Feature Article Masao Horiba Awards

堀場雅夫賞 特別賞受賞者論文

Development of Boron-Doped Diamond Electrodes for Key Analytes in the Aqueous Environment and Beyond

水環境や他の領域において主要分析対象を検出するためのホウ素ドープダイヤモンド電極の開発

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Dissolved oxygen and pH are two of the most important factors in analytical science, affecting processes in the environment and beyond. Given their impact their importance is twofold, firstly their measurement is key to understanding the condition of a given environment, and secondly their control aids in managing the health and quality of those environments for example, the toxicity of potential pollutants such as heavy metals with pH dependent availability. Electrochemistry offers a relatively simple, cheap, and clean analytical method however, conventional electrode materials often struggle with long-term in situ measurements due to fouling, chemical, or physical degradation. Herein, we exploit the robust properties of Boron Doped Diamond electrode materials to explore methods of analysis and in situ control of key environmental analytes such as oxygen, pH, and heavy metals. Negating the need to remove and chemically alter samples before analysis.

溶存酸素とpHは，分析科学において最も重要な要素の一つであり，環境をはじめとするさまざまなプロセスに影響を及ぼす。これらの重要性は二つの側面を持つ。一つ目は，これらの測定が特定の環境の状態を把握する上で不可欠である点である。二つ目は，これらを制御することが，例えば pH に依存する重金属などの潜在的汚染物質の毒性など、環境保全のために管理する上で有効な点である。電気化学測定は，比較的簡便で低コストかつクリーンな分析手法であるが，従来の電極材料は，汚れの蓄積や化学的・物理的な劣化により，長期的な現場測定において課題を抱えることが多い。本研究では，ホウ素ドープダイヤモンド電極材料の堅牢な特性を活用し，溶存酸素，pH，重金属といった重要な環境分析対象の測定および制御方法を検討する。特に，重金属測定では，測定前のサンプル前処理の必要ない分析方法を検討した。

Introduction

Although in the modern analytical science world we are able to measure countless aqueous species via an array of techniques, each important in its own way to a given field of interest, dissolved oxygen and pH are perhaps two of the most widely important analytes of interest. Dissolved oxygen is unequivocally key to the existence of life on our planet, and thus it can be of no surprise that its quantitation is vital in fields from the aqueous environment, to healthcare, and from agriculture all the way through the chain to the food and drinks industry[1],[2]. Furthermore, life and the environment exist in a finely balanced homeostasis of which pH forms a key pillar that when disturbed can have devastating results[3]. Not only is the pH value itself important, but its influence on the speciation and complexation of other key analytes (e.g. heavy metals) can change their bioavailability and thus impact the toxicity of a system[4]. Whilst technologies exist to measure each of these analytes, the sheer breadth of conditions and matrices under which measurement is necessary and range of relevant concentrations necessitates continued development and innovation. For many applications existing technologies suffer drawbacks such as long-term measurement stability, fragility, corrosion, size, and (bio)fouling. Under potentially changeable environmental conditions subtle changes in e.g. pH may cause release of, and therefore increased toxicity of heavy metals[5], it is therefore important to measure both their available and total concentrations; normally achieved by removal and acidification of samples thus prohibiting in situ and continuous monitoring[6]. One of the most commonly used analytical tools in this field is electrochemistry, appealing due to its potential for sensitive, selective, low cost, and easy to use sensing. The body of research highlighted herein aims to combat some of these drawbacks through exploring the use of high-quality Boron Doped Diamond (BDD) for electrochemical control of pH and for the measurement of key environmental analytes[7]-[9]. The superior electrode qualities of BDD have generated much interest in the electrochemistry field over the past few decades, such as chemical and thermal stability, low biofouling, ability to in situ electrochemically clean, low background currents etc[10]-[13]. These same qualities are what give the BDD sensors much potential for solving some of the issues experienced by those interested in measuring dissolved oxygen, pH and pH dependent systems, such as heavy metals. Firstly, this work takes advantage of the robustness of BDD at extreme potentials to explore the ability to control the local pH environment of the measurement electrode[7],[8]; For traditional electrode materials such as gold, or sp^2 carbon (e.g. glassy carbon, screen printed carbon) it is not possible to work at these extremes of potential without causing damage (corrosion) to the electrode surface over time. The resistance to corrosion afforded by the sp^3 bonded structure of BDD offers considerable advantage; in the research highlighted here we demonstrate the use of electrochemical water splitting to produce and control proton concentration at a generator electrode, in turn influencing the pH environment local to a sensing electrode, where the speciation, and concentration of heavy metals of environmental importance can be assessed. This sensor technology is applied to the detection of heavy metals (here Hg[7] and Cu[8]) in aqueous solutions where the pH is non-ideal for the measurement of interest. The sp^3 bonded nature of BDD which produces these excellent qualities also results in a lack of surface sites required for inner sphere reactions, such as the oxygen reduction reaction (ORR), and is not sensitive to pH. Previous research has demonstrated that through surface engineering via laser machining, controlled incorporation of very robust (corrosion stable) forms of sp^2 carbon into the BDD surface is possible. The quinone surface terminations (BDD-Q) introduced with the sp^2 carbon have been demonstrated in previous work to undergo proton-coupled electron transfer, resulting in a Nernstian (~59 mV/pH unit) shift in the voltammetric peak with changing pH[14],[15]. The work discussed herein expands on this, exploring the use of selective incorporation of these sp^2 carbon regions into BDD to enable the simultaneous detection of both pH and dissolved oxygen in aqueous systems on a single electrode (taking ~4 s)[9]. The possibility of negating reference electrode (RE) drift by implementing an internal-referencing mechanism based on the relationship between the two analytical signals is also explored.

