

Electrochemical Measurement of the Dissolved Oxygen Concentration in Water in the Absence of Deliberately Added Supporting Electrolyte

*Richard O.D. Clark, Kamonwad Ngamchuea, Christopher Batchelor-McAuley, Richard G. Compton**

^a Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, United Kingdom

* e-mail: Richard.compton@chem.ox.ac.uk

Abstract

It is commonly assumed that the use and application of electrochemical techniques to natural surface waters requires the presence of high electrolyte concentrations prior to measurement, so limiting the applicability of the technique. We report that even for the complex case of oxygen reduction, an analytically useful electrochemical signal is obtainable using a carbon fibre microcylinder electrode. It is shown to be the case even when using voltammetric signals recorded in potable water that has not been pre-treated or had the addition of any ionic material. The magnitude of the redox wave gives a reliable measure of the oxygen content of these solutions which contain only few millimolar of ions and contains no pH buffer.

Keywords: Oxygen Reduction, Unbuffered Solution, Low Support, Ionic Strength, Mineral Water, Natural Water

1. Introduction

The application of electrochemical techniques to the analysis of real-world samples is often viewed as being limited by the requirement of utilising an excess of supporting electrolyte. The ionic strength of natural surface waters is extremely varied and depends upon the exact source. However, samples regularly have an ionic strength greater than 1mM. For example, Sullivan¹ describes the typical composition of surface waters, and from this an ionic strength of 1.8mM may be calculated. No definite limits for total dissolved solids in drinking water exist, but the EPA have set out a guideline of 500mg L⁻¹ TDS² as a quality control guideline. In reality it is often safe to drink water which has a much higher levels of TDS. A quality of taste study concluded that levels above 1000mg L⁻¹ were generally unacceptable to consumers³. However, These concentrations are still comparatively low as compared to the concentrations of electrolyte commonly utilised in electrochemical experimentation (often ca. 0.1M).

Previous work has investigated the effect of decreased electrolyte on the voltammetric response of both macro and micro electrodes. Under conditions of low support the resulting ohmic drop⁴ can significantly alter the voltammetric waveshape, causing an increase in the voltammetric peak-to-peak separation. Depending on the ionic charge of the reactants, intermediates and products, a concomitant increase or decrease in the magnitude of the signal due to the influence of migration to and from the electrode surface may occur⁵. It should be commented that although a system's mass-transport cannot be suitably described exclusively in terms of diffusion, this does not mean that any such resulting voltammogram is devoid of analytically useful information. On the contrary, voltammetry recorded under conditions of low-supporting electrolyte may in fact yield more information regarding the nature and identity of the redox active species involved⁶.

In the case of the use of low supporting electrolyte concentrations with macroelectrodes combined theoretical and experimental data has evidenced that for a voltammetric response to be completely unperturbed by the influence of migration a support ratio of >100 is commonly necessitated⁴. However, since the 1980s and with the advent of the use of microelectrodes, it has been recognised that for cases involving the use of such small electrode geometries the supporting electrolyte concentration requirements may be at least partially relaxed. This has enabled voltammetry to be recorded in non-conventional solutions of low conductivity⁵. Theoretically the behaviour of both disc⁷ and band microelectrodes⁸ have been previously described, with Amatore providing 'universal' equations for the description of the steady or quasi-steady state behaviour at such microelectrode geometries. Although the electrochemical response of these voltammetric systems is relatively well characterised, the application of such systems for analytical purposes is comparatively under investigated⁹. To this end, previous work by Pletcher has sought to use a platinum microdisc electrode for mechanistic studies on oxygen reduction in weakly supported electrolyte at platinum electrodes¹⁰, and this paper exploits this idea for electroanalytical purposes.

A complicating factor for many analytically useful redox processes is the concomitant transfer of protons associated with the electron transfer. The use of low ionic strength media for electrochemical studies also necessarily implies that the system only has a low buffering capacity. Hence, as a further complication during the course of a voltammetric experiment, the pH local to the electrochemical interface may, due to the occurrence of the redox reaction, vary during the course of a scan¹¹. A paradigm redox process involving the transfer of both protons and electrons is the reduction of oxygen. Oxygen detection is important in a variety of biological and ecological scenarios¹². Due to the non-polar nature of the oxygen molecule its solubility in water is comparatively low with an associated Henry's constant of 1.3x10⁻³M atm⁻¹¹³. Moreover, the gas solubility is relatively insensitive to the presence or absence of electrolyte. Using Henry's Law Constants and the Setchenov equation¹⁴(see SI VIII), the change in dissolved oxygen concentration as a function of electrolyte concentration can be

calculated. The addition of 0.1M KCl is only predicated to decrease the solution phase oxygen content by 3%.

At carbon electrodes the reduction of oxygen is known to proceed via a two-electron reduction process involving the formation of hydrogen peroxide¹⁵. The first pK_a of hydrogen peroxide is 11.62¹⁶ at 298K, and hence in solutions above this pH the resulting product from the reduction processes is the deprotonated form of the peroxide species. Importantly, the electrochemical reduction process at carbon is highly irreversible where the first electron transfer is the rate determining step. Consequently, although the reduction involves proton transfer, on carbon surfaces the position of the voltammetric wave is found to be relatively insensitive to the solution phase pH¹⁷.

