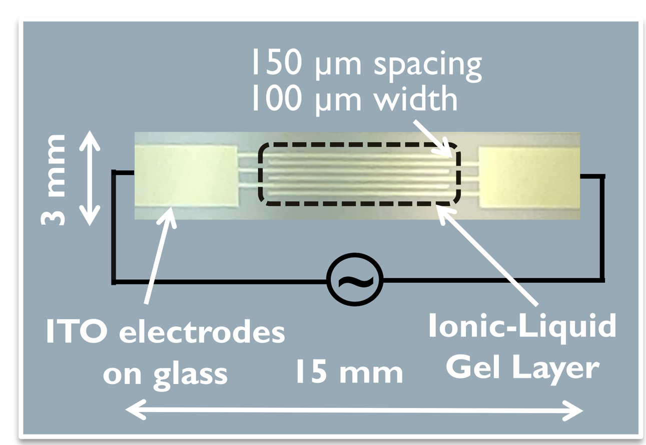


Double Step Chrono-Amperometric (DSCA) response at -0.4V and +0.6V vs. Pt ref shows the improved stability of the sensor

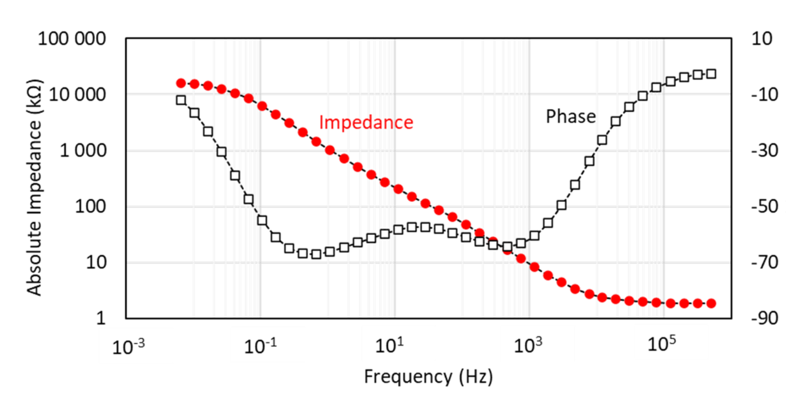
(2) Oudenhoven, J. F. M. et al., (2015). Device and method for electrochemical gas sensing. European Patent EP 2827141 A1

Impedimetric CO_2 sensor

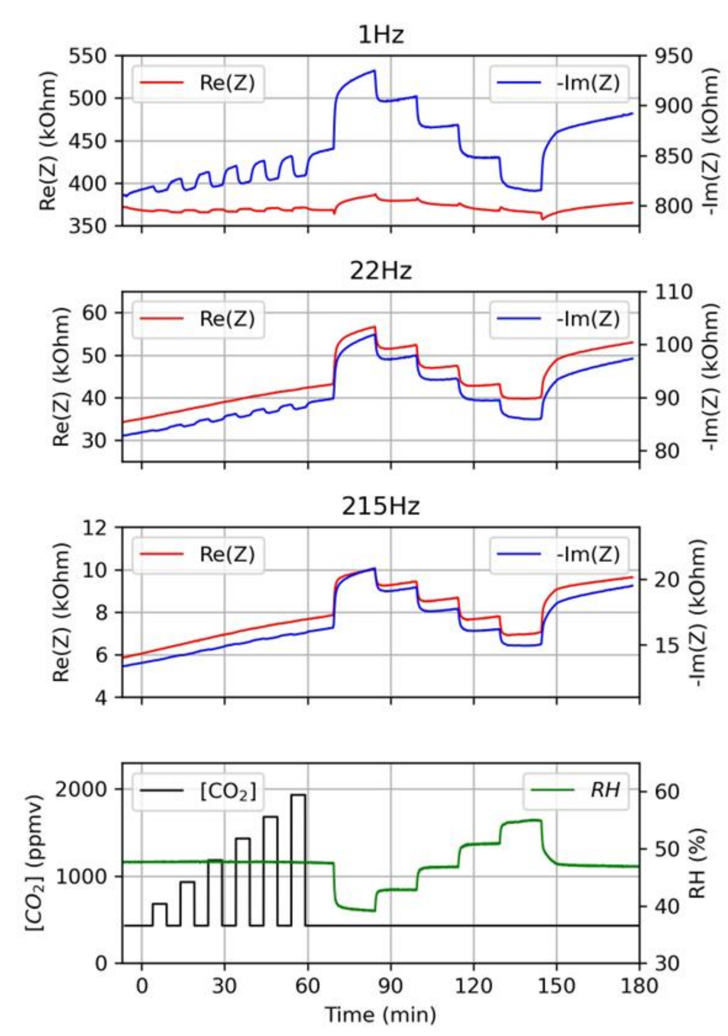
- CO_2 sensor based on **ionic liquid-polymer gel** deposited on top of Indium Tin Oxide **(ITO) electrodes** on glass
- Gel based on poly(vinylidene fluoride-co-hexafluoropropylene) (**PVDF-HFP,** Mw ~400.000) in acetone



