Ionophore-Assisted Electrochemistry of Neutral Molecules: Oxidation of Hydrogen in an Ionic Liquid Electrolyte

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Abstract

The electrochemical properties of gas molecules are of great interest for both fundamental and applied research. In this study, we introduce a novel concept to systematically alter the electrochemical behavior and, in particular, the redox potential of neutral gas molecules. The concept is based on the use of an ion-binding agent, or 'ionophore', to bind and stabilize the ionic electrochemical reaction product. We demonstrate that the ionophore-assisted electrochemical oxidation of hydrogen in a room temperature ionic liquid electrolyte is shifted by almost 1 V towards more negative potentials in comparison to an ionophore-free electrolyte. The altered electrochemical response in the presence of the ionophore not only yields insights into the reaction mechanism but can be used also to determine the diffusion coefficient of the ionophore species. This ionophore-modulated electrochemistry of neutral gas molecules opens up new avenues for the development of highly selective electrochemical sensors.

The electrochemical oxidation and reduction of gas molecules at an electrode surface in liquid electrolytes is of great interest both for the understanding of fundamental electrochemical concepts and for technological applications, e.g. in the fields of electrochemical sensors[1] and electrochemical energy systems.[2] In this respect, the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) in particular have attracted a lot of attention in recent years. In general, electrochemical reactions are influenced by choice of the electrolyte solvent and conducting salt. For example, in the ORR, oxygen is reduced to water in aqueous media (4 e$^-$ transfer), whereas it is reduced to peroxide in aprotic polar solvents containing hard Lewis acids as conducting salts (2 e$^-$ transfer) and to superoxide in aprotic room temperature ionic liquids (RTILs) (1 e$^-$ transfer).[3] While electrolyte properties can be used to modulate electrochemical reactions in a favorable way, interactions with reaction intermediates and products are rather unspecific. In contrast, in a seminal publication, Shao-Horn and co-workers tailored an anion receptor which specifically binds to one target ion only.[4] In this case, the hexacarboxamide cryptand specifically favored peroxide over the superoxide anion, which entirely changed the ORR mechanism. This work clearly shows that selective complexation of an ionic reaction product is an elegant way to alter an electrochemical reaction in a desired way and is a logical extension of electrode reactions with coupled chemical reactions. Nevertheless, to the best of our knowledge, no study has reported the use of an ion receptor to target a specific ionic product formed by the electrochemical reaction of a neutral gas molecule. This might be due, partly, to the tedious work required in the design and synthesis of ion receptors. Fortunately, the field of electrochemical sensors provides vast knowledge relating to ion selective receptors. The ion detection capability of sensors, such as the well-known potentiometric ion selective electrode (ISE), is based on assisted charge transfer across a phase boundary.[5,6] Selectivity is achieved by facilitating this charge transfer with an ion selective receptor molecule, a so called 'ionophore'. A rich library of ionophores is available for a very broad range of target ions.[6]

The goal of this study is to investigate a new concept for electrochemical sensing of neutral gas molecules by exploiting ion-binding reagents, hereafter called 'ionophores', for reaction with a charged electrochemical reaction product. This binding is expected to shift the electrochemical reaction to lower or higher potentials, depending on the nature of the reaction; this shift in potential might be advantageous for applications such as amperometric gas sensing, e.g. enabling the detection reaction to be moved away from the reactions of interferences. The HOR was selected as a model reaction because it yields only ionic reaction products, namely protons, and because of its high technological importance. RTIL-based electrolytes were chosen for their practical advantages, including near-zero vapor pressure, intrinsic ionic conductivity, and, especially, the low coordinating capability of the RTIL anion (bis(trifluoromethylsulfonyl)imide, $[NTf_2]^-$). The latter is a direct consequence of the charge delocalization in the S-N-S- backbone of the $[NTf_2]^-$ anion, which prevents competition with the ionophore for proton-binding. As well as the HOR, we also outline the limitations of the ionophore approach in more complex multi-electron reactions.