This work starts by considering the voltammetric response of two ideal reversible outer-sphere redox probes at carbon surfaces under conditions of low-support. Specifically the behaviour of the ideal redox probes ferrocenemethanol and ruthenium (III) hexaamine are experimentally investigated. These redox processes are studied at both a macro and microcylinder electrode, where the charge on the redox analyte plays an important role in determining the electrochemical response¹⁸. It is demonstrated how by careful selection of the electrode dimensions for both redox probes an analytically useful signal is readily obtainable even with the ionic strengths as low as 1 mM. This work continues by considering the more complex problem of oxygen reduction in the absence of excess supporting electrolyte and without the addition of a pH buffer. At a macroelectrode the position of the oxygen voltammetric wave is shown to be sensitive to the ionic strength of the solution. However, use of a carbon fibre microcylinder electrode enables the recording of virtually undistorted voltammetric responses where the magnitude of the voltammetric waves yield analytically useful information regarding the dissolved oxygen content of the aqueous phase.

2. Experimental

Chemical Reagents

All reagents were purchased from Aldrich at the highest grade available and were used as received, without any further purification. These were ferrocenemethanol, ruthenium hexaamine (III) chloride, potassium chloride, sodium fluoride and sodium chloride. All aqueous solutions of the electro-active species were prepared daily, at 298 K, using deionised water with a resistivity of no less than 18.2MΩ cm (Millipore UHQ, Vivendi, U.K.) as the solvent. All electrolyte solutions were made from a stock solution of 0.1M made up from solid followed by serial dilutions. Oxygen reductions were performed in solutions at atmospheric pressure with no previous saturation.

Equipment and Experimental Setup

Cyclic voltammetric measurements were recorded using a computer controlled μAutolab III potentiostat/galvanostat in a home built Faraday cage. A standard three electrode configuration was used, with a glassy carbon macroelectrode (2.9mm diameter) or a homemade microcylinder electrode (1cm length, 3.5μm radius) made from carbon fibre physically supported on a microscope slide as the working electrode. A detailed schematic can be found in the SI. A platinum wire served as a counter electrode and a saturated calomel electrode (SCE) (BAS Inc. Japan) or a silver/silver chloride leakless electrode (homemade) (3.0M KCl) was used as reference electrodes. The leakless reference electrode was employed in the voltammetric studies at zero electrolyte concentration for ferrocenemethanol and oxygen reduction to ensure that no ion is leaked from the reference electrode into the

solutions. Details about how the leak of ions from the SCE reference electrode to the solutions affect the voltammograms can be found in the SI.

The GC macroelectrode was polished by using alumina particles of decreasing particle size (1.0, 0.3 and 0.05 μm ; Buehler,U.S.A.). The electrode was polished between each measurement and rinsed with deionised water and polished on a brown microcloth strip (Buehler) to remove any alumina particles. The 1cm microwire electrode was cleaned in between each measurement by rinsing with deionised water and drying using N_2 flowing gas. The procedure for the temperature dependent O_2 concentrations in solution involved heating the solutions in question to the stated temperature for two hours before cooling rapidly in an icebath whilst stirring to 298K using an ice bath, such that all measurements were performed so as not to change other parameters such as the diffusion coefficient of the analyte from those previously measured at 298K.

Results and Discussion

We start by considering the experimental behaviour of a neutral versus a charged redox species in solution and their electrochemical responses on a glassy carbon macroelectrode. The voltammetry of both 1.0mM ferrocenemethanol and ruthenium (III) hexamine chloride were studied separately in the presence of a variable supporting electrolyte concentration.

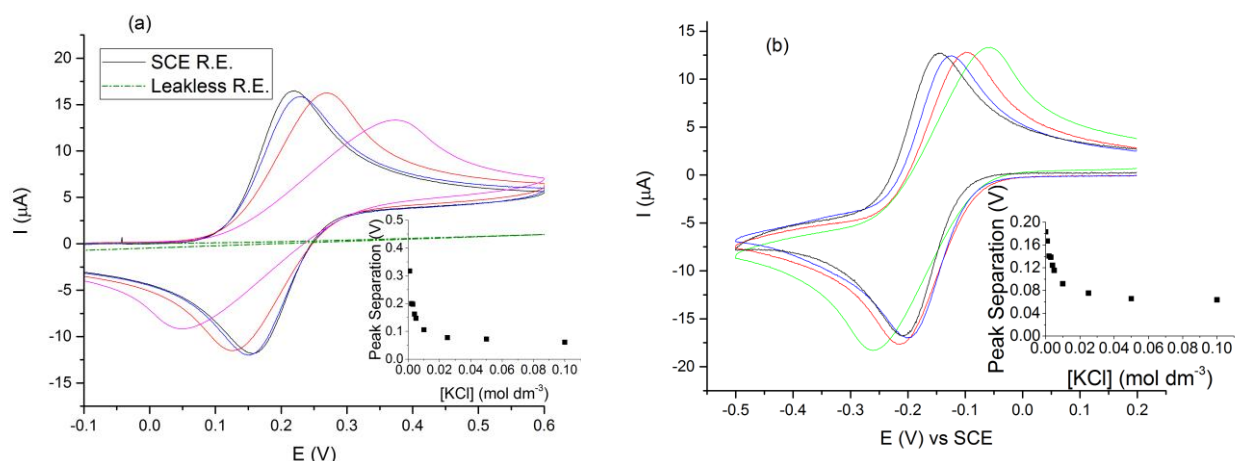


Figure 1:

- (a) Cyclic Voltammetry of 1.0mM Ferrocenemethanol at 298K, measured at a scan rate of 0.1V s^{-1} for 100mM (black), 25mM (blue), 5.0mM (red), 1.0mM (pink) and 0mM (green) KCl solutions on a GC electrode. Inlay shows peak separation vs electrolyte concentration.
- (b) Cyclic Voltammetry of 1.0mM ruthenium hexamine(III) chloride at 298K, measured at a scan rate of 0.1V s^{-1} for 100mM (black), 25mM (blue), 5.0mM (red) and 0.0mM (green) KCl solutions on a GC electrode. Inlay shows peak separation vs concentration of KCl.

Figure 1 (a) depicts the one-electron oxidation of ferrocenemethanol to the corresponding ferrocenium cation, as recorded at 100mV s^{-1} using a glassy carbon macroelectrode (radius = 1.46mm). Under conditions of full support, at 0.1M KCl , the forward peak current is $16.5\mu\text{A}$. Using the reversible form of the Randles-Ševčík equation¹⁹, this corresponds to a diffusion coefficient for the ferrocenemethanol of $8.4 \pm 0.3 \times 10^{-6}\text{cm}^2 \text{s}^{-1}$. This value is consistent with the literature reported value of $7.8 \pm 0.3 \times 10^{-6}\text{cm}^2 \text{s}^{-1}$.²⁰ Moreover, the voltammetric peak-to-peak separation is found to be 61mV and hence the voltammetry is further consistent with the electrochemical redox process being fully electrochemically reversible²¹. As the concentration of the supporting electrolyte is lowered the peak-to-peak separation increases significantly. The inset of Figure 1 depicts the measured peak-to-peak separation as a function of the supporting electrolyte concentration⁵. At an electrolyte concentration of 1.0mM the peak-to-peak separation is found to be 317mV and the voltammetric peak-height has decreased by approximately 21%. Note in the absence of additional electrolyte no redox wave was found to be observable, as will be discussed later, since this is in contrast to the case found for ruthenium (III) hexaamine. The alteration in the voltammetric response as a function of the electrolyte concentration suggest with the presence of an ohmic drop occurring in solution adjacent to the electrode⁴. Over the course of the voltammetric experiment the concentration of the formed ferrocenium ions builds-up in the diffusion layer and in the absence of sufficient ions to support this charge the voltammetric response becomes distorted as evidenced by the increase in the voltammetric peak-to-peak separation.

Having experimentally considered the situation in which the electrochemical reactant is neutral the work now moves to consider the voltammetric response of a charged redox species. $\text{Ru}(\text{NH}_3)_6^{3+}$ is a useful compound for studying the reversible $\text{Ru}^{3+}/\text{Ru}^{2+}$ redox couple²². Although the ruthenium (III) reactant is formally a trication it is possible that this species will to some extent ion-pair with the corresponding chloride counter ion present in solution²³. Figure 1 (b) depicts the voltammetric response of the ruthenium (III) hexaamine reduction in the presence of variable concentrations of supporting electrolyte. Under conditions of full support, at 0.10M KCl , the peak current is found to be $16.79\mu\text{A}$, and the diffusion coefficient calculated from this using the Randles-Ševčík is $8.69 \pm 0.1 \times 10^{-6}\text{cm}^2 \text{s}^{-1}$. The literature diffusion coefficient of this compound is $8.43 \pm 0.03 \times 10^{-6}\text{cm}^2 \text{s}^{-1}$.²⁴ Again the voltammetry has a peak-to-peak separation of 64mV consistent with the redox process being fully reversible. However, in contrast to the oxidation of ferrocenemethanol, the voltammetry is far less sensitive to the presence of the additional supporting electrolyte. In the case where no additional supporting electrolyte has been added to the solution a clear voltammetric wave is still observable, and although the experimental peak-to-peak separation has increased to 183mV , the peak current has increased by approximately 9%. This increase in the peak-current it is not related to a change in the solutions viscosity (discussed later.) This relative insensitivity to the absence of supporting electrolyte arises due to the charged nature of the reactant; such that even in the absence of additional electrolyte the solution phase ionic strength is still millimolar (the exact value will be sensitive to the extent of ion-pairing present in the system). Hence, the system is electrochemically 'self-supported' so a voltammetric response is still observable even in the absence of *additional* electrolyte.

Since the 1980s it has been recognised through the use of micro electrodes that a system's requirement for the use of excess supporting electrolyte is at least partially relaxed²⁵. However, in terms of their use electro-analytically, microdisc electrodes present separate and distinct problems to their more widescale application. Issues include problems of reproducibility in terms of the electrodes requiring calibration and the associated small scale (nA) electrical signals which are susceptible to electrochemical noise and require more sensitive electronics for measurement²⁶. One widely used route to circumventing these problems is through the development of arrays of microelectrodes²⁷, this however comes at the expense of more complex fabrication procedures²⁸. As an alternative, there has been some resurgent interest in the use of microcylinder electrodes both for the detection of

nanoparticulate material²⁹ and of molecular species³⁰. These electrodes commonly have a radius in the order of microns but their length can be macroscopic (ca. cm in length). Advantageously for molecular species this electrode design still exhibits relatively high mass-transport (leading to pseudo-steady-state fluxes), but due to their length they also give relatively larger electrochemical signals (cf. μA). In the following section we seek to evidence the voltammetric behaviour of these electrodes towards the ideal outer-sphere redox probes of ferrocenemethanol and ruthenium (III) hexaamine under conditions of low supporting electrolyte.

