Graphite Screen-Printed Electrodes Applied for the Accurate and Reagentless Sensing of pH

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Abstract

A reagentless pH sensor based upon disposable and economical graphite screen-printed electrodes (GSPEs) is demonstrated for the first time. The voltammetric pH sensor utilises GSPEs which are chemically pre-treated to form surface immobilised oxygenated species that when their redox behaviour is monitored, give a Nernstian response over a large pH range (1-13). An excellent experimental correlation is observed between the voltammetric potential and pH over the entire pH range of 1-13, such a response is not usually expected but rather deviation from linearity is encountered at alkaline pH values; absence of this has previously been attributed to a change in pK_a value of surface immobilised groups. This non-deviation, which is observed here in the case of our facile produced reagentless pH sensor and also reported in the literature for pH sensitive compounds immobilized upon carbon electrodes/surfaces,where a linear response is observed over the entire pH range, is explained alternatively for the first time. The performance of the GSPE pH sensor is directly compared with a glass pH probe and applied to the measurement of pH in real samples where an excellent correlation between the two protocols is observed validating the proposed GSPE pH sensor.

Introduction

The accurate measurement of pH is crucial to a diverse array of scientific fields,[1, 2] where for example, the slightest fluctuation can potentially result in substantial changes to the kinetics of a reaction.[3, 4] From the on-line monitoring of proton ions in extreme conditions such as those postured by a nuclear reactor to waste water treatment plants and the observing of blood pH by clinicians,[1, 2] the determination of pH is vital.

Typical approaches for the measurement of pH are based upon electrochemical methods but face issues that need to be overcome. The most commonly used technique, potentiometric glass electrodes, have a limited shelf life due to the degradation of the glass membrane and the fragility that is associated with glass. In addition, the glass membrane pH electrodes have significant inaccuracy at high pH values,[5] a so-called "alkali error" and regular calibration of the pH sensor is necessary as a pre-treatment; consequently they have little potential of the development into a portable hand-held device or be used easily in-the-field.[2, 5]

A different approach for the pH measurement of a solution is based again on the application of electrochemical techniques, however using voltammetric techniques.[3, 4, 6-8] In this case, a pH dependent mediator is selected [9-12] and its electrochemical activity is monitored (reduction or oxidation). A popular choice is quinone moieties which have been utilised previously in the literature: a carbon-epoxy electrode with pH sensitive species anthraquinone and phenanthrenequinone [11] and the modification of a glassy carbon electrode with an anthraquinone–ferrocene film have been reported.[13] In such instances, the peak potential (E_p) of the redox peak is dependent on the pH of the solution in which the mediator is present (as per the Nernst equation), and whilst using potentially cheaper electrodes and no further specialist equipment (such as a pH meter) it could prove to be a cost-effect approach to pH sensing. Using a voltammetric method requires quantification of pH via the Nernst equation[14] (eqn. 1) and the measured potential (E_p) as given by:

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{nF} \log \frac{[Red]}{[Ox]} \qquad (1)$$

where n is the number of electrons involved in the reaction, R the ideal gas constant, T is the temperature, F is the Faraday constant and E^0_f is the formal potential of the redox process.

This paper reports the preparation of a voltammetric pH sensor based upon cost-effective and disposable screen-printed graphite electrodes (GSPEs) which are chemically pre-treated to form surface oxygenated species that, when their redox behaviour is observed, give rise to a Nernstian response relative to the pH of the solution and as a result, a quantifiable signal to determine pH. GSPEs are of a benefit because of their robustness, especially when compared to the previously mentioned glass membrane electrodes, low purchase cost, rapid utilisation and simplicity.[15-18]

Previous literature reports the utilisation of carbon electrodes (glassy carbon [GC], edge plane pyrolytic graphite [EPPG]) with extensive mechanical polishing (20 minutes prior to each experiment) to generate oxygenated (quinone) species which monitor pH.[3, 4] It is theorised that a near perfect calibration plot ranging from pH 1.0 − pH 13.0 can be obtained with a Nernstian response corresponding to a 2 proton/2 electron system, which would relate to the redox processes of the quinone groups upon the electrode surface following extensive polishing. However, it is noticed that surface characterisation to confirm such inferences of surface immobilised groups are clearly lacking. Typically, a solution-based mediator undergoing such a reaction will affect the slope of a potential vs pH plot with a change in linearity occurring at the mediator's pK_a. For example, quinone moieties in solution have a reported pK_a value of *ca*. 9.2 which would give rise to two linear regions either side of this value over the entire pH range; however Lu *et al*., along with other groups, observed no change in linearity when the quinone moiety was bound to the surface of GC and EPPG electrodes.[3, 4, 19, 20]

In this paper a novel reagentless electrochemical approach for the sensing of pH based using disposable GSPEs that are chemically pre-treated to form oxygenated species on the electrode surface for the accurate sensing of pH utilising square-wave voltammetry (SWV) is reported for the first time. Such work allows an economical and disposable sensor to be realised that does not need surface modification with quinone-type compounds nor extensive surface pre-treatment via mechanical polishing;[3, 4] since the electrodes are chemically pre-treated multiple electrodes can be readily prepared at once. The electrochemical response of the GSPEs are explored at different pHs demonstrating an exceptional linear response from pH 1.76 to 13.12 with a gradient predicting a theoretical shift in reduction potentials of 57 mV per pH unit which is in excellent agreement with the value for a Nernstian response of a 1:1 proton:electron

process (59 mV per pH unit, T= 298 K). The protocol is also validated against the traditional glass probe in the measurement of pH in "real" unbuffered samples.

