Supporting information

Electrochemical sensing of ethylene employing a thin ionic-liquid layer

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Device fabrication

The ethylene sensor was fabricated according to the scheme shown in Figures S1a and b (cross-sectional and top view, respectively) and consisted of four steps. First, 10 nm Ti as adhesion layer and 100 nm Pt were sputtered on a Si wafer with a 1 μm thermally grown SiO₂ insulating layer. These were then patterned by photolithography and ion beam etching into a disk Pt working electrode (WE, radius 550 μm) surrounded by a ring Pt quasi-reference electrode (REF, inner and outer diameter 1200 μm and 2000 μm, respectively), a rectangular counter electrode (CE, 1800 μm × 500 μm), feed wires and bond pads. Second, 200 nm Si₃N₄, 600 nm SiO₂ and 200 nm Si₃N₄ (nitride-oxide-nitride, NON-layer) were deposited by plasma enhanced chemical vapor deposition as a capping layer preventing leakage from the feed wires. Third, disk (radius 500 μm), ring (inner and outer diameter 1300 μm and 1900 μm, respectively) and rectangular (1700 μm × 400 μm) holes were etched through the capping layer and centered on the electrodes fabricated in the first step. This step defined the area exposed to solution. Finally, the WE was modified by sputtering 10 nm Ti and 200 nm Au centered in the well by photolithography and by lift-off.

Before casting the IL, the working electrode was extensively cleaned by depositing a droplet of freshly prepared piranha on the device for 5 minutes and rinsing with deionized water afterwards. We note that such a harsh cleaning was necessary to remove any fabrication residues and to obtain reproducible results between devices. Next, cyclic voltammetry between -0.1 V and 1.5 V vs Pt in 0.5 M sulphuric acid (H₂SO₄) with a scan rate of 0.5 V/s or 0.1 V/s was performed until stable voltammograms were obtained that showed the characteristic behavior of gold. The sensor was then rinsed with deionized water, isopropanol and dried in a stream of nitrogen.
The device was mounted in a custom built flow chamber and could be exposed to various ethylene concentrations in a nitrogen carrier flow. Part of the carrier flow was directed through water bubblers and mixed with dry nitrogen to control the humidity. The volume of the chamber was 10 cm\(^3\) and a mass flow controller set the gas flow to 150 sccm through the chamber. After injection in the main flow, the ethylene flowed through \(~50\) cm tubing before arriving at the sensor surface. The main flow was turbulent and the ethylene was therefore completely mixed in the transversal direction of the tubing and arrived as a plug flow in the measurement chamber. The sensors response on flow rate was investigated and above 90 sccm, the response became independent of flow rate (see section below). At 150 sccm the mixing in the measurement chamber thus occurs on a time scale much faster than the sensor response and is in principle a step-wise increase of the concentration.

![Figure S1. Cross-sectional (a) and top view (b) of the various stages in the sensor fabrication process.](image)

1. A disk Pt working electrode (WE) surrounded by a ring Pt quasi-reference electrode (REF) and rectangular counter electrode (CE) were patterned and 2. covered by a capping layer consisting of 200 nm Si\(_3\)N\(_4\), 600 nm SiO\(_2\) and 200 nm Si\(_3\)N\(_4\) (NON-layer). 3. Holes were etched through the NON-layer. 4. The WE was modified by patterning a layer of Au aligned in the well.

**Theory**

We derive the steady-state current and transient response for a disk working electrode covered by a thin film of ionic liquid that is exposed to a sudden increase of a target gaseous analyte. Buzzeo and Compton derived steady-state currents for various gas sensor geometries, some covered by a gas permeous membrane.\(^1\) Here we extend their formalism for the case where the radius of the working electrode is much larger than the ionic liquid layer thickness \((r_0 \gg L)\) and we include electron-transfer kinetics for completeness. Since \(r_0 \gg L\), the concentration profile
of the electroactive species in reduced form, \( c(z,t) \), where \( z \) is the distance from the working electrode, is described by the one-dimensional diffusion equation (ignoring radial diffusion)

\[
\frac{\partial c(z,t)}{\partial t} = D \frac{\partial^2 c(z,t)}{\partial z^2}
\]  

(S1)

Here \( D \) is the diffusion coefficient and the initial condition is given by \( c(z,0) = 0 \). The boundary condition at the working electrode is the Butler-Volmer equation for a totally irreversible oxidation:

\[
\frac{i}{nFA} = D \left. \frac{\partial c}{\partial z} \right|_{z=0} = k_{\alpha} c(0,t) = k^0 \exp\left((1-\alpha)f \left[ E - E^0 \right] \right) c(0,t)
\]  