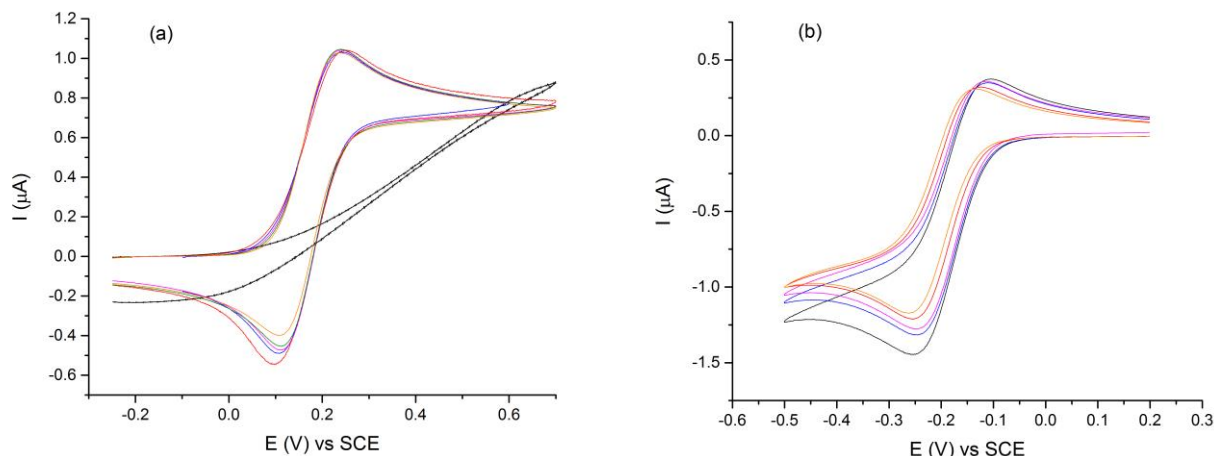


Figure 2:

- (a) C.V. of 1mM Ferrocenemethanol at 298K, 0.1V s^{-1} scan rate in 100mM (orange), 25mM (green), 10mM (pink), 5mM (blue), 1.4mM (red) and 0mM (black) KCl solutions on a 1cm microcylinder electrode.
- (b) C.V. of 1mM ruthenium hexaamine(III) chloride at 298K, 0.1V s^{-1} scan rate in 100mM (orange), 50mM (red), 10mM (pink), 5mM (blue) and 0mM (black) KCl solutions on 1cm microcylinder electrode.

The oxidation of 1.0mM ferrocenemethanol was studied at a surface supported microcylinder carbon fibre electrode (radius = $3.5\mu\text{m}$, length = 1cm). The resulting voltammetric responses are as depicted in Figure 2 (a). In the presence of 0.1M KCl a clear voltammetric peak is observed at 0.24V vs SCE, with a peak current of $1.03\mu\text{A}$. For an *isolated* microcylinder electrode the peak current for a reversible one-electron transfer has been analytically approximated by Aoki *et al.* as¹⁴

$$\frac{I_p}{2\pi nFC_0D_0l} = 0.446p + 0.335p^{0.15}; \quad p = \sqrt{\frac{nFr_0^2v}{RTD_0}} \quad (1)$$

where I_p is the peak current in amps, n is the number of electrons transferred in the reaction, r_0 is the electrode radius, v is the scan rate, D_0 is the diffusion coefficient of the analyte and l is the length of the microcylinder. In the present experimental case the microcylinder is supported on a non-conductive surface. This surface serves to partially diffusional block the electrode, hence in order to use the above equation to describe the present system it must be multiplied by a dimensionless factor of 0.61. The exact value of this conversion factor depends upon a variety of factors including the diffusion coefficient of the analyte, the radius of the cylinder and the experimental scan rate³¹. Using the above equation and the

corresponding correction factor to account for the electrode geometry a peak-current of 1.1 μA is predicted for the oxidation of ferrocenemethanol at a scan rate of 0.10 V s^{-1} .

As the concentration of the supporting electrolyte is decreased the voltammetric response is found to be relatively insensitive to the electrolyte concentration, where at high over potentials the quasi-steady state currents are within 2.5 percent of each other (above 1.0 mM KCl). Only under conditions of no additional supporting electrolyte does the voltammetry appear significantly distorted. This response is consistent with that found with the use of a micro disc electrode, where for a neutral redox species the voltammetric response is found to be relatively insensitive to the presence of supporting electrolyte, at least in the present case to concentrations as low as 1 mM ²⁵.