First, we briefly discuss the oxidation of H_2 at a platinum disc electrode in carefully dried 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$) without ionophore present. The respective voltammograms (Figure 1 a) largely agree with previous results in RTILs, showing single broad oxidative and reductive peaks with a peak-to-peak separation of 245 mV at 100 vol-% H_2.[7–9] The reversibility increases with increasing H_2 concentration and decreasing scan rate; this is probably a result of the higher proton concentration that facilitates the second order back reaction of:

$$H_2 \rightleftharpoons 2H^+ + 2e^- \tag{1}$$

Analysis of the peak current normalized by H_2 concentration reveals that H_2 pre-adsorption occurs and significantly contributes to the current amplitude at a low H_2 concentration of 1% (see SI Figure S1). This is consistent with the report by Barrette and Sawyer for the aprotic HOR at platinum electrodes in a range of molecular aprotic solvents,[10] and with the mechanism proposed by Tang et al. in ionic liquids.[11] The quasi-steady-state-current observed at high overpotentials in the voltammograms for 10 and 50 vol-% H_2 also agrees well with expected diffusion limited current (see SI), thus validating the experimental data. The potential of the oxidative peak varies from 0 to 150 mV vs. the lithium iron phosphate (LFP) reference electrode[12] which corresponds to 10 to ~ 160 mV vs ferrocene (see SI Figure S3). These values are slightly higher than in a previous report in which a peak position of ~-80 mV vs. ferrocene was reported in the same RTIL.[13] The more positive HOR potential in Figure 1 a is probably a consequence of our rigorous solvent drying procedure as discussed below.
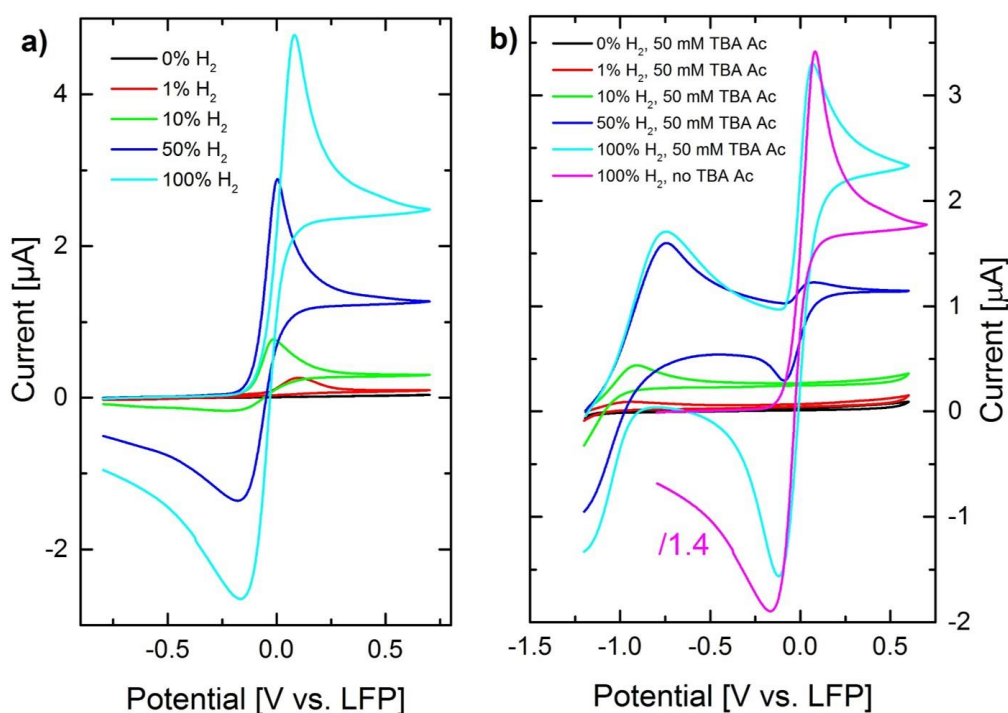

Figure 1 Cyclic voltammograms (25 mVs^{-1}) showing the hydrogen oxidation in [C$_2$mim][NTf$_2$] a) in the absence and b) presence of 50 mM TBA acetate for various hydrogen gas phase concentrations. Nitrogen makes up the remainder of the mixture. Pt disc, 1 mm diameter. The negative side of the potential window is limited by the reductive stability of the acetate anion (see discussion in the SI).