Experimental

All chemicals used were of analytical grade and were used as received without any further purification from Sigma-Aldrich (Gillingham, UK). All solutions were prepared with deionised water of resistively no-less than 18.2 Ω cm. All solutions (unless stated otherwise) were vigorously degassed with nitrogen to remove oxygen prior to analysis.

Voltammetric measurements were carried out using a μ-AutolabII (Eco Chemie, The Netherlands) potentiostat/galvanostat and controlled by Autolab GPES software version 4.9. Experiments were performed using screen-printed graphite macroelectrodes (denoted as GSPEs herein) which have a 3 mm diameter working electrode were fabricated in-house with appropriate stencil designs using a DEK 248 screen printing machine (DEK, Weymouth, UK). For the fabrication of the screen-printed sensors, firstly, a carbon-graphite ink formulation (Product Code: C2000802P2; Gwent Electronic Materials Ltd, UK) used previously was screen-printed onto a polyester (Autostat, 250 μm thickness) flexible film (denoted throughout as standard-SPE). This layer was cured in a fan oven at 60 degrees for 30 minutes. Next a Ag/AgCl reference electrode was included by screen printing Ag/AgCl paste (Product Code: C2040308D2; Gwent Electronic Materials Ltd, UK) onto the polyester substrates. Finally, a dielectric paste (Product Code: D2070423D5; Gwent Electronic Materials Ltd, UK) was then printed onto the polyester substrate to cover the connections. After curing at 60 degrees for 30 minutes the screen-printed electrodes are ready to be used. The reproducibility and repeatability of the batch fabricated screen-printed sensors were found to correspond to a % relative standard deviation (%RSD) no greater than 0.82% ($N = 20$) and 0.76% ($N = 3$) for The heterogeneous rate constant, k^o for the $Ru(NH_3)^{2+/3+}$ redox probe in 1M KCl was found to be equal to 1.08×10^{-3} cm s^{-1}. Because of the removal of the Ag/AgCl reference in forming the surface immobilised oxygenated species, via the proposed chemical pretreatment (see later), an external saturated calomel electrode (SCE) was used as the reference and a platinum counter was also utilised in a 3 electrode set-up. Independent pH measurements were performed using a SevenCompact pH meter (Mettler Toledo) which was calibrated prior to use with pH standard. The various tested solutions ranged from pH 1.76 – 13.12 and were composed of HCl (pH 1.76), phosphate buffer solution (PBS; pH 2.48, 3.51, 4.29, 6.47, 7.32, 8.26, 9.27, 10.16, 11.20, 12.10, 13.12). Real pH samples consisted of a commonly available antacid (Rennies) and malt vinegar: The

antacid (1.3 g) was dissolved in water before analysis and the malt vinegar was analysed without any pre-treatment or dilution.

The chemical formation of surface groups involved immersion of GSPEs (with Ag/AgCl reference removed) in to a percarbonate solution ([10% w/v] Na_2CO_3/H_2O_2) and was left overnight (18 h). Note: electrodes were also left for a longer duration (45 h); however no significant difference in electrochemical response was observed (see Figure S1). This procedure is optimal, meaning that all electrodes pretreated via this approach are successfully prepared.

X-ray photoelectron spectroscopy (XPS) was used to analyse the electrode surface and its hypothesised oxygenated groups. All spectra were collected using a bespoke ultra-high vacuum system fitted with a Specs GmbH Focus 500 monochromated Al Kα X-ray source, Specs GmbH PHOIBOS 150 mm mean radius hemispherical analyser with 9-channeltron detection, and a Specs GmbH FG20 charge neutralising electron gun . Survey spectra were acquired over the binding energy range 1100 – 0 eV using a pass energy of 50 eV and high resolution scans were made over the C 1s and O 1s lines using a pass energy of 20 eV. The analysis area was approximately 1.4 mm in diameter. Under these conditions the full width at half maximum of the Ag $3d_{5/2}$ reference line is ~0.7 eV. The energy scale of the instrument is calibrated according to ISO standard 15472, and the intensity scale is calibrated using an in-house method traceable to the UK National Physical Laboratory. Data were quantified using Scofield photoelectric cross sections corrected for the energy dependencies of the electron attenuation lengths and the instrument transmission. Data interpretation was carried out using CasaXPS software v2.3.16.

Scanning electron microscope (SEM) micrographs were obtained with a Zeiss Supra 40vp model. Fourier-transform infra-red spectroscopy (FT-IR, Nicolet iS5, Thermo Scientific) was performed on the surface with the iD5 ATR-Diamond accessory. Eight Scans were performed over the range 4000-525 cm^{-1} with 1.928 cm^{-1} data spacing and recorded with a DTGS KBr detector utilizing a KBr beam-splitter. From this % transmittance was obtained the values compared to commonly available IR transmittance tables.

Results and Discussion

Characterisation of the chemically pre-treated electrodes

GSPEs were chemically pre-treated to form surface immobilised oxygenated species, as detailed in the experimental section, which introduces oxygenated species upon the electrode surface. These pre-treated GSPES were characterised with Scanning Electron Microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Fourier-transform infra-red spectroscopy (FT-IR). Apparent from the SEM images in Figure 1 is an increase in porosity for the pre-treated GSPE (Figure 1B) which is likely the result of the chemical pre-treatment with percarbonate solution ([10% w/v] Na_2CO_3/H_2O_2); (see experimental section). FT-IR and XPS were performed to aid the hypothesised presence of generated oxygenated species immobilised on the electrode surface as a result of the chemical pre-treatment process. The chemically pre-treated and un-treated GSPEs were measured with FT-IR, and expecting an increase in peaks in the $1665 – 1760$ cm^{-1} range for the chemically pre-treated GSPE, which would be indicative of carbonyl moiety. However, following experimentation there was found to be no distinct variation between both chemically pre-treated and un-treated GSPEs – this could be related to the "depth" to which the IR beam penetrates the electrode surface (the generated oxygenated species are only theorised to be on the surface).