BDD Sensor Design For Electrochemical pH Control

An individually addressable ring-disk electrode system is designed; Ring and disk shaped electrodes are each laser machined out of a wafer of freestanding BDD and placed concentrically, separated and encapsulated by electrically-insulating material such that the electrode faces are coplanar but not touching. The electrochemistry at each electrode is separately controlled via copper wires connected to the BDD through Ohmic sputtered Ti-Au contacts. This arrangement enables the control of local pH through water electrolysis on the ring electrode upon the application of a sufficiently large current, whilst analytical voltammetric measurements of a species of interest can be conducted independently on the disk. The relationship between applied ring-current and resultant local pH at the disk surface were characterised through use of an electrodeposited pH sensitive IrOx film for both applications. Figure 1 illustrates (a) the ring-disk format and (b)

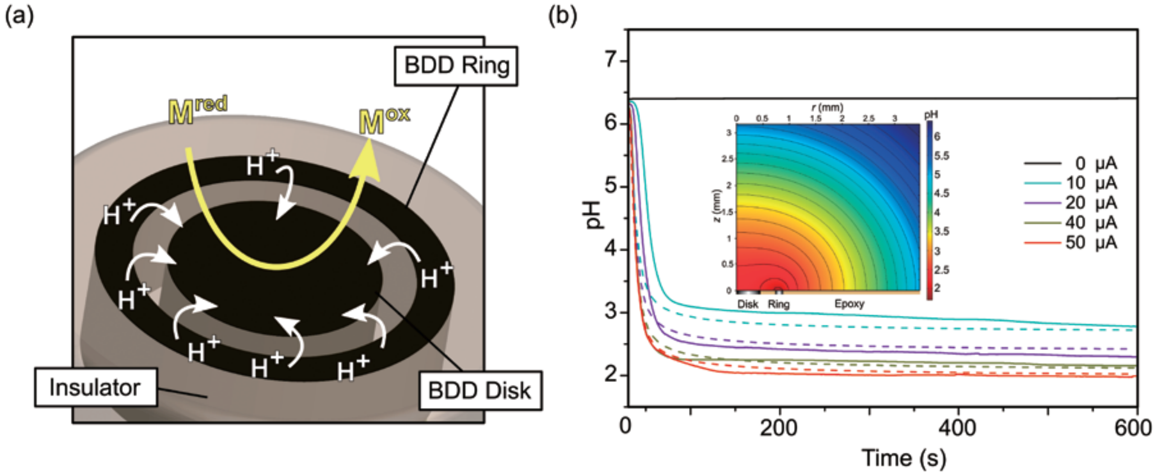

Figure 1 (a) Illustration of the BDD ring-disk design for pH control and simultaneous electrochemical heavy metal analysis.
(b) Comparing simulated (dashed line) and experimental (solid line) data for the pH change generated at different applied ring currents. Inset shows 2D axisymmetric simulation of the pH profile extending into bulk solution.
Figure adapted from [7] *copyright 2014 American Chemical Society.*

experimental data for the pH change associated with different applied ring-currents compared with data produced using finite element methods[7].