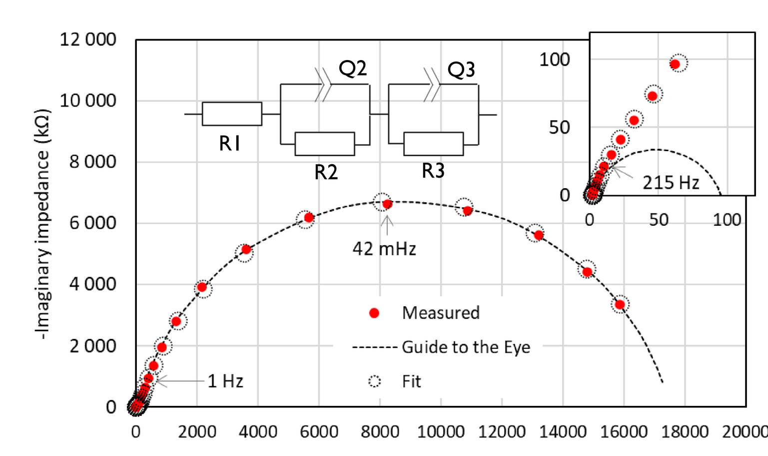
AC signal with a sine amplitude of 141 mV and a DC bias of 2.7V was applied



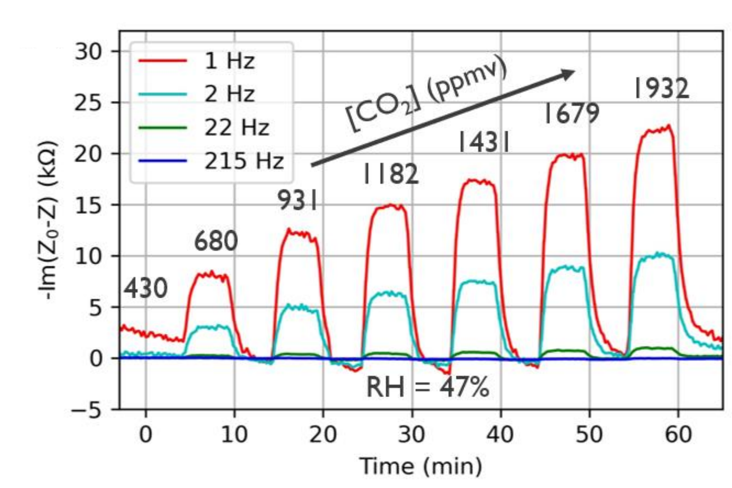
Bode plot shows capacitive behavior (phase angle minima around 0.5 and 400 Hz)



Real (red) and imaginary (blue) impedance measurements shows the sensor sensitivity towards CO_2 and RH



Nyquist plot. Insert: zoom of the high frequency points. The data was fit to the displayed equivalent circuit.



Change in imaginary part of the impedance as function of CO_2 concentration

Conclusion

- We have developed **miniaturized electrochemical gas sensors** using a **Room Temperature Ionic Liquid** (RTIL) as electrolyte.
- We optimized the sensors for detection of $\mathbf{O_2}$ **and** $\mathbf{CO_2}$ based on **Amperometric** and **Impedimetric** detection respectively.
- We explicitly evaluated the **cross-sensitivity towards Relative Humidity**, something that is often neglected in the literature but highly relevant for targeted applications such as **on-demand ventilation** and **bioreactor headspace monitoring**.
- Benefits of these sensors are their **small form factor**, potential for **low-cost fabrication** and possibility to integrate with **low-power micro-electronics**.

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Outlook: Bioreactor monitoring