The XPS results from the electrodes (Table 1) showed the regular GSPE working electrode surface to be composed of 87.3% carbon and 3.9% oxygen with the carbon 1s spectrum of the un-treated GSPE typical of an oxidised graphite-like material. The chemically pre-treated electrode surface had an increased oxygen content of 16.7% and a reduced carbon content of 71.1% indicating oxidation of the electrode surface. The carbon 1s spectra from the pre-treated and the reference GSPE samples are shown in Figure S2. In both cases the spectra show a strong asymmetric and narrow component at approximately 284.8 eV binding energy which is typical of graphitic carbon. They both also show a strong shoulder at approximately 286.3 eV. This is due to carbon in either C-O or C-Cl bonds, which cannot generally be resolved by XPS. However, analysis of the relative intensity of this component and the proportion of Cl detected showed that similar levels of C-O bonds were present in both cases, accounting for approximately 50% of the intensity of this component. Both spectra showed intensity at approximately 289.3 eV, attributed to surface acid groups, COO⁻. A significant difference was seen at higher binding energy where the treated GSPE sample showed intensity at approximately 291.3 eV not seen on the untreated surface. This is in the spectral region

typically associated with graphitic plasmon loss features, but is rather intense and suggests the presence of carbon in a further highly chemically-shifted configuration such as a carbonate ester *i.e.* R-O-C(=O)-O-R. Note that an inorganic carbonate group such as may be expected from any Na2CO3 residue would be expected at approximately 289.4 – 289.5 eV and no significant difference in seen between the untreated and treated samples in this binding energy range. It is clear from the XPS data that the treated surface is more highly oxygenated (higher oxygen surface composition, and evidence of a highly oxygenated component in the C 1s spectrum) but it has not been possible to determine the *exact* composition of oxygenated species on the GSPE surface.

Electrochemical testing

Several different accurately measured 0.01 M buffers (HCl, phosphate buffer solution [PBS] and acetate buffer) ranging from pH 1.76 – 13.12 were electrochemically tested with square-wave voltammetry (SWV) on both the chemically pre-treated GSPEs ([10% w/v] Na_2CO_3/H_2O_2) and un-treated GSPEs. Scanning cathodically from positive to negative potentials a single reduction peak is realized. As can be observed from Figure 2A, increasing the pH results in more negative overpotentials as well as there being peaks with much lower intensity; this could be since at high pHs there are less protons available, limiting the amount of species that can be reduced. Note: peaks with lower intensities in acidic conditions (>pH 5) could be attributed to deprotonation of carboxylic acid groups on the surface[21] or pH dependent charge trapping of the quinones electrostatically bound in an electron-confined polymer (polyvinyl chloride [PVC], a polymer, is used as a binder in the GSPE ink)[22]. The use of background correction and smoothing were employed by the GSPE software to give clarity to the responses, as is common in the literature.[4] As can be seen from Figure S3 there is an electrochemical response with *untreated* GSPEs, likely due to a small amount of oxygenated species naturally occurring on the GSPE surface; however, note that this is much lower in intensity (approximately 1000 times lower). The use of an *untreated* electrode provides inconsistent voltammetric responses when utilised to monitor changes in pH and instead the proposed chemical pretreatment produces optimal responses. The approach herein attempts to negate the use of any mechanical effort as reported in the literature[3, 4] to solely rely on the chemical pre-treatment. Note that the chemical pre-treatment for a longer duration (45 h) was

explored; however, slight variations in peak current notwithstanding the overwhelming similarities in the response showed 18 h is adequate for pre-treatment (Figure S1).

Next, a plot of peak potential (*E*) *vs*. pH was constructed (Figure 2B) where a gradient of 57 mV was observed (*E/V* = - 57mV + 0.4 *E/pH*, R^2 = 0.99). This value is indicative of a 1:1 proton/electron process as described from the Nernst equation (equation 1). It is important to note that there is no deviation across the pH range explored. It is hypothesised by Lu *et al*. that, when bound to the surface, there are significant changes in pK_a between bulk aqueous solution and surface immobilized species; naturally leading to the conclusion that the pK_a value of a selected mediator (in this instance quinones; normal pKa value *ca.* 9.2) must have altered, exceeding pH 13.0, consequently not changing the linearity of any calibration plots.

As is evident from the literature, new electrodes that are proposed for the sensing of pH mostly neglect to apply them to the sensing of pH in real samples. [3, 4] Consequently, the proposed analytical pH sensing protocol herein is validated against the laboratory standard glass probe pH sensor in the real samples: malt vinegar and a commonly available antacid (Rennies). The electroanalytical SWV signals gained are visible in Figure 3 and comparable values of pH were obtained in both cases; with malt vinegar a pH value of 2.98 was obtained by the glass probe compared to 2.86 from the pre-treated GSPE (±0.12; RSD 3.72%) and the antacid 10.43 versus 10.08 (±0.35; RSD 4.81%). This demonstrates there is potential for this approach to be developed into a portable, hand-held, voltammetric pH sensor using GSPEs.

Returning to the origin of the observed correlation between the voltammetric potential and pH over the *entire* pH range of 1-13 where no deviation is encountered at alkaline pH values has previously been reported[19-21] to be caused by a change in pKa value of surface immobilised groups in comparison to that of a solution phase species. A new alternative approach is proposed herein is that the pK_a value of a surface bound mediator (oxygenated species) does not interfere with the linear Nernstian response because of its activity (α).