Electrochemical Measurement of Hg with simultaneous pH Control

Stripping voltammetry measurements conducted in Hg containing solutions at different bulk pH values, Figure 2(a), demonstrate the effect of pH on the analytical signal. At low pH values, where Hg is completely in the Hg2+ form, a single sharp stripping peak is observed. However, as the pH increases the peak is seen to shift on the potential axis, broadening and decreasing in current magnitude as the Hg speciation changes to less electroactive forms. In Figure 2(b) measurements conducted in bulk pH 6.40 and pH 2.0 solutions are compared to the resulting data when a current is applied to the ring electrode during measurement in bulk pH 6.40 solution. Application of a 50 µA current is expected to result in a pH change to ~pH 2.0 as found in Figure 1(b), here we see the stripping peak transformed from a broad peak at ~0.2 V in bulk pH 6.4 solution to a much sharper peak at ~0.5 V, which is similar to that recorded in bulk pH 2.0 solution. Some shoulder peaks are observable, indicating that the local pH may not have completely reached pH 2.0 at the point of measurement however, this data demonstrates the power of such electrodes for in situ analysis of heavy metals such as Hg in solutions of non-ideal pH without the need for manual acidification.

Controlling Cu speciation and detection with simultaneous pH Control

Copper is another common contaminant in natural water, which can cause issues such as Wilsons Disease when it accumulates in the body[16]. The binding of copper by ligands in water systems or therapeutics can be used to remove it – but this process is also pH dependent. In this work the same ring disk pH control sensor format is applied to measurement and manipulation of the speciation of copper by common therapeutic ligand triethylenetetramine (TETA). The effect of Cu-ligand binding is demonstrated using UV-Vis Spectroscopy in combination with speciation simulations in Figure 3(a), here demonstrating good agreement and a move from free copper to bound systems as pH increases. Electrochemical measurements using the disk electrode to measure in solutions at

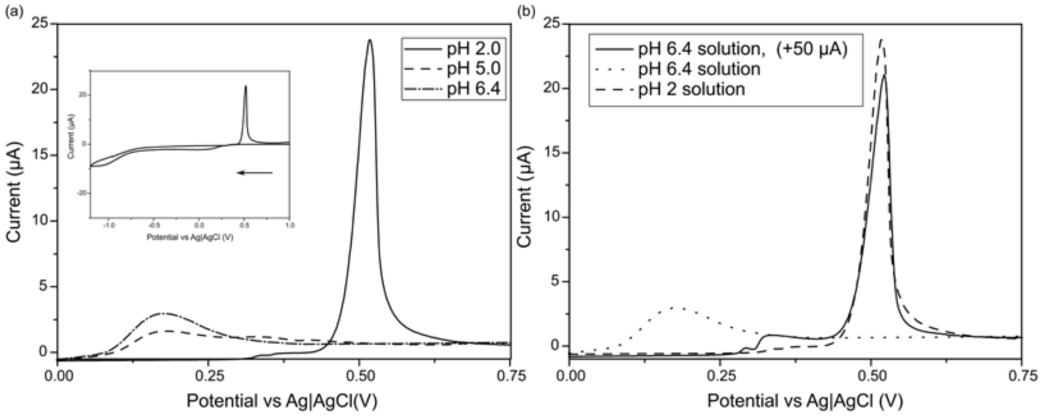

Figure 2 (a) Comparing Hg stripping peaks from cyclic voltammetry at different bulk solution pH values. inset shows full CV and direction of scan. (b) Comparing stripping peaks for Hg in bulk pH 2 and pH 6.4 solutions with that in bulk pH 6.4 solution with 50 µA simultaneously applied to the ring electrode. Figure adapted from [7] *copyright 2014 American Chemical Society.*