In contrast to the above result, for the case in which the electrochemical reactant is charged the magnitude – but not the potential – of the voltammetric wave is seen to be sensitive to the supporting electrolyte concentration. The reduction of the charged redox species ruthenium (III) hexamine chloride was studied at a carbon fibre microcylinder electrode under conditions of varying supporting electrolyte concentrations, as shown in Figure 2 (b). Again, under conditions of full support (100 mM KCl), the measured peak current, 1.172 μA , is consistent with that anticipated for a diffusion limited one-electron reduction at a surface supported microcylinder electrode, 1.20 μA . As the supporting electrolyte concentration is lowered a marked increase in the magnitude of the reductive signal is observed, where in the presence of only an additional 5 mM supporting electrolyte the magnitude of the reductive current is 11% larger than that found in the presence of fully support. It is noted that on decreasing the electrolyte concentration the viscosity of the solution decreases by only 0.6% ³². On this basis it is unlikely that the change in viscosity can account for the observed increase in the voltammetric wave. Moreover, if the viscosity change was dominant, one would anticipate the observation of a similar magnitude increase for the oxidation of ferrocenemethanol. Consequently, it is concluded that the larger currents in this case reflect the enhanced mass-transport due to the influence of migration of the charged species into the diffuse layer surrounding the electrode. Again this result is consistent with analogous results for microdisc electrodes where the electrochemical response of charged species are found to be influenced by migration ³³.

Although the microcylinder electrodes used within this work have one dimension that is of macroscopic proportions, in terms of their electrochemical response they are found to provide voltammograms more comparable to that found for microdiscs than macroelectrodes. ⁹ Moreover, on the basis of the above results we may tentatively conclude that if a charged species is to be analytically studied under conditions of low-supporting electrolyte this is likely best achieved using a macrodisc electrode. Conversely, in the case that the electroactive analyte of interest is neutral in the solution phase, the use of a microcylinder electrode presents a potentially optimal route for its detection and analytical quantification.

Having studied the voltammetric response of both a macro and microcylinder electrode towards two ideal outer-sphere redox probes the work next turns to consider the more complex but analytically important case of electrochemical oxygen reduction.

Oxygen reduction is a multi-step electron transfer process involving the concomitant transfer of protons and at a carbon electrode. Depending on the solution phase pH the process is reported to proceed via surface adsorbed superoxide species on the carbon electrode ¹⁷. The voltammetric reduction of oxygen was studied under *non-buffered* conditions at a glassy carbon macroelectrode, as shown in Figure 3. A broad irreversible reduction wave is observed at 0.527 V vs SCE. Tafel analysis showed that $\alpha \approx 0.55$ (see SI) From the irreversible form of the Randles-Ševčík equation ³⁴:

$$I_p^{irrev} = \pm 0.496(n'\alpha)^{\frac{1}{2}}nFAC\left(\frac{FDv}{RT}\right)^{\frac{1}{2}} \quad (2)$$

where:

- I_p is the peak current in amps;
- n' is the number of electrons transferred before the rate determining step;
- n is the total number of electrons transferred;
- A is the area of the electrode;
- D is the diffusion coefficient;
- v is the scan rate in $V s^{-1}$;
- α is the transfer coefficient measured to be 0.55 from Tafel analysis;
- C is the bulk concentration of oxygen.

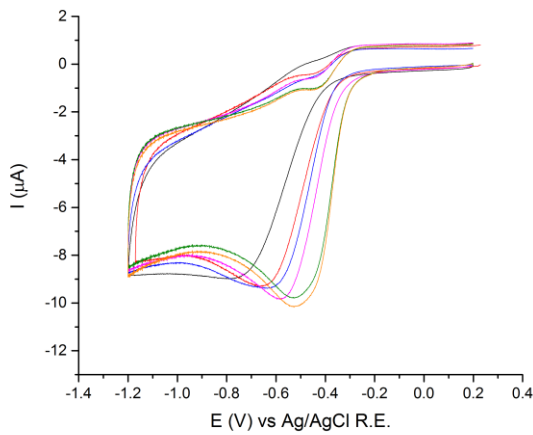


Fig. 3 Cyclic voltammetric response of O_2 reduction in the absence of a buffer, at 298K and $0.1V s^{-1}$ scan rate in 100mM (orange), 80mM (green), 50mM (pink), 25mM (blue), 10mM (red) and 1mM (black) KCl solutions on a GC electrode at atmospheric pressure.

The peak current for the reduction processes is experimentally found to be $10.2\mu A$, whereas a value of $11\mu A$ is estimated from the equation using values of $n = 2$, $\alpha = 0.55$ and $D = 1.98 \pm 0.06 \times 10^{-9} m^2 s^{-1}$ ³⁵ Consequently, the reduction is inferred to be a two electron reduction of oxygen to hydrogen peroxide, consistent with many literature reports for the reduction of O_2 at carbon in supported media³⁶. On the basis of the experimentally determined transfer coefficient the first electron-transfer resulting in the formation of superoxide is inferred to be the rate determining step.

