Amperometric Measurement of Gaseous Hydrogen Sulfide *via* a Clark-type Approach

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Electronic Supplementary Information

Figure S1 SEM image of the surface of the papyex material employed.



Figure S2

SEM image of the surface of the carbon fibre mesh material employed.



Figure S3

SEM image of the surface of the 30 μ m thick PTFE membrane supported by a PTFE mesh employed in some experiments at two different length scales.



A crude physicochemical model to understand the non-interference of molecular hydrogen within the sensing system

The surprising and remarkable observations that dihydrogen does not interfere with the direct amperometric oxidation of hydrogen sulfide at first appears counterintuitive, especially since the sensing electrode was cleaned and polished before experimentation (and so cannot be rationalised by the formation of a poorly-conducting sulphurous deposit^{S1} remaining from a previous experiment). However, given that air was the diluent for those experiments, these data can be plausibly understood in a three-step mechanism, in which dioxygen adsorbs on the polycrystalline platinum electrode, to form a monolayer, in a first step:

$$Pt(s) + O_2(g) \rightleftharpoons Pt - O_2(ads) \tag{S1}$$

Evidence for this type of reaction occurring is given in small change in baseline when air is first introduced to the cell whilst the electrode is potentiostated at 0.0 V *vs.* Ag | AgCl | Cl⁻(aq, 0.1 M). The small reduction current observed for this reaction likely steps from pseudocapacitiative interfacial charge transfer in forming the adsorbate. This type of process is well-known^{S2} within the literature. Assuming this forms a monolayer, if the adsorption is sufficiently tight, it may prevent other species from adsorbing directly to the electrode surface. Since gaseous hydrogen sulfide is able to form both monolayers and multilayers on platinum,^{S3} we propose that initially this gas weakly adsorbs on top of the oxygen layer in a non-dissociative form, and that this intermediate and transient state is sufficiently small-lived with respect to the non-dissociated and directly platinum-adsorbed species H₂S(ads), so that overall the following reaction may be written.

$$H_2S(g) \xleftarrow[k_{off}]{k_{off}} H_2S(ads)$$
(S2)

Given the large driving form for the dissociation of H_2S on platinum (Pt-H bonds are strong^{S4} at 270 kJ mol⁻¹), we speculate that reaction (S2) occurs as an equilibrium on the introduction of the H_2S species, with further displacement of the O_2 adsorbate, if necessary:

$$H_{2}S(ads) \xrightarrow{k_{trap}} Pt - S(ads) + 2Pt - H^{\bullet}(ads)$$
(S3)

This reaction, for which the rate constant will follow a Gaussian distribution for the polycrystalline material employed throughout this work, is tantamount to a trapping of the adsorbed hydrogen sulfide. It is written as an irreversible process due to the stability of the Pt-S species and the rapid subsequent oxidation of H• (the rate constant for proton evolution is maximal for Pt electrodes^{S4}):

$$Pt - H^{\bullet}(ads) - e^{-} \xrightarrow{} Pt(s) + H^{+}(aq)$$
(S4)

If this reaction occurs at a three-phase boundary of electrode | gas | aqueous solution, it is likely to be Nernstian and rapid, else it will suffer kinetic limitations which may be modelled phenomenologically using an heterogeneous rate constant (k_s) and a Butler-Volmer symmetry factor, α . Under these conditions, and noting that reaction (S1) occurs before the introduction of H₂S thereby allowing for exclusion of oxygen species, we may express the kinetics of reactions (S2)-(S4) *via* the following rate laws, where total surface coverage, Γ_{tot} (number of moles of adsorbate per unit surface area) is constant

and is assumed to be equal to the monolayer coverage of oxygen species, viz. $1 = \frac{\Gamma_{H_2S} + \Gamma_S + \Gamma_H}{\Gamma_{tot}} = a + s + h$

where the subscripts H_2S , S and H refer to $H_2S(ads)$, Pt-S(ads) and Pt-H•(ads) respectively, with the lower case letters representing the reduced surface concentrations. Note that incorporated within k_{on} is the mass transfer rate of H_2S through

the membrane and electrolyte thin layer,^{S5} and, therefore, following a Smoluchowski approach,^{S6} holds a weak dependence on p_{H_2S} , whilst being dominated by the slowness of the mass transport through the membrane and the electrolyte layer.