For simplicity, envisage the example of the electrochemical reduction of 1,2-benzoquinone(1,2-BQ) into 1,2-hydroquinone(1,2-HQ); (Scheme S1) which has been utilised previously in the literature;[3, 4, 22] (such as Prissanaroon-Ouajai *et al*.[22] who used a novel pH sensor based on hydroquinone monosulfonate-doped conducting polypyrrole). First, consider the Nernst equation which quantitatively predicts the cell potential relating it to the redox behaviour of two species, utilised in the above analysis of the electrochemical reduction of 1,2-BQ as described in the following equation (2):

$$1,2\ BQ + 2e^- + 2H^+ \rightleftharpoons 1,2\ HQ \tag{2}$$
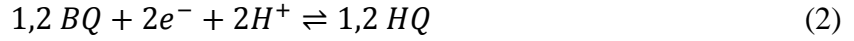
which when applied to the Nernst equation leads to:

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{nF} \log \frac{[Red]}{[Ox]} \tag{3}$$

If one takes into account the activity where *a* is the symbol for alpha used in all the equations such as in equation 4 of the 1,2-benzoquinone(1,2-BQ)/1,2-hydroquinone(1,2-HQ) redox behaviour, equation (3) leads to:

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{2F} \log \frac{\alpha\ 1,2\text{-}HQ}{\alpha\ 1,2\text{-}BQ \cdot \alpha H^{+2}} \tag{4}$$

However, if it is considered that the surface immobilised groups are a solid since they are immobilised upon the electrode surface, and therefore have an activity of 1, this results in:

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{2F} \log \frac{1}{a_{H^{+2}}} \tag{5}$$

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{2F} \log a_{H^{+-2}} \tag{6}$$

Application of the logarithmic power rule results in the following series of equations:

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{2F} (-2) \log a_{H^+} \tag{7}$$

$$E_p = E^0_{f\ Ox/Red} + 2.303\ \frac{RT}{F} \log a_{H^+} \tag{8}$$
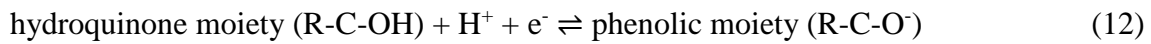
$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{F} -\log a_{H^+} \tag{9}$$

$$E_p = E^0_{f\ Ox/Red} - 2.303\ \frac{RT}{F} pH \tag{10}$$

which show the electrochemical response is *dependent solely* on the pH (and obviously other thermodynamic effects *e.g.* temperature) and negates the pK_a values of the quinone species. This offers an alternative explanation as to why there is no change in linearity when surface immobilised oxygenated species (for example quinone groups) are utilised for pH sensing. This also explains data obtained by other groups using oxygenated species immobilised on an

electrode surface and solid quinone compounds for pH sensing which observe similar results of a linear Nernstian response that is dependant only on pH and not a change in linearity at a surface bound mediators pKa.[3, 4, 27, 28] Although this worked example (equations 1 to 9) offers an explanation to the previously mentioned reports, the protocol presented within following elucidation of XPS spectra reveals the process of 1,2-benzoquinone(1,2-BQ) into 1,2-hydroquinone(1,2-HQ) cannot be the sole contributor to the electrochemical response when sensing pH in this instance (and perhaps others). An inadequate amount of carbonyl moieties (such as those present on 1,2-BQ) suggest instead that the electrochemical response, which is the origin of the pH sensor could possibly be dominated, for example, by either

quinone moiety (R-C=O) + 2H$^+$ +2e$^-$ $\rightleftharpoons$ bisphenol moiety (R-C-OH)   (11)

or

hydroquinone moiety (R-C-OH) + H$^+$ + e$^-$ $\rightleftharpoons$ phenolic moiety (R-C-O$^-$)   (12)

or resonance structures in the graphite lattice; though, as noted above, the exact kinetics of the surface remain unknown and the actual "step by step" mechanism that occurs is likely to be rather complex. What is clear, however, is that it is an equal electron-proton process. Therefore, a generic example of the mathematic resolution is reported below:

$$Ox + ne^- + mH^+ \rightleftharpoons Red \tag{13}$$

$$E_p = E_f^0 - \frac{RT}{nF}\ln\frac{a\,[Red]}{a[Ox]aH^{+m}} \tag{14}$$

$$E_p = E_f^0 - \frac{RT}{nF}2.303\log\frac{a\,[Red]}{a[Ox]} + 2.303\frac{RT}{nF}\log aH^{+m} \tag{15}$$

$$E_p = E_f^0 - \frac{RT}{nF}2.303\log\frac{a\,[Red]}{a[Ox]} + 2.303\frac{RTm}{nF}\log aH^+ \tag{16}$$

$$E_p = E_f^0 - \frac{RT}{nF}2.303\log\frac{a\,[Red]}{a[Ox]} - 2.303\frac{m}{n}\frac{RT}{F}\log aH^+ \tag{17}$$

$$E_p = E_f^0 - \frac{RT}{nF}2.303\log\frac{a\,[Red]}{a[Ox]} - 2.303\frac{m}{n}\frac{RT}{F}pH \tag{18}$$

This offers an explanation as to why the electrochemical response is dependant only on the pH and not the p*Ka* of a surface immobilised mediator and as such, also explaining the linear

response over the *entire* pH range observed in this work (Figure 2B) and critically in all prior literature in which this unique response is routinely observed.. [3, 4, 19, 20, 26]