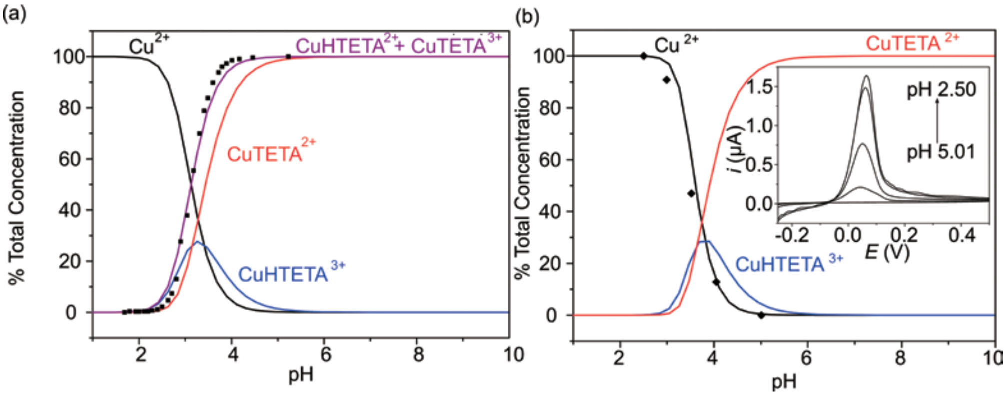

Figure 3 (a) Simulated speciation curves for copper in TETA containing solutions at different pH compared to experimental UV-Vis data (black squares), (b) Copper speciation simulation compared with peak currents (black dots) for electrochemical stripping peaks of Cu in solutions at different pH.
Figure adapted from [8].

chemically adjusted pH values showed good agreement to simulated speciation curves, confirming that the change in binding was observable via electrochemical measurement, Figure 3(b).

Finally, the ring electrode was used to influence the local pH enabling in situ local control over the binding of the copper with simultaneous electroanalysis. The current density applied to the ring is compared to the resultant Cu detection peak current measured on the ring as a percentage of the maximum recorded current (representing complete availability of all copper species) in Table 1; Used in combination with the electrochemical speciation curve in Figure 3(b) it is therefore possible to calculate the local pH generated at each current density. This study further highlights potential of BDD electrodes for control of metal ligand binding and therefore measurement of free and total metal concentrations in complex aqueous systems.

BDD Sensor Design for Electrochemical pH and Oxygen Measurement

The ability to measure pH using BDD based electrode materials with robust laser-induced sp^2 carbon regions ($BDD\text{-}sp^2$) has been demonstrated by researchers in the Macpherson group[14],[15]. Sp^2 carbon also catalyses reactions which require surface interaction and are therefore not measurable by high quality sp^3 diamond carbon surfaces, such as the key environmental analyte dissolved oxygen. This study aimed to assess the use of such sensors for simultaneous pH and oxygen measurement. In order to achieve this it was first necessary to optimize the pattern of sp^2 regions to achieve clear and sensitive electrochemical signals for both analytes (not just pH). Figure 4 presents the three patterns assessed: (a) a microspot array of pits with overlapping diffusional fields akin to a microelectrode array, (b) a single pit of equivalent total machined area to (a), and (c) a microspot array of smaller, diffusionally isolated spots. Cyclic voltammetry was used to assess the electrochemical performance of each, and the resultant

Table 1 Comparing data for the applied current at the ring electrode with electroanalytical response on the disk electrode for Cu detection and the effective local pH change. Table from [8].

Applied Current Density (mA cm^{-2})	% Maximum LSV Peak Current	Generated pH from Speciation Curve
0.10	0	5.01 ≤
0.20	34.98	3.76
0.395	78.92	3.35
1.98	100	≤ 2.50