$$\frac{da}{dt} = k_{on} p_{H_2S} \left(1 - a - s - h \right) - k_{off} a - k_{trap} a \tag{S5}$$

$$\frac{ds}{dt} = k_{trap}a \tag{S6}$$

$$\frac{dh}{dt} = 2k_{trap}a - k_s e^{-\frac{\alpha F}{RT}\left(E-E^{0^{\circ}}\right)} \left\{ \frac{C_{H^+}}{\Gamma_{tot}} - he^{\frac{F}{RT}\left(E-E^{0^{\circ}}\right)} \right\} = \frac{i}{FS\Gamma_{tot}}$$
(S7)

In equation (S5), p_{H_2S} is the partial pressure of H₂S(g), whilst in equation (S7), F, R and T respectively refer to the Faraday constant, the molar gas constant and the absolute temperature, with c_{H^+} representing the surface concentration of protons, E the potential applied to the working electrode with respect to the reference electrode, E^o being the formal potential for proton reduction to form adsorbed H•, with S and i referring to the electrode area and the current flowing between working and counter electrodes, respectively. It is important to note that in reaction (S7) k_s may be represented as $k_s^0(1-\theta)$, where k_s^0 is the value of k_s at a non-blocked electrode and θ is the fraction of the electrode which is partially-blocked. The heterogeneous kinetics in (S7) take on two limiting forms. First, if the reaction is electrochemically reversible,

then $\frac{C_{H^+}}{\Gamma_{tot}} = he^{\frac{F}{RT}(E-E^{0^+})}$, and the bracketed expression reduces to zero. Alternatively, if the oxidation is fully driven, *viz.*

 $E \gg E^{0'}$, the heterogeneous kinetics return the irreversible expression $+k_s he^{\frac{F}{RT}(E-E^{0'})}$. As experiments are undertaken at 0.0 V *vs.* Ag | AgCl | Cl-(aq, 0.1 M) and at pH 6.5, the oxidation is likely fully driven, and may be considered to be reversible.^{S7} Thus, considering the reaction scheme outline in (S2)-(S4), and noting that the current transients illustrated in Figure 3 and 5 of the main manuscript approach and attain a steady-state value in the presence and absence of H₂S, application of the steady-state hypothesis to H₂S(ads) furnishes the following expression for the observed current.

$$\frac{i}{FS\Gamma_{tot}} = \frac{2k_{trap}k_{on}p_{H_2S}(1-s-h)}{(k_{off}+k_{trap})+k_{on}p_{H_2S}}$$
(S8)

For very low partial pressures of hydrogen sulfide, such as those in typical environmental samples, a limit to the expression in (S8) occurs when $k_{on}p_{H_2S} \ll (k_{off} + k_{trap})$. This corresponds physically to the faster loss of the intermediate H₂S(ads) compared with its formation. As the trapping kinetics will reflect the competition between the energy barrier for concerted dissociation and the driving force for reaction (S3), it is likely that the limiting inequality will be upheld for small partial pressures of H₂S, and when transport of the latter is slow, as demonstrated in the main manuscript. For this case, plots of the observed current against hydrogen sulfide concentration should be linear, if only a small amount of adsorption occurs such that $1 - s - h \approx 1$.

It is insightful to examine, within the framework of the crude model described above, the temporal variation of the current at a constant hydrogen sulfide concentration as it tests the robustness of the sensing system, since the platinum sulfide

species will build-up on the electrode surface. Accordingly, integration of equation (S6) at constant H₂S partial pressure, suggests that the PtS species builds up in an exponential manner, reaching to the limiting value of $\frac{1}{2}$, as expected:

$$s = \frac{1}{3} \left\{ 1 - e^{-\frac{3k_{on}k_{trap}p_{H_2S}t}{(k_{off} + k_{trap}) + k_{on}p_{H_2S}}} \right\}$$
(S9)

The effect of this is that the current is then predicted to fall exponentially with time:

$$\frac{i}{FS\Gamma_{tot}} = \frac{2k_{on}k_{trap}p_{H_2S}}{\left(k_{off} + k_{trap}\right) + k_{on}p_{H_2S}} e^{-\frac{3k_{on}k_{trap}p_{H_2S}t}{\left(k_{off} + k_{trap}\right) + k_{on}p_{H_2S}}}$$
(S10)