Although in this experiment the pH of the solution is not controlled and during the course of the reduction process the proton activity local to the electrode will vary, due to the protonation occurring *after* the rate determining electron transfer the oxygen reduction process is likely relatively insensitive to the systems buffering capacity. Notably, when we studied O_2 reduction on a glassy carbon macroelectrode in the presence of 0.1M KOH, the reduction process is found to have a peak potential of $-0.43V$ at a scan rate of $0.1V s^{-1}$ (see SI V,) which is comparable to that reported above for the reduction in the non-buffered electrolyte, further emphasising the relative insensitivity of the irreversible electrochemical process to the local pH shifts at the electrode surface. For situations in which this insensitivity breaks down the

interested reader is referred to the work of Humffray et al. who study the influence of variable buffer concentration on the potential of the oxygen reduction wave³⁷. Generally however, assuming the buffering capacity is not significantly above micromolar levels then the voltammetry will predominantly appear as if the oxygen reduction processes is unbuffered with a voltammetric peak potential at ≈ -0.53 V on a macroelectrode.

Having shown the ability to reduce oxygen at the carbon electrode surface in the absence of buffer the work now considers the influence of the supporting electrolyte concentration. Figure 3 shows the voltammetric response for the reduction in the presence of decreasing concentrations of the supporting electrolyte. Over the range of concentrations, the peak position shifts from -0.527 V to -0.809 V, and the peak height decreases by ca. 12%. The origin of this altered voltammetric behaviour as a function of the electrolyte concentration was investigated further by considering the possible influence of the identity of the additional salt. Figure 4 depicts the peak potential for the reduction of oxygen in three different supporting electrolytes as a function of electrolyte concentration. In all three cases upon lowering the electrolyte concentration the oxygen reduction peak is found to shift to more negative electrode potentials. This result mirrors that found for the oxidation of ferrocenemethanol; for both neutral species a decrease in the supporting electrolyte concentration leads to an ohmically distorted voltammetric wave. However, given the large differences in the molar conductivities of the three electrolytes utilised, ($\text{KCl} = 149.9 \text{ S cm}^2 \text{ mol}^{-1}$, $\text{NaCl} = 126.5 \text{ S cm}^2 \text{ mol}^{-1}$, $\text{NaF} = 105.5 \text{ S cm}^2 \text{ mol}^{-1}$)³⁸ the similarities in the oxygen reduction peak positions as a function of the differing ionic species is notable. For comparison, in the SI the peak positions for the oxygen reduction are replotted against the solution phase conductivities, and here the lack of correlation is clear. Hence, it is concluded that the peak position for the oxygen reduction signal in the non-buffered low electrolyte supported media is pre-dominantly a reflection of the solution phase ionic strength and not the conductivity of the ionic solution. It is on this basis that the oxygen reduction peak position at a macro-glassy carbon electrode may plausibly be used as an analytical method for the determination the ionic strength of an electrolytic solution.

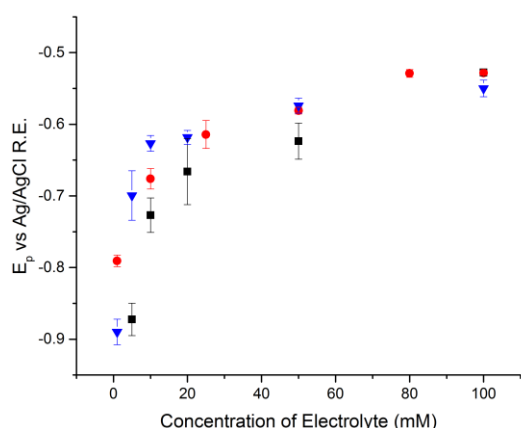


Fig 4. Graph showing peak position vs concentration of supporting electrolyte at 298K, with a scan rate of 0.1 V s^{-1} for KCl (red), NaCl (blue) and NaF (black) solutions on a glassy carbon electrode and at atmospheric pressure.

Finally, we consider the electrochemical response of oxygen reduction at a carbon fibre electrode in non-buffered media and under conditions of low-electrolyte support. Figure 5 depicts the reduction of oxygen at a carbon fibre micro electrode with varying (1-100mM) concentrations of supporting electrolyte. A clear reductive feature is observed at around -

0.8V vs a Ag/AgCl reference electrode. As found for the oxidation of ferrocenemethanol the electrochemical response is essentially invariant with the concentration of the supporting electrolyte. Moreover, oxygen reduction was also performed in an as supplied mineral water sample, also depicted in Figure 5. This mineral water is suitable for human consumption and is an ionic strength of approximately 1.5mM(see SI for full specifications.) Again a clear voltammetric reduction wave is observed. Hence, even in the absence of buffer or excess supporting electrolyte it is proposed that the electrochemical reduction of oxygen at a single carbon fibre microcylinder electrode readily enables the detection and quantification of the dissolved oxygen concentration in a given aqueous solution.

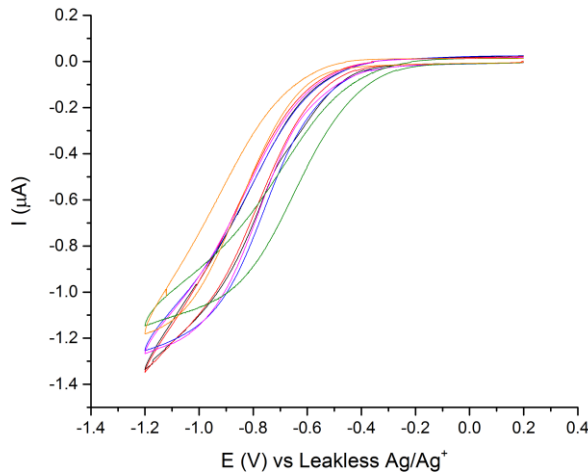


Fig. 5 Cyclic Voltammetry of O₂ reduction at 298K and a scan rate of 0.1V s⁻¹ in 100mM (black), 50mM (red), 25mM (blue), 10mM (pink), 1mM (green) solutions of KCl and bottled mineral water (orange) on a 1cm microcylinder electrode.