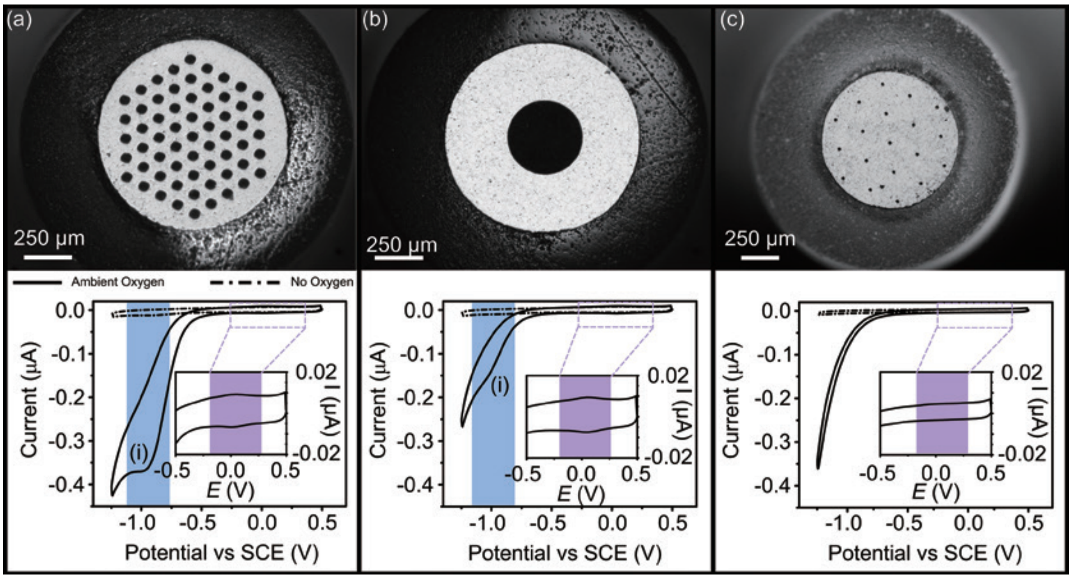

Figure 4 Optical images and cyclic voltammograms comparing BDD electrodes with (a) a microarray of machined spots with diffusional overlap, (b) a single spot of equivalent machined area to (a), and (c) a microspot array with no diffusional overlap and decreased machining area. Cyclic voltammograms show pH signatures (purple highlighted region) and oxygen signatures (blue highlighted region labelled (i)) under ambient and degassed conditions. Figure adapted from [9] *copyright 2019 American Chemical Society.*

data is also presented. For each electrode a clear signal at ~0.1 V associated with the proton coupled electron transfer reaction at quinone surface terminations is observed (purple highlighted regions) as expected based on previous work. It is notable that the signature for (c) whilst present is significantly smaller, which is expected as the lower machined area results in a lower surface coverage of quinone species. For (a) and (b) a signal associated with the reduction of oxygen can also be observed at ~-1.0 V (blue highlighted region, labelled (i)), however this is not present in (c) and is likely masked by the onset of solvent reduction. As the signal for oxygen reduction was found to be larger and more clearly distinguishable from solvent reduction in (a) and no significant difference in pH response was observed this pattern was used for further studies.

Rapid Simultaneous Measurement of Oxygen and pH

For full characterization of simultaneous oxygen and pH response on BDD-sp^2 electrodes, square wave voltammetry was applied as it enables reduction of background currents increasing signal-to-noise and is significantly faster than other voltammetric techniques. Calibration curves were collected for both analytes simultaneously, where the concentration of oxygen in a series of solutions at different pH values was varied using mass flow controllers to change the ratio of oxygen to balance gas (argon). Figure 5 presents an example measurement (centre) with the resultant aggregate mean data from measurements conducted at 5 different pH values in the range 4.00-10.20, with 5 different oxygen values over 0.1-8 mgL^{-1} in each. For both oxygen (blue, left) and pH (purple, right) a clear signature is observed, and calibration plots for each (left and right respectively) are produced demonstrating linear behaviour ($R^2 = 0.999$ for oxygen and 0.998 for pH). The slope of the pH calibration plot, 60 mV pH^{-1}, is also found to be close to that predicted by the Nernst equation, 59 mV pH^{-1}. Each measurement conducted to produce the calibration plots was obtained in ~4 s, clearly demonstrating the potential of these BDD-sp^2 electrodes for the rapid simultaneous measurement of oxygen and pH in aqueous media.

Potential to Correct for Reference Electrode Drift

As a linear relationship is observed between the aggregate mean oxygen peak current and the mean dissolved oxygen concentration (measured independently via commercial optical dissolved oxygen probe) across the whole pH range assessed, the assumption can be made that the magnitude of the oxygen current response is unaffected by pH over the pH range 4–10. One of the most significant issues for real-world analysis is the necessity for a long-term stable reference electrode, to which the potential at the sensing electrode is compared. However, in real-world systems these reference electrodes often suffer drift due to fouling or other influences thus impacting the accuracy of the measurement and impeding continuous or long-term in situ measurements, particularly when they rely on peak potential as with the proton coupled electron transfer reaction signals used to measure pH here. As the two analytical signals (oxygen and pH) are seemingly independent, the relationship between them has potential to act as an internal referencing mechanism where any reference electrode drift would impact both equally and thus be

$$\text{Equation 1} \qquad O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad pH = 7 \qquad E^0 = 0.456\ V\ vs\ SCE$$