(S2)

where \( i \) is the overall current, \( n \) the number of electrons transferred, \( F \) Faraday’s constant, \( A \) the electrode area, \( k^0 \) the heterogeneous rate constant, \( \alpha \) the transfer coefficient, \( f = F / RT \) where \( R \) is the gas constant, \( T \) the temperature, \( E \) the applied potential to the working electrode and \( E^0 \) the formal potential. During experiments, a constant gas flow was forced towards the device, therefore we assume a constant analyte concentration at the ionic liquid–gas boundary

\[ c(L,t) = c_B \]  

(S3)

which is given by the partial pressure \( p \) via Henry’s law \( p = Hc_B \) (\( H \) is Henry’s constant). For the case \( r_0 \sim L \), radial diffusion towards the electrode cannot be ignored anymore and the problem becomes two dimensional but mathematically unwieldy. The diffusion equation was numerically solved using finite-element calculations described below.

**Steady-state current**

The steady-state solution of the diffusion equation obeying the boundary conditions (Equations (S2) and (S3)) is a linear concentration profile and the steady-state current

\[
i_s = nFAD \left. \frac{\partial c}{\partial x} \right|_{x=0} = nFADk_{\alpha} c(0,t)
\]

at a given applied potential \( E \) is given by

\[
i_s = \frac{nFADk_{\alpha} c_B}{1 + \frac{Lk_{\alpha}}{D}}
\]  

(S4)

We now discuss two limiting cases. First, at high applied potential \( E \gg E^0 \), the electron-transfer rate exceeds mass-transport towards the working electrode \( (Lk_{\alpha} / D \gg 1) \) because
Diffusion limits the current and Equation (S4) reduces to the steady-state current through a thin film:

\[ i_s = \frac{nFADc_B}{L} \quad (S5) \]

Second, at low applied potential \((E \ll E^0)\), \(Lk_{ox}/D \ll 1\), the current is initially kinetically limited and Equation (S4) can be simplified to:

\[ i_s = nFAk_{ox}c_B \quad (S6) \]

which is insensitive to \(D\) and \(L\) but depends exponentially on \(E\). In the full range of \(Lk_{ox}/D\), \(i_s\) is always smaller than the maximum diffusion-limited current given by Equation (S5). Therefore, the largest current magnitude is achieved in the mass-transport limited regime \((E \gg E^0)\), and can be enhanced by decreasing the IL layer thickness or careful choice of the IL for which the product of analyte solubility and diffusion coefficient is largest.

**Current-time step response**

The full solution to Equations (S1)-(S3) can be calculated for the two limiting regimes. First, in the mass-transport limited regime, the target analyte is fully oxidized due to fast kinetics leaving no reduced species at the surface. Boundary condition (S2) therefore reduces to \(c(0,t) = 0\) and the concentration profile is

\[
\frac{c(z,t)}{c_B} = \frac{z}{L} - \sum_{m=1}^{\infty} \frac{2(-1)^{m+1}}{m\pi} \sin \left[ \frac{m\pi z}{L} \right] \exp \left[ -\frac{m^2 \pi^2 Dt}{L^2} \right]
\]

Concentration profiles at various normalized times are shown in Figure S2a. Applying Equation 2 yields the current step response, which is shown in Figure S2c (black line):

\[
\frac{i(t)}{i_s} = 1 - \sum_{m=1}^{\infty} 2(-1)^{m+1} \exp \left[ -\frac{m^2 \pi^2 Dt}{L^2} \right]
\]

Second, in the kinetically limited regime, \(k_{ox} \approx 0\), which implies \(D \frac{\partial c}{\partial z}\bigg|_{z=0} \approx 0\) and the current can be determined using \(i(t) = k_{ox}c(0,t)\). The concentration profiles and current response are respectively:

\[
\frac{c(z,t)}{c_B} = 1 - \sum_{m=0}^{\infty} \frac{4(-1)^m}{(2m+1)\pi} \cos \left[ \frac{(2m+1)\pi z}{2L} \right] \exp \left[ -\frac{(2m+1)^2 \pi^2 Dt}{4L^2} \right]
\]
\[ \frac{i(t)}{i_s} = 1 - \sum_{m=0}^{\infty} \frac{4(-1)^m}{(2m+1)\pi} \exp\left[ -\frac{(2m+1)^2 \pi^2 Dt}{4L^2} \right] \]  

(S10)

The concentration profiles are shown in Figure S2b, while the (normalized) current step response is depicted in Figure S2c (red line). The sensor response times are \( t_r = 4L^2 / \pi^2 D \) in the kinetically limited regime and \( t_r = L^2 / \pi^2 D \) in the mass-transport limited regime. A sensor operating in the mass-transport limited regime reaches \( i_s \) faster, as can be seen in Figure S2c.