Conclusions

For the first time, the accurate measurement of pH using chemically pre-treated low cost, disposable GSPEs has been shown as a practicable analytical protocol. This inspires the potential for a handheld, portable and reproducible pH sensor that has also been validated against a traditional pH sensing protocol and demonstrated accurate quantification capabilities when applied to 'real' pH samples without the need for further specialist equipment (such as a pH meter) nor extensive mechanical pre-treatment. The monitoring of surface immobilised oxygenated species redox potentials across the range of pH 1.76-13.12 display a linear response ($R^2 = 0.99$) with a gradient of 57 mV ($N = 3$). Also presented is an alternative explanation as to why surface immobilised mediators do not influence the Nernstian response, suggesting molecules immobilised on the surface have an activity equal to 1, excluding them from the Nernst equation meaning the measured potential depends solely on the pH. A mathematical model for all cases involving surface immobilised mediators is proposed in equations 13 – 18. This is contrary to previous reports of a mediator immobilised on the surface's pKa; such work is of huge importance in the electroanalytical field which forms the basis of voltammetric pH sensors.

Acknowledgements

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Scheme 1. Mechanism of electrochemical reduction of 1,2-benzoquinone into 1,2-hydroquinone leads to pH dependent responses, one of the many proposed mechanisms occurring on the chemically pre-treated surface.
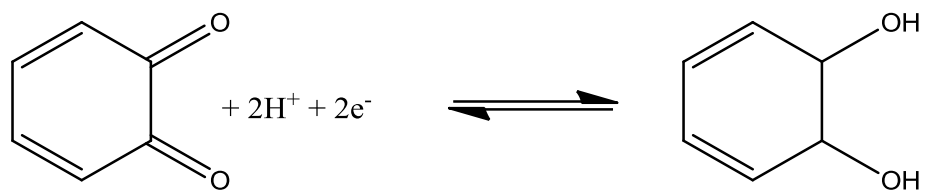

$+\ 2H^+ + 2e^-$

Table 1. De-convolution of the XPS spectra obtained for the GSPE before and after chemical pre-treatment (denoted Na_2CO_3/GSPE). Note the presence of chloride is due to the polyvinyl chloride (PVC) binder in the GSPE ink, and the low level additional species found on the pre-treated surface make no significant contribution to the interpretation of the carbon surface chemical state as discussed in the text.

Element	GSPE				GSPE with pre-treatmet			
	Element atom %	Moeity			Element atom %	Moeity		
		assignment	BE (eV)	atom %		assignment	BE (eV)	atom %
C 1s	87.2	C-C	284.7	68.86	71.1	C-C	284.7	59.08
		C-O/C-Cl	286.55	15.63		C-O/C-Cl	286.58	9.92
		COO-	288.8	2.77		COO-/CO32-	289.27	2.1
						plasmon/high oxygenation	290.09	3.53
Cl 2p	8.8	C-Cl	200.3		5.6	C-Cl	200.4	
O 1s	3.9	unresolved, consistent with C-O			16.7	broad, consistent with C 1s assignments and low level inorganics		
Na 1s	-				2.8	Na+, non-specific	1072.4	
Si 2p	-				1.7			
S 2p	-				0.4			
Mg 2p	-				1.5			
N 1s	-				0.2			

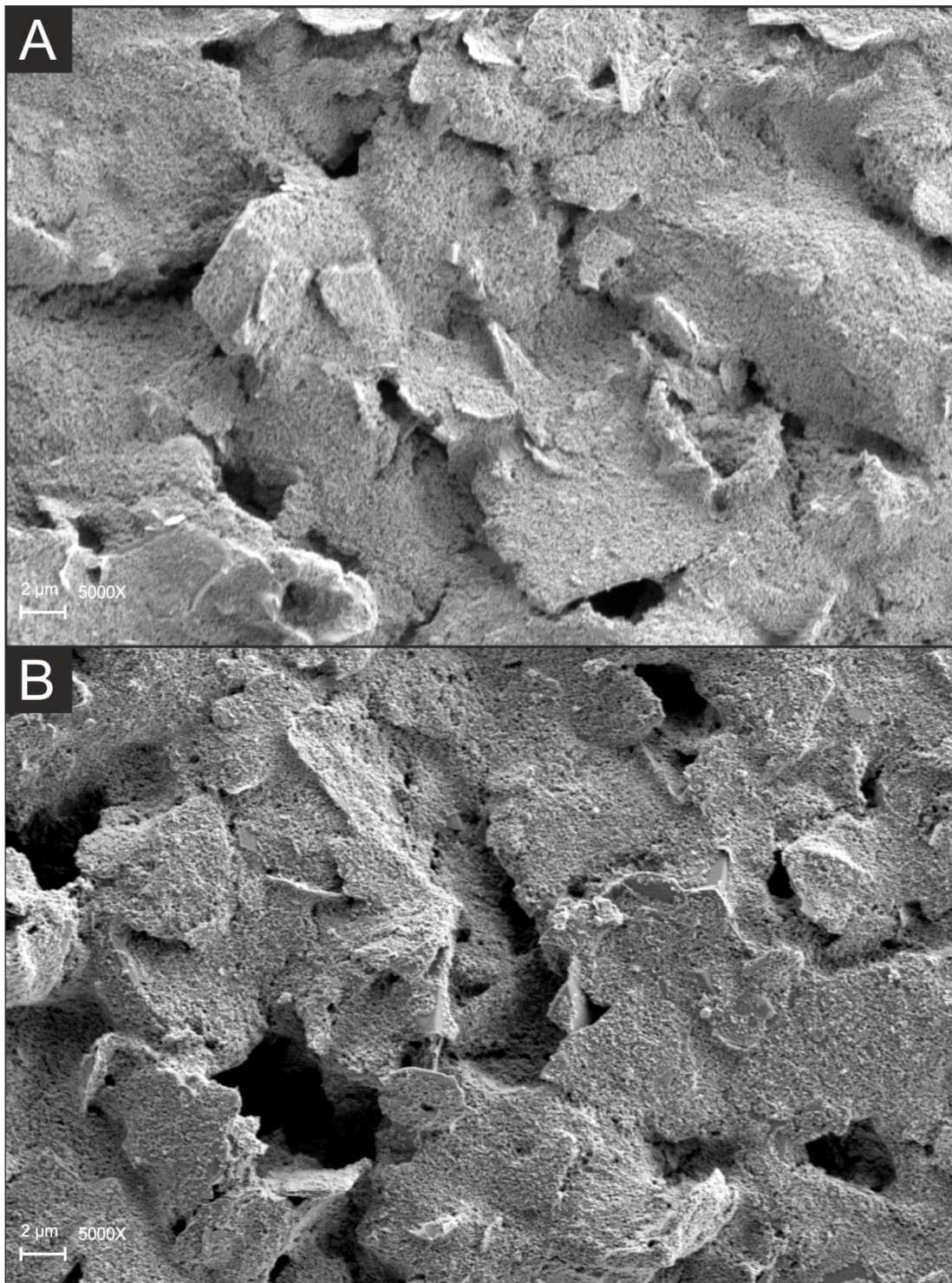**Figure 1.** SEM images of untreated (A) and chemically pre-treated (B) GSPEs