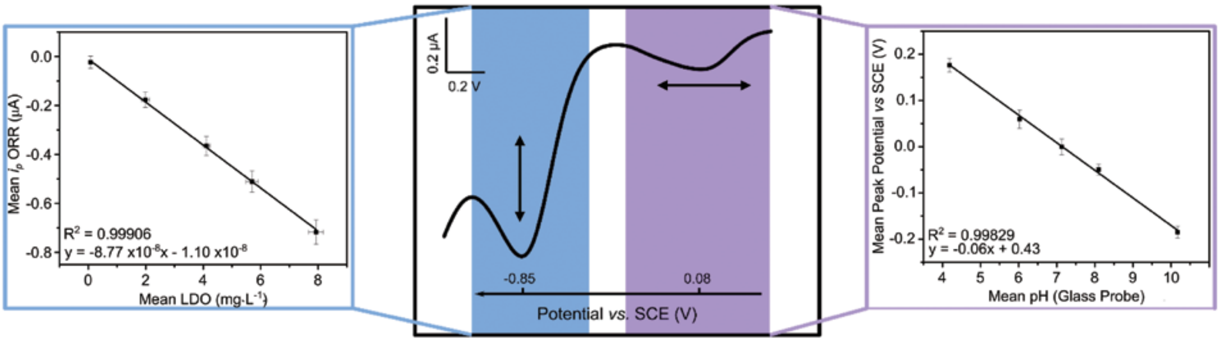

Figure 5 Example measurement of both oxygen (blue) and pH (purple), centre, compared with (left) aggregate mean oxygen calibration data and (right) aggregate mean pH calibration data conducted in solutions at a range of pH and dissolved oxygen concentrations. Figure adapted from [9] *copyright 2019 American Chemical Society.*

negated, a concept first proposed by Wrighton et al.[17]. Although the equation for two electron reduction of oxygen on sp^2 C, Equation 1, indicates the involvement of protons in the reaction, as there are no proton transfer reactions occurring before or in the rate-determining step, the peak position for electron transfer should not be affected[18]-[21].

This is assessed in Figure 6, where the relationship between the pH and oxygen signatures is explored in more detail. The peak potential for oxygen reduction from Figure 5 was analyzed for a statistically significant dependence using a Kruskal–Wallis analysis of variance (ANOVA) and a One-Way ANOVA at a 5 % significance level, with the Bonferroni correction for multiple comparisons. No statistical dependence of the oxygen reduction peak potential was observed for either dissolved oxygen concentration or pH, Figure 6(a) and (b), respectively. Figure 6(c) shows the separation between the pH and oxygen peaks in one measurement, ΔE_p, as a function of dissolved oxygen concentration, at set pH values. ΔE_p can thus be used to inform on solution pH, as shown in Figure 6(d), where a gradient of 57 mV is observed, close to that predicted by Nernst, for a plot of mean ΔE_p for all oxygen concentrations as a function of pH. This highlights the potential for using the ORR signal as an internal reference for voltammetric pH measurements, negating any reference electrode fouling when applied in real world systems.