For completeness, the blue line in Figure S2c is the sensor response when mass transport is comparable to the electron-transfer kinetics \( (L_{k_{ox}} / D = 1) \) which is in between the two limiting regimes, as expected. This response was obtained by numerically solving Equations (S1)-(S3) using Matlab 2010a. Equation (S8) was used to fit the traces of Figures 3a and 4a of the main text, while the the traces of Figure 5 were fitted with the full numerically determined solution of Equations (S1)-(S3).
Figure S2. Concentration profiles and current-time responses to a stepwise increase of the analyte concentration to \( c_B \) at the edge of a thin ionic-liquid film. The working electrode is located at \( z = 0 \) while the gas-phase – ionic liquid interface is at \( z = L \). At this boundary, the concentration remains fixed \( (c(L, t) = c_B) \), because the edge is in equilibrium with the gas phase and a constant gas flow towards the sensor is assumed. The concentration profile and current response is plotted at various normalized times \( \tau = \pi^2Dt/L^2 \). (a) Mass-transport limited regime \((Lk_{ox}/D \gg 1)\). The electron-transfer kinetics are much faster than diffusion and therefore ethylene is depleted at the electrode surface \( (c(0, t) = 0) \). (b) Kinetically limited regime \((Lk_{ox}/D \ll 1)\) The electrochemical reaction is limited by sluggish kinetics and therefore the surface concentration approaches \( c_B \) for \( \tau \to \infty \). (c) Normalized \((i/i_s)\) current-time response to an increase of the target analyte concentration to \( c_B \) at the ionic liquid – gas interface. The response is shown for the mass-transport limited (black line), kinetically limited regime (red line) and an intermediate regime for which \( Lk_{ox}/D = 1 \) (blue line). The sensor response time is larger in the kinetically limited regime.
Finite-element calculations

The model introduced in the previous section ignores radial diffusion to the electrode. When the IL layer thickness is comparable or exceeds the working electrode radius, radial diffusion can no longer be ignored. Here we determine for which ratio $L/r_0$ the thin-film approach is accurate. The steady-state two-dimensional axisymmetric diffusion equation,

$$\frac{\partial^2 c(r, z)}{\partial r^2} \frac{1}{r} \frac{\partial c(r, z)}{\partial r} + \frac{\partial^2 c(r, z)}{\partial z^2} = 0$$  \hspace{1cm} (S11)

was numerically solved for the geometry of Figure S3a using Comsol Multiphysics 4.1. The geometry represents the disk working electrode with $r_0 = 500 \, \mu m$ covered by an IL layer with thickness $L$ that was varied during the simulations. Boundary equation (S2) was applied to the working electrode surface while the concentration at the edge of the IL layer was held constant, $c(r, L) = c_B$. Figure S3a shows a concentration profile and the current was determined by integration over the electrode surface.

Figure S3b shows the current as a function of $L/r_0$ for various $k_{ox}$ in the range $10^{-7}$ m/s (kinetically limited) to $\infty$ (mass-transport limited). The current was normalized by the steady-state current of a disk electrode, $i_s = 4nFDc_n r_0$, depicted by the dotted line. For each curve in Figure S3b a transition can be seen from thin-film behavior (gray shaded area) to a radial diffusion limited region (purple shaded area, $L/r_0 > 10$). The dashed lines are drawn according to Equation (S4). The deviation from the thin-film model is within 10% when $L/r_0 < 0.13$ (gray shaded area). The current magnitude for the largest investigated thickness (142 $\mu m$, $L/r_0 = 0.28$) is thus partly governed by radial diffusion and expected to deviate from the thin-film model. Figure S3b predicts that the current scales as most as $L^{-1}$. The $\sim 4\times$ decrease of the current when the IL layer was thickened from 63 $\mu m$ to 142 $\mu m$ cannot be attributed to the influence of radial diffusion alone, as discussed in the main text.
Figure S3. (a) Geometry for modeling and cross-section of a concentration profile. (b) Current as a function of $L/r_0$ for various $k_m$. The current is normalized by the diffusion-limited current for a disk electrode $i_n = 4nFADc_0r_0$ (dotted line). The dashed lines are the currents predicted by Equation 4 in the main text. For $L < 10r_0$, the current is dominated by diffusion through the thin film (gray shaded area), while for $L > 10r_0$, radial diffusion towards the working electrode limits the current (purple shaded area).