Figure 2A. Electrochemical signal (SWV) obtained over the pH range 1.76 – 13.12 using the chemically pre-treated GSPEs. Note the electrochemical signal is obtained from scanning potential from positive to negative to induce the electrochemical reduction of the surface immobilised oxygenated species (see Scheme 1). SWV parameters: Frequency 20 Hz, step potential 2 mV, amplitude 200 mV. (vs. SCE).
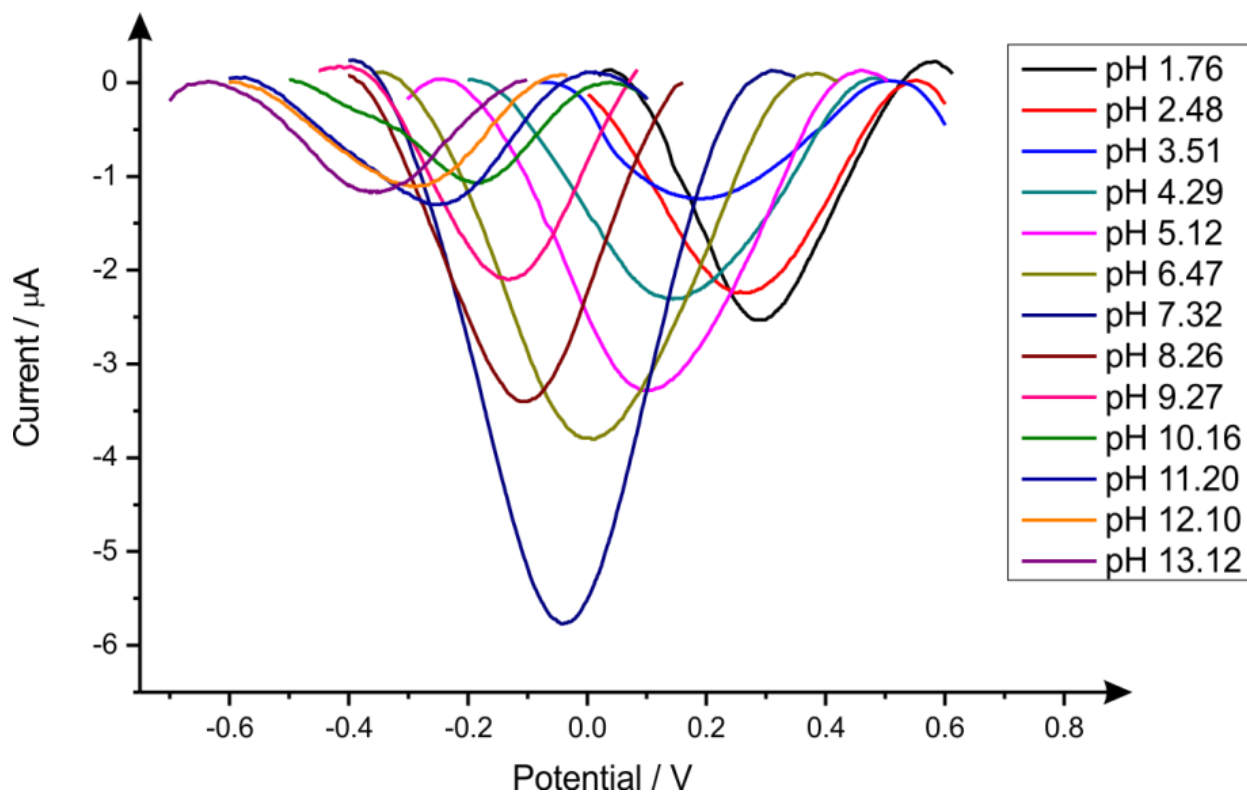
Figure 2B. Calibration plot resulting from the analysis of SWV peak potential (date shown in figure 