In order to demonstrate the analytical applicability of this oxygen reduction response an air equilibrated mineral water sample was heated under atmospheric conditions and the subsequently sealed and cooled back to room temperature (298K). The solubility of oxygen is lower at higher temperatures. This reflects the slightly exothermic solvation of oxygen in water ($\Delta H = -12.1\text{kJ mol}^{-1}$)³⁹ hence in accordance with the Van't Hoff equation at higher temperatures the solubility of oxygen is decreased. By heating the water the oxygen content is lowered. The exact oxygen content of the heated water can be readily estimated from calculating the concentration in solution from combining the Henry's Law Coefficient with the integrated form with respect to temperature of the Van't Hoff equation⁴⁰:

$$\frac{\hat{H}_i(T_1)}{\hat{H}_i(T_0)} = \exp \left[\left(\frac{\Delta H_{sol}}{R} \right) \left(\frac{1}{T_1} - \frac{1}{T_0} \right) \right] \quad (3)$$

where \hat{H}_i are the Henry's law coefficients at temperatures T_1 and T_0 , and ΔH_{sol} is the enthalpy of solution.

From this equation, variations in Henry's Law Coefficients as a function of temperature can be calculated, and in turn predict the peak currents relative to the 298K peak current. Having heated and subsequently cooled the water a carbon fibre microcylinder electrode was used to measure the remaining oxygen content. The results of which are depicted in Figure 6. The voltammetric peak current has been converted directly to a measured solution phase oxygen concentration using a conversion of multiplying by 224.7M A⁻¹, the factor between the peak current and literature concentration of O₂. Herein we can conclude that even a potable water sample containing no additional supporting electrolyte or buffer can yield an accurate and

readily available route to determining the concentration of oxygen analytically in solution via the magnitude of the peak current.

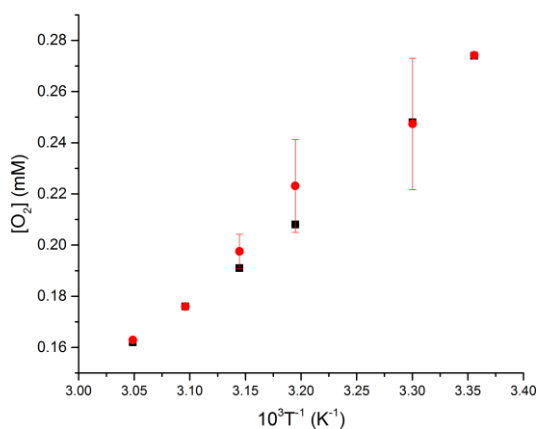


Fig. 6 Predicted O_2 concentrations from Van't Hoff equation (black) vs experimentally determined concentrations from peak currents (red) as a function of T^{-1} on 1 cm microcylinder electrode at atmospheric pressure.

Conclusions

The use of electrochemical techniques in real-world samples has often been viewed as limited by the requirement of the addition of excess supporting electrolyte. Herein this work has demonstrated that for solutions of ionic strength above ca. 1.0mM, as is very commonly found for natural surface waters, then although the voltammetric signal may be partially distorted appropriate electrode selection can still enable analytically useful signals to be obtained. Specifically it is shown that the oxidation or reduction of neutral redox active species may be successfully undertaken using a carbon fibre microcylinder electrode.

Beyond the application of this technique to idealised redox active species the work demonstrates how even for the more complex case of oxygen reduction an analytically useful signal can be obtained in the absence of a pH buffer or excess supporting electrolyte. For this example, the redox processes is highly irreversible. However, due to protonation occurring after the rate determining electron transfer step, the voltammetric wave is found to be essentially insensitive to the pH local to the electrode and hence it is not dramatically altered by the absence of buffer. This technique has been applied to the determination of the oxygen content of varying aqueous solutions without prior sample treatment.

References

- (1) Sullivan, P. J.; Agardy, F. J.; Clark, J. J. J. In *The Environmental Science of Drinking Water*; Butterworth-Heinemann: Burlington, **2005**, pp. 1-28.
- (2) Environmental Protection Agency, Secondary Drinking Water Standards: Guidance for Nuisance Chemicals
- (3) Bruvold, W. H.; Ongerth, H. J. J. - *Am. Water Works Assoc.* **1969**, *61*, 170-174.