**Scan rate**

Figure S4a shows corrected cyclic voltammograms recorded with different scan rates in the presence of 3000 ppm ethylene at 40% RH and Figure S4b indicates that the peak current scales as $v^{1/2}$ up to 1 V/s (solid line is a fit). At higher scan rates, the cyclic voltammograms were distorted due to significant ohmic drop and the peak current deviated from the square root dependence. The $v^{1/2}$-dependence confirmed that the peak shape in Figure 2b of the main text originated from mass-transport limitation followed by inhibition of the reaction by a layer of gold oxide.
Figure S4. (a) Cyclic voltammograms recorded in the presence of 3000 ppm ethylene (40% RH) for different scan rates, corrected for the background charging current. The layer of [BMIM][NTf₂] had a thickness of 63 ± 10 μm. (b) Peak current as a function of scan rate $\nu$. The symbols and error bars represent the mean and standard deviation of three different CVs recorded with the same device. The solid line is a fit $\sim \nu^{1/2}$ while the dashed line has a slope 1 for comparison.

**Gold oxide**

At high applied potential, ethylene oxidation is inhibited by formation of a gold oxide layer, which was observed both in the cyclic voltammograms and amperometric current-time traces. Prior to sensing, the surface has to be completely free of gold oxide, otherwise the layer can significantly affect the measurement. This is illustrated in Figure S5, which shows current-time traces for a bare gold working electrode (black line) and the same electrode covered by a surface oxide layer (red line) upon exposure to 20 ppm stepwise increases of the ethylene concentration. The surface oxide layer was formed by conditioning the working electrode at 1.5 V vs Pt for 90 s, which is just before the onset of water hydrolysis and sufficient to oxidize gold. The IL layer thickness was 60 μm and the RH 40%, while the applied potential was 0.9 V vs Pt during recording of the traces. The sensitivity to ethylene was 5× smaller when a surface oxide layer was present: the inset of Figure S5 shows the calibration curves of which the slopes are 17 pA/ppm and 3.4 pA/ppm in the presence and absence of gold oxide, respectively. We note that the absolute sensitivity is smaller than Figure 6 of the main text, because a thicker IL layer and smaller RH was used.
Figure S5. Amperometric current-time traces for a gold working electrode in the absence (black line) and covered by a surface oxide layer (red line) upon exposure to increasing concentrations of ethylene (RH = 40%, \( L = 60 \mu m \)). The inset shows the calibration curves with slopes 17 pA/ppm (black line) and 3.5 pA/ppm (red line). The oxide layer significantly inhibited ethylene oxidation.

**Ohmic drop**

Ionic liquids are more viscous than other commonly used electrolytes and therefore exhibit a lower conductivity that could lead to significant ohmic drop. For our sensor geometry, the resistance, \( R \), between the working electrode and reference electrode was governed by a thin ring-shaped ionic liquid film with inner radius \( r_{in} = 500 \mu m \) and outer radius \( r_{out} = 650 \mu m \), and was given by \( R = \ln\left(\frac{r_{out}}{r_{in}}\right) / (2\pi \kappa L) \). To estimate an upper limit for \( R \), we used the conductivity of [BMIM][NTf₂], \( \kappa = 0.33 \) S/m, obtained under dry conditions and the thinnest IL layer thickness investigated, \( L = 30 \mu m \), which yielded \( R \approx 4 \) k\( \Omega \). Ohmic drop became significant (> 1 mV) when the current exceeded \( \sim 0.25 \mu A \), in line with the voltammograms of Figure S4a which are significantly distorted for scan rates > 0.6 V/s. We note that the actual ohmic drop was smaller because the IL thickness during cyclic voltammetry was 63 \( \mu m \) and the IL conductivity increases with the amount of water present. Furthermore, ohmic drop could be neglected for the amperometric current-time traces because the maximum current was approximately two orders of magnitude smaller than the current during cyclic voltammetry.
Flow rate

The mixing time in the analysis chamber depends on the flow rate at the inlet and could influence the amperometric current-time traces if mixing occurs at a time scale comparable to or longer than the sensor response time. Figure S6 shows current-time traces as a function of flow rate recorded when the sensor response is fastest ($L = 30 \, \mu\text{m}$ and RH = 60%). The response time decreases in the range 15 sccm to 60 sccm. Above 90 sccm, the responses overlapped, indicating that the sensor itself governs the step response. The flow rate was set to 150 sccm during experiments.

![Figure S6. Normalized current-time responses as a function of gas flow rate at the inlet of the measurement chamber. Above 90 sccm, the step response is independent on flow rate.](image)

References