Initial experiments showed that the H_2 oxidation potential is highly dependent on the presence of residual water in the RTIL – the higher the water content, the lower the oxidation potential (see Figure S4). In pure and water-free ionic liquids, the generated proton (see equation 1) is only very poorly solvated by the [NTf$_2$]$^-$ anion, resulting in high oxidation potentials. Water, in contrast, is a much stronger base than the [NTf$_2$]$^-$ anion[14,15] and can therefore effectively bind to, and stabilize, the generated protons according to:

$$H_2 + 2H_2O \rightleftharpoons 2H_3O^+ + 2e^- \tag{2}$$

resulting in lower oxidation potentials. To the best of our knowledge, the strong dependence of the H_2 oxidation potential on the residual water content in RTILs has not yet been reported in the literature. This effect can be perceived as an example of our concept to influence a redox reaction by stabilizing the ionic product. However, water is known to readily solvate many types of cations and anions because of its high dipole moment, thus rendering its stabilizing effect rather unspecific. Therefore, all experiments in this study were carried out under strict water exclusion conditions (see experimental section for details).

We now consider the influence of acetate and another commercial ionophore on the electrochemical HOR. The acetate anion is a base of moderate strength (aqueous pK_a of acetic acid = 4.76)[16] which is expected to bind to protons generated during the electrochemical H_2 oxidation according to the following overall reaction:

$$H_2 + 2Ac^- \rightleftharpoons 2HAc + 2e^- \tag{3}$$

which can also be perceived to be reaction (1) followed by:

$$2H^+ + 2Ac^- \rightleftharpoons 2HAc \tag{4}$$

We use acetate here as a simple ion-binding reagent, operating via an acid-base reaction to capture available protons, in the same manner as commercially available proton ionophores. Figure 1 b shows H_2 oxidation in [C_2mim][NTf_2] in the presence of 50 mM tetrabutylammonium acetate (TBA Ac) for various H_2 concentrations, from 1 to 100 vol-%, at a scan rate of 25 mVs^{-1} (for data at 500 mVs^{-1} see SI). A cyclic voltammogram recorded in the absence of TBA Ac (pink curve, same data as Figure 1a) is also included. At H_2 concentrations of 1 and 10 vol-% (red and green curves), an oxidation peak appears at -0.8 V vs LFP which is followed by a H_2 diffusion limited current. In the absence of acetate, H_2 oxidation is not possible within this potential range (see Figure 1a); accordingly, the H_2 oxidation peak at -0.8 V vs LFP can be assigned to the ionophore-assisted reaction (4). As no second oxidation peak occurs at higher potentials at H_2 concentrations of 1 and 10 vol-% (corresponding to H_2 concentrations of 0.014 and 0.14 mmol L^{-1} in the RTIL),[17] the acetate concentration at the electrode surface must be sufficiently high throughout the entire voltammogram to consume all generated protons.

At a H_2 concentration of 50 vol-% (dark blue curve), the oxidation peak at -0.8 V is significantly larger and a second oxidation peak starts to emerge at ca. 0 V vs LFP. Based on its position (compared to the pink curve in Figure 2b), the second oxidation can be assigned to the oxidation of H_2 in the absence of the acetate ionophore, according to equation (1). The depletion of the acetate ionophore at the electrode surface is caused by its much slower diffusion in comparison to molecular H_2. The reason for this is the larger size and the negative charge of the acetate anion, two factors which slow down diffusion in RTILs.[18] Note that at potentials above 0 V vs LFP, the ionophore assisted reaction (4) continues (controlled by acetate diffusion towards the electrode surface) in parallel with reaction (1), which consumes surplus H_2 at the electrode surface.