2) against pH for using the chemically pre-treated GSPEs over the pH range of 1.76 to 13.12. A linear response is observed with a gradient of 57 mV $R^2 = 0.99$; $N = 3$. (vs SCE).
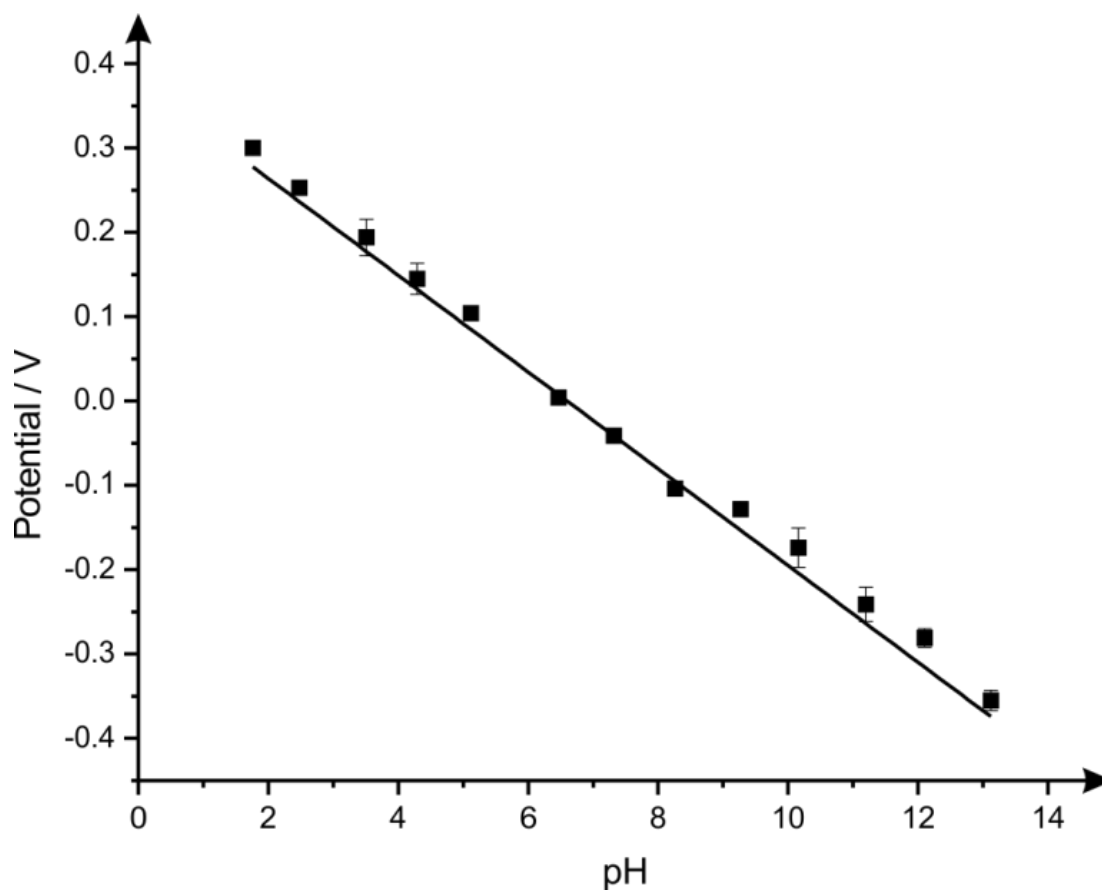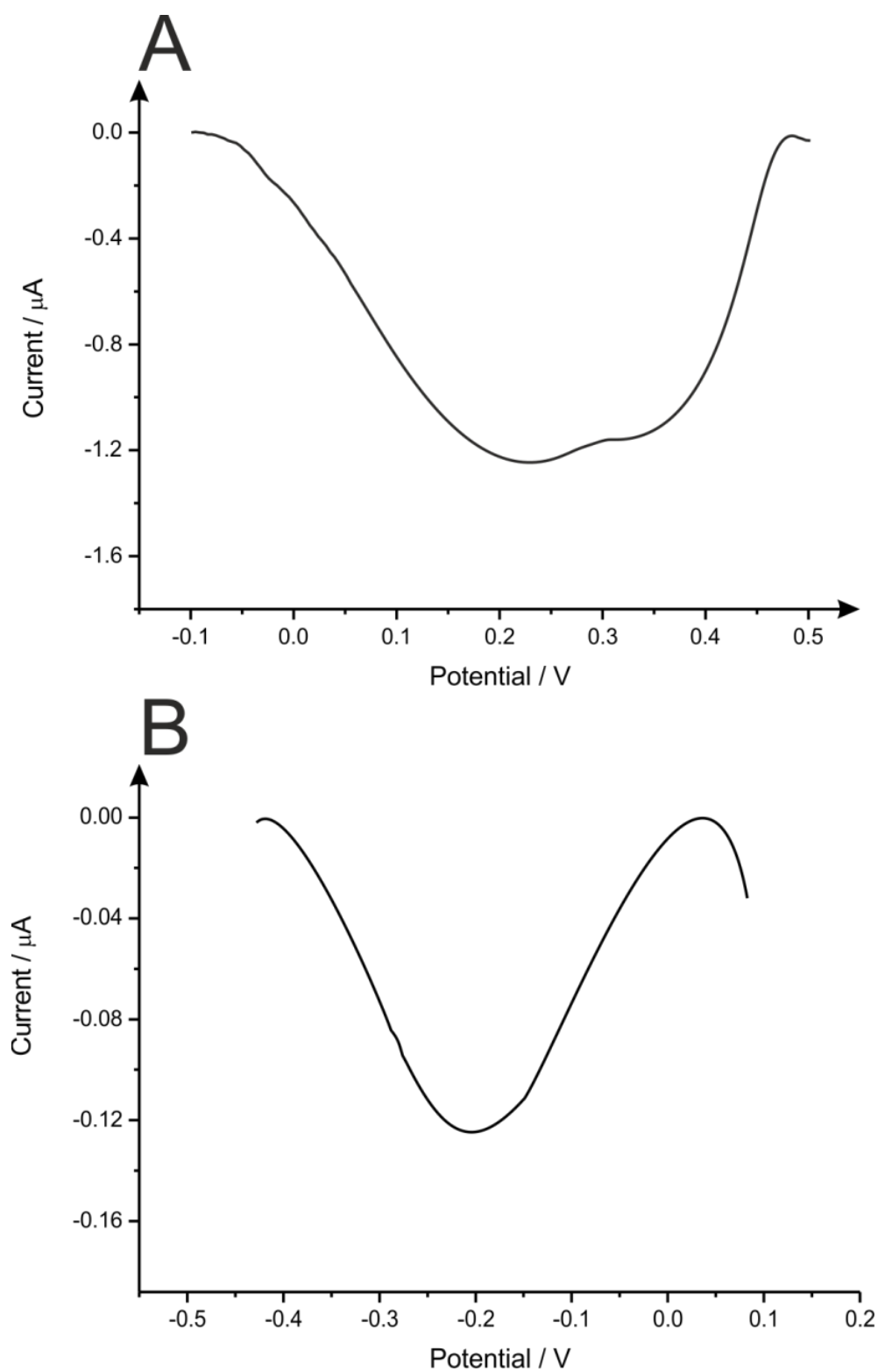
Figure 3. Electrochemical signals (SWV) obtained in real samples for A: Malt Vinegar and B: Rennies® antacid using the chemically pre-treated GSPEs. SWV parameters: Frequency 20 Hz, step potential 2 mV, amplitude 200 mV. (vs. SCE). Peak of maximum inflection is used throughout.