- (4) Dickinson, E. J. F.; Limon-Petersen, J. G.; Rees, N. V.; Compton, R. G. *J. Phys. Chem. C* **2009**, *113*, 11157-11171.
- (5) Bond, A. M.; Coomber, D. C.; Feldberg, S. W.; Oldham, K. B.; Vu, T. *Anal. Chem.* **2001**, *73*, 352-359.
- (6) Belding, S. R.; Limon-Petersen, J. G.; Dickinson, E. J.; Compton, R. G. *Angew. Chem.* **2010**, *49*, 9242-9245.
- (7) Cooper, J. B.; Bond, A. M.; Oldham, K. B. *J. Electroanal. Chem.* **1992**, *331*, 877-895.
- (8) Amatore, C.; Fosset, B.; Maness, K. M.; Wightman, R. M. *Anal. Chem.* **1993**, *65*, 2311-2316.
- (9) Ciszowska, M.; Stojek, Z. *J. Electroanal. Chem.* **1999**, *466*, 129-143.
- (10) Pletcher, D.; Sotiropoulos, S. *J. Electroanal. Chem.* **1993**, *356*, 109-119.
- (11) Batchelor-McAuley, C.; Kozub, B. R.; Menshikau, D.; Compton, R. G. *J. Phys. Chem. C* **2011**, *115*, 714-718.
- (12) Glud, R. N. *Marine Biology Research* **2008**, *4*, 243-289.
- (13) Sander, R. *Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry*. **1999**, 1-13.
- (14) Battino, R.; Rettich, T. R.; Tominaga, T. *J. Phys. Chem. Ref. Data* **1983**, *12*, 163.
- (15) Brito, P. S. D.; Sequeira, C. A. C. *J. Power Sources* **1994**, *52*, 1-16.
- (16) Perin, D. D. *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution, Second Edition Pergamon*, Oxford, **1982**.
- (17) Yang, H.-H.; McCreery, R. L. *J. Electrochem. Soc.* **2000**, *147*, 3420.
- (18) Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1987**, *225*, 23-36.
- (19) Compton, R. G.; Banks, C. E. *Understanding Voltammetry*, World Scientific, **2011**, p. 121.
- (20) Cui, L.; Gadde, S.; Li, W.; Kaifer, A. E. *Langmuir* **2009**, *25*, 13763-13769.
- (21) Batchelor-McAuley, C.; Yang, M.; Hall, E. M.; Compton, R. G. *J. Electroanal. Chem.* **2015**, *758*, 1-6.
- (22) Limon-Petersen, J. G.; Han, J. T.; Rees, N. V.; Dickinson, E. J. F.; Streeter, I.; Compton, R. G. *J. Phys. Chem. C* **2010**, *114*, 2227-2236.
- (23) Josefsson, I.; Eriksson, S. K.; Rensmo, H.; Odelius, M. *Struct. Dyn.* **2016**, *3*, 023607.
- (24) Wang, Y.; Limon-Petersen, J. G.; Compton, R. G. *J. Electroanal. Chem.* **2011**, *652*, 13-17.
- (25) Amatore, C.; Deakin, M. R.; Wightman, R. M. *J. Electroanal. Chem.* **1987**, *225*, 49-63.
- (26) Cinková, K.; Clark, M.; Sokolov, S. V.; Batchelor-McAuley, C.; Švorc, L.; Compton, R. G. *Electroanalysis* **2016**, DOI: 10.1002/elan.201600693.
- (27) Fletcher, S.; Horne, M. D. *Electrochem. Commun.* **1999**, *1*, 502-512.
- (28) Prehn, R.; Abad, L.; Sánchez-Molas, D.; Duch, M.; Sabaté, N.; del Campo, F. J.; Muñoz, F. X.; Compton, R. G. *J. Electroanal. Chem.* **2011**, *662*, 361-370.
- (29) Lees, J. C.; Ellison, J.; Batchelor-McAuley, C.; Tschulik, K.; Damm, C.; Omanovic, D.; Compton, R. G. *ChemPhysChem* **2013**, *14*, 3895-3897.
- (30) Weber, J.; Wain, A. J.; Marken, F. *Electroanalysis* **2015**, *27*, 1829-1835.
- (31) Ngamchuea, K.; Lin, C.; Batchelor-McAuley, C.; Compton, R. G. Supported Microwires for Electroanalysis: Sensitive Amperometric Detection of Reduced Glutathione, *Anal. Chem.* **2017**, *Just Accepted*.
- (32) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions: Second Edition Revised*; Butterworths, **1959**, p. 571.
- (33) Daniele, S.; Ugo, P.; Bragato, C.; Mazzocchin, G. A. *J. Electroanal. Chem.* **1996**, *418*, 29-34.
- (34) Brownson, D. A. C.; Banks, C. E. In *The Handbook of Graphene Electrochemistry*; Springer London, **2014**, pp. 23-77.

- (35) Han, P.; Bartels, D. M. *J. Phys. Chem.* **1996**, *100*, 5597-5602.
- (36) Sljukic, B.; Banks, C. E.; Compton, R. G. *J. Iran Chem. Soc.* **2005**, *2*, 1-25.
- (37) Taylor, R. J.; Humffray, A. A. *J. Electroanal. Chem.* **1975**, *64*, 95-105.
- (38) Coury, L. *Conductance Measurements Part I: Theory, Current Separations*, **1999**, pp. 91-96.
- (39) Li, Q.; Batchelor-McAuley, C.; Lawrence, N. S.; Hartshorne, R. S.; Compton, R. G. *J. Electroanal. Chem.* **2013**, *688*, 328-335.
- (40) Smith, F. L.; Harvey, A. H. *Chem. Eng. Prog.* **2007**, *103*, 33-39.