At a H_2 concentration of 100 vol-% (cyan curve), the oxidation peak at -0.8 V vs LFP has a similar current as 50 vol-%. This confirms that at high H_2 concetrations, it is not H_2 but acetate diffusion towards the electrode surface that limits the ionophore-assisted H_2 oxidation. The second oxidation peak at ca. 0 V vs. LFP is significantly higher than for 50 vol-% in the presence of acetate (dark blue curve), but still smaller than the same oxidation peak at H_2 concentration of 100 vol-% in the absence of the acetate ionophore (pink curve).

Let us now take a closer look at the reduction peak at about -0.15 V vs LFP (Figure 1 b) which can be assigned to the reduction of "free" protons (reversal of reaction 1). At 100 vol-% H_2, this reduction peak is very high due to the large amount of free protons formed in the preceding oxidative scan, while it is entirely absent at a H_2 concentrations of 1 and 10%. At 50 vol-% H_2, a clear reduction peak is visible at -0.15 V vs LFP while the overall current is still positive, i.e. oxidative. This can be interpreted as a superposition of the ionophore-assisted H_2 oxidation (reaction 4) with the simultaneous reduction of free protons (reverse of reaction 1). The rate of the former reaction must slightly exceed the rate of the latter in order to obtain an overall oxidative current. Accordingly, the voltammetric shapes shown in Figure 1b can be simulated by a combination of reactions 1 and 4 (see Figure S5 and discussion in the supporting information).

Below -0.8 V vs. LFP, the onset of the HAc reduction (reverse of reaction 3) can be observed. Due to the limited reductive stability of the acetate ionophore, scanning through the full HAc reduction peak was avoided to prevent fouling of the working electrode (see discussion in the SI). Nevertheless, it appears that the peak-to-peak separation of this reaction is greater than that of the ionophore-free process, suggesting that the former has slower electrode kinetics.

From the separation of the formal redox potential $E°'$ values of reactions (1) and (4), it is possible to estimate the Gibbs free energy of the proton binding by the acetate ionophore according to:

$$\Delta G = - z_e F \Delta E^{0\prime} \qquad (5)$$

where z_e is the number of electrons transferred per hydrogen molecule (= 2), F is the Faraday constant and $\Delta E^{0\prime}$ is the difference between the formal potentials for reactions (1) and (4) (the formal potentials are taken as the average of the oxidative and reductive peak potentials for each process). Unfortunately, the formal potential for reaction (4) cannot be precisely determined as its reduction peak is not fully resolved but it can be estimated that $\Delta E^{0\prime} \geq 1$ V (from Figure 1b), resulting in a Gibbs free energy for acetate-proton binding of < -200 kJ mol^{-1}. This value for acetate-proton binding can be compared to -53 kJ mol^{-1} in water (based on an aqueous pK_a of 4.76) and -1400 kJ mol^{-1} in the gas phase,[19] and is a consequence of the comparably weak solvation of ionic species (i.e. acetate and protons) in RTILs compared to a high dielectric solvent like water.