ESI Figure 1 - Electrochemical signal (SWV) obtained over the pH range 1.81 − 13.16 using chemically pre-treated GSPEs (45 hours). SWV parameters: Frequency 20 Hz, step potential 2 mV, amplitude 200 mV. (vs. SCE). Inset: Calibration plot resulting from the analysis of SWV peak potential against pH for a chemically pre-treated GSPE (45 hour treatment − see experimental solution) in 0.01 M buffer solutions (HCl, and PBS) ranging from pH 1.81 − 13.16. A linear response is observed with a gradient of 57 mV $R^2 = 0.99$, N=3. (vs. SCE).
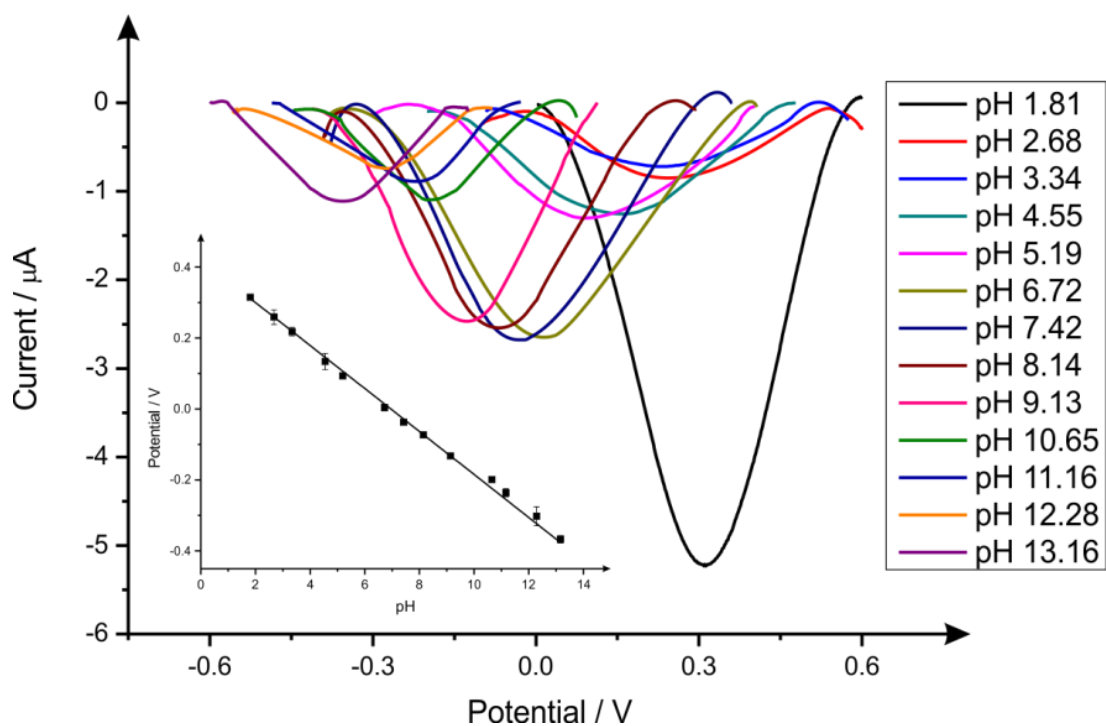
ESI 2 – Electrochemical reduction of oxygenated species at the chemically pre-treated GSPEs (solid line) and un-treated GSPEs (dashed line, inset) using SWV using ~ pH 7.4 PBS. Visible from the inset is a zoom of the un-treated GSPEs where a small voltammetric peak is evident (Note nA scale). Square-wave parameters: Frequency 20 Hz, step potential 2 mV, amplitude 200 mV. (vs. SCE).