The exponent can be linearised for small values:

$$\frac{i}{FS\Gamma_{tot}} \approx \frac{2k_{on}k_{trap}p_{H_2S}}{\left(k_{off} + k_{trap}\right) + k_{on}p_{H_2S}} \left(1 - \frac{3k_{on}k_{trap}p_{H_2S}t}{\left(k_{off} + k_{trap}\right) + k_{on}p_{H_2S}}\right)$$
(S11)

suggesting that the current may indeed fall in a linear fashion, and that this effect is greatest for high concentrations of H₂S. However, the typical and representative data reported in Figure 3 of the main manuscript suggest that the current at constant H₂S concentration is not a function of time. This means that equation (S11) can be further truncated to afford equation (S8) with $1 - s - h \approx 1$ in the latter. Since plots of current against p(H₂S) exhibit direct proportionality for the data in Figure 3 of the main manuscript, under the assumption that $k_{on} p_{H_2S} \ll (k_{off} + k_{trap})$, both data sets may be

employed to determine values of $k' = \frac{k_{on}k_{trap} p_{H_2S}}{\left(k_{off} + k_{trap}\right)}$, which is effectively a measure of the sensitivity of the analytical

signal. At 20 ppmv H₂S, the data in Figure 3c suggest^{S8} k' = $0.035 \pm 0.002 \text{ s}^{-1}$, whilst those from Figures 3d allow a value of $0.019 \pm 0.008 \text{ s}^{-1}$ to be calculated; *mutatis mutandi*, for 2.0 ppmv H₂S, k' = $3.5 \pm 0.8 \times 10^{-3} \text{ s}^{-1}$ (from the data in Figure 3c), or k' = $1.9 \pm 0.8 \times 10^{-3} \text{ s}^{-1}$ (if the data in Figure 3d are used). Whilst these data sets give results which are in reasonable order-of-magnitude agreement, but crucially differ by a factor of *ca*. two, it is clear that the optimal use of this measurement methodology for pragmatic operational gas concentration quantification requires the measurement to be made with *periodic* rather than *continuous* exposure to a test-gas sample – this type of approach allows for longevity of sensor working lifetime.

References and Notes

- (a) This has been suggested for the case of platinum electrodes immersed in highly alkaline sulfide solutions, *q.v.* references S1b and S1c;
 (b) S. Kapusta, A. Viehbeck, S. M. Wilhelm, N. Hackerman, *J. Electroanal. Chem.*, 1983, 153, 157;
 (c) J. Szynkarczuk, P. G. Komorowski, J. C. Donini, *Electrochim. Acta*, 1995, 40, 487.
- S2 For relevant work for platinum in aqueous solutions for which $pH < pK_{a_1}$, as for the case considered in this work, see N. Ramasubramanian, *J. Electroanal. Chem.*, 1975, 64, 21.
- S3 (a) T. Loučka, *Collect. Czech. Chem. Commun.*, 2000, 65, 161; (b) R. J. Koestner, M. Salmeron, E. B. Kollin, J. L. Gland, *Surf. Sci.*, 1986, 172, 668; (c) V. A. Sethuraman, L. A. Wise, S. Balasubramanian, J. W. Weidner, *ECS Trans.*, 2006, 1, 111.
- S4 S. Trasatti, *J. Electroanal. Chem.*, 1972, 39, 163.
- S5 (a) Reaction (S2) can be re-written as:

$$H_2S(g) \xrightarrow{k_{t_1}} H_2S(membrane) \xrightarrow{k_{t_2}} H_2S(aq) \xrightarrow{k_{a_f}} H_2S(ads)$$

involving transport terms (k_{t_1} and $k_{t_{-1}}$), partition and transfer kinetics (k_{t_2} and $k_{t_{-2}}$), and heterogeneous

(activation) kinetics ($k_{a_{\ell}}$ and $k_{a_{h}}$). Note that we neglect the reactions of other sulfide species such as HS⁻; this

is reasonable since the electrolyte pH is less than the reported pK_{a_1} for H₂S, furnishing undissociated H₂S(aq)

at a concentration of more than twice that of HS (aq). Moreover, the proton evolution Faradaic reaction proposed will ensure that the pH local to the electrode surface is sufficiently small so as to maintain this view, even with buffer action, *q.v.* reference S5b; (b) C. Amatore, S. Arbault, Y. Bouret, M. Guille, F. Lemaître, *ChemPhysChem*, in press, DOI: 10.1002/cphc.201000102.

- S6 M. von Smoluchowski, Z. Physik. Chem., 1917, 92, 129.
- S7 See, for example, V. Climent, B. A. Coles, R. G. Compton, J. Phys. Chem. B, 2002, 106, 5988.
- S8 (a) Assuming S = 0.05 cm² and Γ_{tot} = 10⁻¹⁰ mol cm⁻². The latter is reasonable (*q.v.* reference S8b); (b) J. D. Wadhawan, P. J. Welford, E. Maisonhaute, V. Climent, N. S. Lawrence, R. G. Compton, H. B. McPeak, C. E. W. Hahn, *J. Phys. Chem. B*, 2001, *105*, 10659.