Based on the acetate diffusion limited current for 50 and 100 vol-% H_2 (Figure 1 b), the diffusion coefficient of acetate, $D(Ac^-)$ was estimated to be ~3×10^{-8} cm^2 s^1 (see SI for details). To the best of our knowledge, this is the first experimental determination of a diffusion coefficient of a carboxylate anion in RTILs. The reported value of $D(Ac^-)$ is smaller by a factor of about three than the diffusion coefficients reported for chloride[20] and superoxide anions[21] (both $D = 1.1 \times 10^{-7}$ cm^2 s^1) in similar RTILs, which is a consequence of the larger size of the acetate anion. The ionophore-assisted electrochemistry concept is an interesting option for the indirect determination of the diffusion coefficients of molecules such as the acetate anion, which might otherwise be hindered by complex electrode reactions.
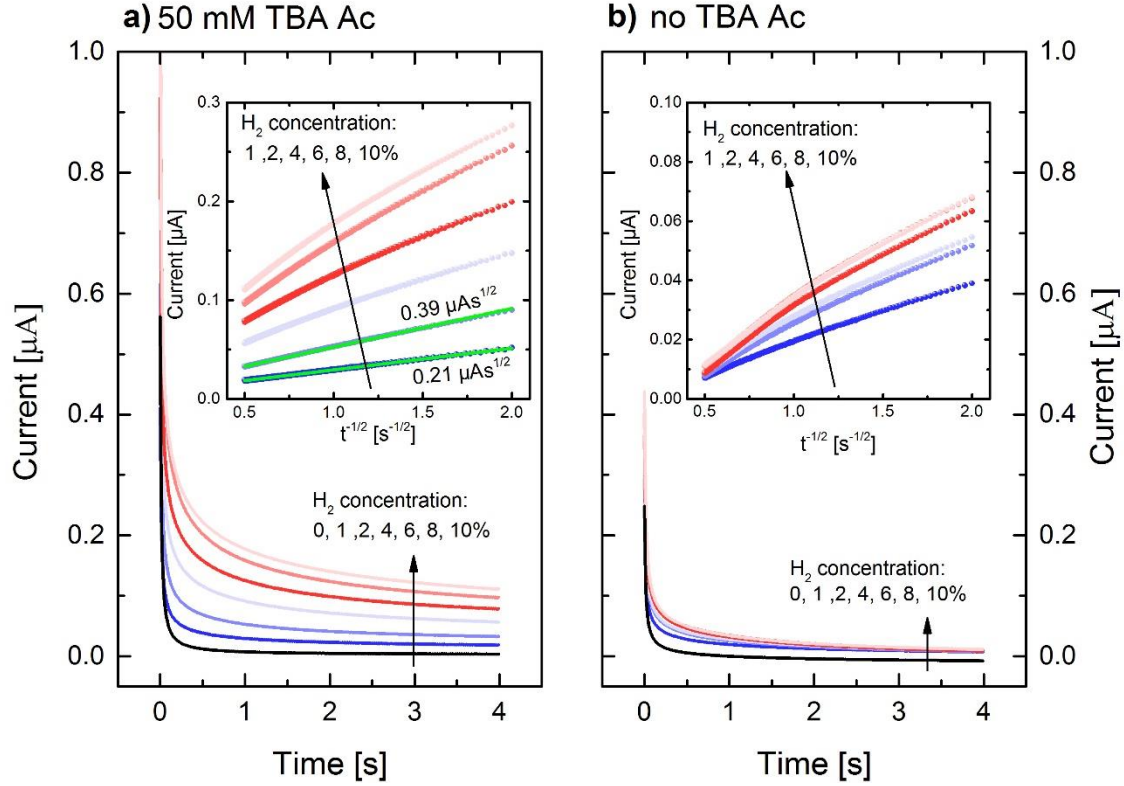
Figure 2 Current transients recorded after stepping the potential from -1.2 to -0.35 V vs LFP in [C$_2$mim][NTf$_2$] in the presence (a) and absence (b) of 50 mM TBA acetate for various hydrogen gas phase concentrations. The inset shows the linearized plot based on the Cottrell equation; note that the first 250 ms were omitted in the linearized plot because of double layer charging effects.

A possible practical application for the ionophore-assisted concept is to lower the oxidation potential (or magnitude of the reduction potential) of the targeted analyte to avoid cross-sensitivities which are a major obstacle for electrochemical gas sensors.[22] Figure 2a shows a chronoamperometric experiment in the presence of 50 mM TBA Ac. First, the potential was held at -1.2 V vs. LFP (the open circuit potential in the presence of TBA Ac and H$_2$) for a few seconds and then stepped up to -0.350 V vs LFP for four seconds while current transients were recorded. A potential of -0.350 V vs LFP was chosen so that the acetate-assisted HOR (equation 4) is in a diffusion-limited regime while the unassisted HOR (equation 1) does not occur (see Figure 1 b). As expected, the current increases with H$_2$ concentration as shown in Figure 2a, yielding a linear dependence of current on the hydrogen concentration, i (A) = 1.0 x 10^{-8} (A/vol-% H$_2$).c (vol-% H$_2$) + 1.2 x 10^{-8} (A), R^2 = 0.991. Diffusion controlled current transients in a potential step experiment at a mm-sized disk electrode can be described by the Cottrell equation[23]