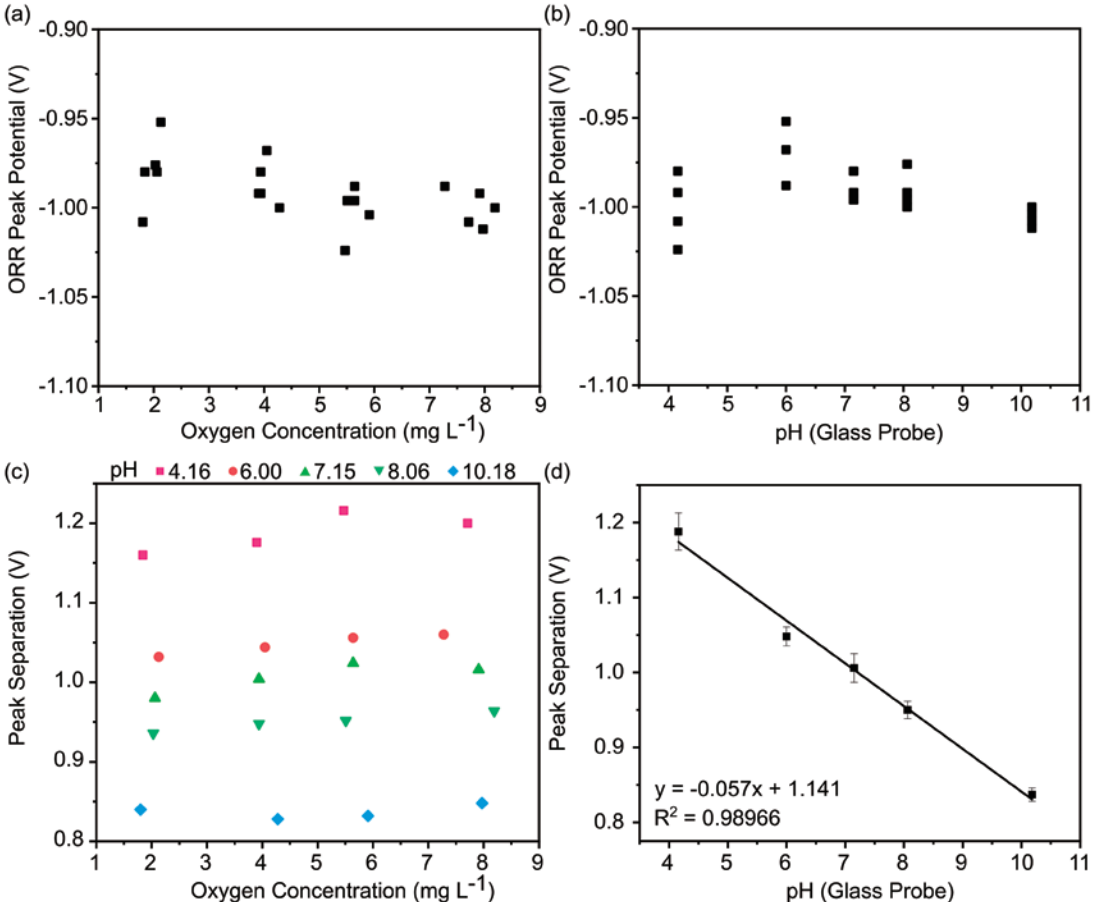

Figure 6 Comparison of oxygen and pH peak parameters to assess the potential for internal referencing. Figure from [9] *copyright 2019 American Chemical Society.*

Conclusion

This manuscript highlights the use of BDD electrodes to improve measurement and local-control of key environmental analytes. We present the first published examples of the use of electrochemical pH control in aqueous systems, and its application to heavy metal detection and speciation control. Firstly, the method is used to electrochemically measure Hg concentrations in solutions of non-ideal measurement pH without manual adjustment of the bulk pH. This technique is subsequently used to control the local speciation of Cu ions in the presence of binding ligands, thus providing a route to assess total and bound concentrations of heavy metals using a single in situ sensor. This work has since inspired further work by unrelated international research groups (see work by e.g. O'Riordan et al on interdigitated electrodes for agricultural, chlorination applications). The ability to control the local pH environment, and therefore speciation of analytes, in a system of interest could offer new approaches to in situ analyses in fields ranging from waste-water treatment and environmental analysis to medicine (e.g. chelation based cancer therapeutics) and human function (e.g. oxygen and hemoglobin interactions). Proof of concept work on the use of high quality laser-modified BDD electrodes for dissolved oxygen and pH measurements is also described; The ability to simultaneously measure both species on a single electrode (as opposed to separate sensing electrodes within a device) offers a route to the reduction of material usage and manufacturing steps, and therefore a potential decrease in the environmental impact of production. Whilst the work described herein proves the initial concept, going forwards assessments of sensor function in a wider range of environmentally relevant conditions and matrices will be conducted.

Whilst BDD may initially be considered both monetarily and resource expensive, the ability to grow it in the laboratory in a free-standing form at the wafer scale (~6" diameter) and the fact that the sensors demonstrated here are ≤1 mm in diameter (with potential to go smaller limited only by the current laboratory manual electrode fabrication and handling methods) means a huge quantity of sensors could be produced from a single wafer. Furthermore, the robustness of BDD as a material implies a significant longevity over other electrode materials and other existing methods (e.g. optical) of measuring dissolved oxygen and pH and counters these initial costs. The material qualities of BDD, such as hardness and resistance to fouling, could offer solutions for dissolved oxygen and pH measurement over long periods in challenging or hazardous to access aqueous environments, improving not only sensor longevity and measurement frequency but also personnel safety.

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