$$i = \frac{z_e \, F \, A \, c_j^0 \sqrt{D_j}}{\sqrt{\pi}\sqrt{t}} \qquad (6)$$

where z_e is the number of electrons, F is the Faraday constant, A is the electrode area, c^0 is the initial bulk concentration and D is the diffusion coefficient, t is the time; the index j refers to the redox active species, in this case H$_2$. The experimental current transients for 1 and 2 vol-% H$_2$ in the presence of acetate nicely follow the Cottrell equation, but above 2 vol-% H$_2$, the experimental current transients increasingly fall below the values predicted by the Cottrell equation (see Figure S6). The linearized plot of the Cottrell equation (inset Figure 2a) also shows that the ratio of the slopes for 1 and 2 vol-% H$_2$ come close to the

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expected value of 2, while the transients cannot be properly linearized for higher H_2 concentrations. This means that for up to 2 vol-% H_2, the acetate concentration at the electrode surface is high enough to ensure that only H_2 diffusion is rate limiting, whereas at higher H_2 concentrations the availability of acetate at the electrode surface also starts to affect the rate. In the absence of the ionophore, the current transients at a constant potential of -0.35 V vs LFP are much smaller and also do not depend on the H_2 concentration (Figure 2b). This shows that the ionophore-assisted electrochemistry concept can be used to effectively change the potential window in which an analyte can be detected.

We also investigated the HOR using hydrogen ionophore IV (see Figure S7), a commercial pyridine-based hydrogen ionophore that interacts with protons in an acid-base reaction. Qualitatively, the results were similar to the acetate ionophore results, but the intensities of the ionophore-assisted H_2 oxidation peaks were much lower due to the lower diffusion coefficient of hydrogen ionophore IV and its lower solubility. We are planning to extend the ionophore-assisted electrochemistry concept to other reactions – such as the electrochemical reduction of chlorine gas to chloride anions[24] and the more complex iodine/iodide/tri-iodide system[25] – and to investigate the limitations of the ionophore concept. Our preliminary data for the oxidation of ammonia, which produces ammonium cations (see Figure S8), suggests that the concept may not be usefully applied for such a complex multi-electron reaction. As a result, future work will elucidate the exact criteria that render electrochemical reactions of neutral gas molecules susceptible to the influence of ionophores.

In conclusion, we have shown that by addition of an ion-binding reagent (ionophore) to the electrolyte solution, the oxidation of a neutral gas molecule can be shifted to lower potentials by virtue of the binding of the ionized electrochemical reaction product. This capability opens up prospects for the use of such ionophores to modulate the electrochemistry of gases, including tuning the sensitivity and selectivity of amperometric gas sensors. The design of ionophores that specifically bind to electrochemical reaction products and which possess good solubility in the chosen electrolyte medium will greatly improve the expansion of this line of investigation.

Supporting Information Available:
Experimental description, evidence of hydrogen pre-adsorption on the working electrode, reference electrode choice, estimation of diffusion limited current and acetate diffusion coefficient. Influence of water impurities, Cottrell behaviour of current transients, simulation of cyclic voltammograms, and behaviour with commercial hydrogen ionophore IV and ammonia oxidation. This material is available free of charge via the Internet at http://pubs.acs.org.
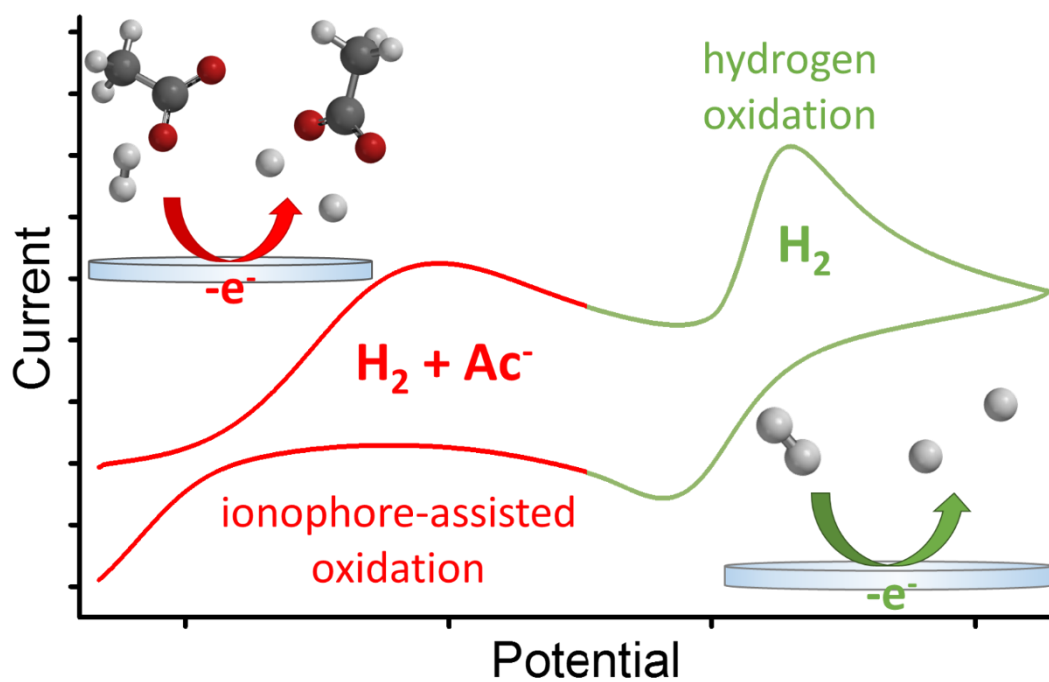
The authors declare no competing financial interest.

References

(1)   Hahn, C. E. W. Tutorial Review Electrochemical Analysis of Clinical Blood-Gases , Gases and Vapours. *Analyst* **1998**, *123* (June), 57–86.

(2)   Carrette, L.; Friedrich, K. A.; Stimming, U. Fuel Cells : Principles , Types , Fuels , and Applications. *Chem. Phys. Phys. Chem.* **2000**, *1*, 162–193.

(3)   Sawyer, D. T. *Oxygen Chemistry*; Oxford University Press: New York, 1991.

(4)   Lopez, N.; Graham, D. J.; McGuire, R.; Alliger, G. E.; Shao-Horn, Y.; Cummins, C. C.; Nocera, D. G. Reversible Reduction of Oxygen to Peroxide Facilitated by Molecular Recognition. *Science* **2012**, *335* (6067), 450–453.

(5)   Bakker, E.; Pretsch, E. Modern Potentiometry. *Angew. Chemie Int. Ed.* **2007**, *46*, 5660–5668.

(6)   Bühlmann, P.; Pretsch, E.; Bakker, E. Carrier-Based Ion-Selective Electrodes and Bulk Optodes . 2 . Ionophores for Potentiometric and Optical Sensors. *Chem. Rev.* **1998**, *2665* (97), 1593–1688.

(7)   Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. An Electrochemical Study of the Oxidation of Hydrogen at Platinum Electrodes in Several Room Temperature Ionic Liquids. *J. Phys. Chem. B* **2007**, *111* (18), 5000–5007.

(8)   Silvester, D. S.; Ward, K. R.; Aldous, L.; Hardacre, C.; Compton, R. G. The Electrochemical Oxidation of Hydrogen at Activated Platinum Electrodes in Room Temperature Ionic Liquids as Solvents. *J. Electroanal. Chem.* **2008**, *618* (1–2), 53–60.

(9)   Sandoval, A. P.; Suárez-Herrera, M. F.; Feliu, J. M. Hydrogen Redox Reactions in 1-Ethyl-2,3-Dimethylimidazolium Bis(Trifluoromethylsulfonyl)Imide on Platinum Single Crystal Electrodes. *Electrochem. commun.* **2014**, *46*, 84–86.

(10)   Barrette, W. C.; Sawyer, D. T. Determination of Dissolved Hydrogen and Effects of Media and Electrode Materials on the Electrochemical Oxidation of Molecular Hydrogen. *Anal. Chem.* **1984**, *56* (4), 653–657.

(11)   Tang, Y.; Zeng, X. Electrochemical Oxidation of Hydrogen in Bis(Trifluoromethylsulfonyl)Imide Ionic Liquids under Anaerobic and Aerobic Conditions. *J. Phys. Chem. C* **2017**, *41* (120), 23542–23551.

(12)   Wandt, J.; Lee, J.; Arrigan, D. W. M.; Silvester, D. S. A Lithium Iron Phosphate Reference Electrode for Ionic Liquid Electrolytes. *Electrochem. commun.* **2018**, *93* (June), 148–151.

(13)   Meng, Y.; Aldous, L.; Belding, S. R.; Compton, R. G. The Formal Potentials and Electrode Kinetics of the Proton/Hydrogen Couple in Various Room Temperature Ionic Liquids. *Chem. Commun.* **2012**, *48* (45), 5572.

(14)   Thomazeau, C.; Olivier-Bourbigou, H.; Magna, L.; Luts, S.; Gilbert, B. Determination of an Acidic Scale in Room Temperature Ionic Liquids. *J. Am. Chem. Soc.* **2003**, *125*, 5264–5265.

(15)   Chiappe, C.; Pieraccini, D. Ionic Liquids: Solvent Properties and Organic Reactivity. *J. Phys. Org. Chem.* **2005**, *18* (4), 275–297.

(16)   Rumble, J. *CRC Handbook of Chemistry and Physics, 98th Edition*; 2017.

(17)   Lei, Z.; Dai, C.; Chen, B. Gas Solubility in Ionic Liquids. *Chem. Rev.* **2014**, *114* (2), 1289–1326.

(18)   Barrosse-Antle, L. E.; Bond, A. M.; Compton, R. G.; O'Mahony, A. M.; Rogers, E. I.; Silvester, D. S. Voltammetry in Room Temperature Ionic Liquids: Comparisons and Contrasts with Conventional Electrochemical Solvents. *Chem. - An Asian J.* **2010**, *5* (2), 202–230.

(19)   Cumming, J. P.; Kebarle, P. Summary of Gas Phase Acidity Measurements Involving Acids AH. Entropy Changes in Proton Transfer Reactions Involving Negative Ions. Bond Dissociation Energies D(A-H) Abd Electron Affinities EA(A). *Can. J. Chem.* **1978**, *56* (1), 1–9.

(20)   Villagrán, C.; Banks, C. E.; Hardacre, C.; Compton, R. G. Electroanalytical Determination of Trace Chloride in Room-Temperature Ionic Liquids. *Anal. Chem.* **2004**, *76* (7), 1998–2003.

(21)   Herranz, J.; Garsuch, A.; Gasteiger, H. A. Using Rotating Ring Disc Electrode Voltammetry to Quantify the Superoxide Radical Stability of Aprotic Li–Air Battery Electrolytes. *J. Phys. Chem. C* **2012**, *116* (36), 19084–19094.

(22)   Silvester, D. S. New Innovations in Ionic Liquid-Based Miniaturised Amperometric Gas Sensors. *Curr. Opin. Electrochem.* **2019**, *15,* 7–17.

(23)   Bard, A. J.; Faulkner, L. R. Electrode Reactions with Coupled Homogeneous Chemical Reactions. In *Electrochemical Methods Fundamentals ad Applications*; 2011; p 471.

(24)   Murugappan, K.; Arrigan, D. W. M.; Silvester, D. S. Electrochemical Behavior of Chlorine on Platinum Microdisk and Screen-Printed Electrodes in a Room Temperature Ionic Liquid. *J. Phys. Chem. C* **2015**, *119* (41), 23572–23579.

(25)   Zhao, Y.; Wang, L.; Byon, H. R. High-Performance Rechargeable Lithium-Iodine Batteries Using Triiodide/Iodide Redox Couples in an Aqueous Cathode. *Nat. Commun.* **2013**, *4* (May), 1896–1897.

TOC Graphic

Graphical Abstract text:

An ionophore is used to bind and stabilize the ionic product of the electrochemical reaction of a neutral gas species, resulting in shifting of the reaction potential to lower values.