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Voltammetric pH sensing using Carbon Electrodes : Glassy Carbon behaves similarly to EPPG

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Abstract

Developing and building on recent work based on a simple sensor for pH determination using unmodified edge plane pyrolytic graphite (EPPG) electrodes¹, we present a *voltammetric* method for pH determination using a bare unmodified glassy carbon (GC) electrode. By exploiting the pH sensitive nature of quinones present on carbon edge-plane like sites within the GC, we show how GC electrodes can be used to measure pH. The electro-reduction of surface quinone groups on the glassy carbon electrode was characterised using cyclic voltammetry (CV) and optimised with square-wave voltammetry (SWV) at 298 K and 310 K. At both temperatures, a linear correlation was observed, corresponding to a 2 electron, 2 proton Nernstian response over the aqueous pH range 1.0 to 13.1. As such, unmodified glassy carbon electrodes are seen to be pH dependent, and the Nernstian response suggests its facile use for pH sensing. Given the widespread use of glassy carbon electrodes in electroanalysis, the approach offers a method for the near-simultaneous measurement and monitoring of pH during such analyses.

Introduction

Chemical and biochemical reactions are often extremely sensitive to proton concentrations and even the slightest fluctuation in pH levels can result in significant changes of rate, so that pH often has to be carefully monitored and controlled. As such, pH determination is necessarily carried out in a huge diversity of environments, such as industrial, medical and environmental²⁻⁴.

There are a wide range of different pH sensors available, which can be voltammetric⁵, amperometric⁶⁻⁹ or potentiometric in nature^{10, 11}. Whilst potentiometric glass electrodes¹² are the

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3 most common approach for pH detection due to their high sensitivity and selectivity, commercial
4 availability and fast response, the electrodes are fragile due to their glass nature and can often be
5 impractical for “in-field” analysis. In addition, they can suffer from “alkali errors”¹³, instability and
6 potential drift¹⁴ which needs to be frequently calibrated prior to use. As an effort to move away
7 from the conventional glass electrode, many different methods and materials have been explored,
8 including but not limited to metal oxides, conductive polymers, optical pH sensors based on
9 fluorescent indicator dyes^{15, 16} and NMR methods¹⁷.

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15 Many techniques and materials have been used for amperometric pH sensing. However a
16 widely used electrode material in electrochemistry is carbon due to its relatively large potential
17 window, commercial availability, versatility and low cost¹⁸⁻²⁰. A review by Kahlert²¹ summarises
18 many methods in which carbon materials have been modified for sensing pH. There are a great
19 number of functional groups at carbon surfaces, including oxo-groups, which lends itself to
20 interesting chemistry²²⁻²⁴. Figure 1 shows an example of the diverse nature of the surface functional
21 groups present^{22, 25}. Such groups can show reactivity with other molecules in solution; in this paper
22 we are concerned with the interaction with protons.
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29 The characterisation of carbon surfaces has been extensively studied using both physical and
30 chemical techniques²². Using methods such as XPS^{26, 27}, thermal decomposition methods²⁸,
31 vibrational spectroscopy²⁹ and electrochemistry^{30, 31}, many functional groups have been realised.
32 Edge plane sites present on graphitic carbons present many functional groups which can react with
33 the oxygen in the atmosphere to form various surface oxo-groups²². These have been suggested as
34 sites for electron transfer processes³². Of the range of functional groups present, such as carbonyl,
35 quinonyl, hydroxyl, quinone groups have shown to be pH dependent and have been developed for
36 the determination of pH. Many researchers have exploited this and patents using carbon electrodes
37 for pH determination have been filed³³⁻³⁶.
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44 The Nernst equation³⁷ can be used to quantify voltammetric redox processes involving the
45 surface oxo-groups, such as quinones where the response is electrochemically reversible. The Nernst
46 equation is:
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$$E_p = E_{\text{formal}}^{\circ} - \frac{2.3 RTm}{nF} \text{pH}$$

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53 where m represents the number of protons, n represents the number of electrons. One can note
54 that there is a direct relationship between the peak potential and pH, whereby for n = 2, slopes of
55 ca. 0, 30 and 60 mV per pH unit are seen for m = 0, 1 and 2. pK_a values for ortho-benzoquinone in
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3 aqueous solution at 298 K have been quoted in the literature as 9.25 and 13.0 for pK_{a1} and pK_{a2} ,
4 respectively.³⁸ Figure 2 shows a schematic where there are three possible reduction pathways of an
5 ortho-benzoquinone with their associated protonations, where $n = 2$ and $m = 0, 1, 2$.
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9 In this paper, we investigate the use of a glassy carbon (GC) electrode and its ability to
10 function as a pH sensor by highlighting the pH dependence of intrinsic quinone groups. We have
11 previously reported using an unmodified EPPG electrode as a simple method for pH determination¹
12 by exploiting the pH sensitive nature of intrinsic quinone groups on the surface edge plane sites. The
13 presence of quinone functional groups on graphitic carbon has been confirmed by XPS and chemical
14 labelling by Thorogood et al.^{23, 24}. Developing this, one can assume other forms of carbon with
15 intrinsic edge-plane sites might behave in an analogous manner. Using the edge plane sites as a basis
16 for quinone presence, we hereto investigate the pH nature of a glassy carbon electrode. The glassy
17 carbon electrode is a widely used carbon electrode material in electrochemistry due to its low
18 electrical resistance, high temperature resistance and hardness. It is composed of sp^2 carbons, and
19 upon polishing, edge plane surface functionalities may be revealed including pH dependent quinone
20 functional groups. The glassy
21 carbon electrode is a widely used carbon electrode material in electrochemistry due to its low
22 electrical resistance, high temperature resistance and hardness. It is composed of sp^2 carbons, and
23 upon polishing, edge plane surface functionalities may be revealed including pH dependent quinone
24 functional groups.
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29 Previously, Paixao et al.³⁹ have shown the use of electrochemically pre-treated glassy
30 carbon electrodes as pH sensors in *potentiometric* titrations, suggesting the presence of
31 electrochemically reversible redox couples on the surface of glassy carbon. The authors found that
32 the electrode could be used in pH potentiometric titrations with excellent agreement with
33 corresponding measurements at a glass electrode. The potential varied linearly with pH over the
34 range pH 1.0 to 13.1, with a slope of ca. 60 mV per pH, making it a suitable pH sensor for
35 potentiometric experiments. Whilst potentiometric measurements are useful, in this paper we
36 report a method using *voltammetric* pH sensing at a glassy carbon electrode.
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43 Cyclic voltammetry (CV) and square wave voltammetry (SWV) were used to study the
44 behaviour of a bare GC electrode in a range of buffer solutions. The experiments were carried out at
45 room temperature (298 K), and a higher temperature of 310 K. The response of the GC electrode at
46 higher ionic strength was also investigated. A linear correlation was seen in all cases between the pH
47 and peak potential, corresponding to a Nernstian response. One can therefore infer that glassy
48 carbon electrodes have analogous edge-plane sites to edge plane pyrolytic graphite electrodes and
49 can similarly function as a pH sensor through their intrinsic pH sensitive quinone functional groups.
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55 It is common to use glassy carbon electrodes in electroanalysis. The method
56 proposed in this paper suggests a basis for a near-simultaneous measurement of pH during such
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3 analyses. The use of the same electrode for pH measurement and as a working electrode is
4 extremely useful in electroanalytical measurements. A proof of concept of combined measurements
5 at a single pH has been reported by Henstridge et al⁴⁰ whereby theory and experimental evidence
6 shows that the single-electrode generator-collector approach is capable of detecting local pH
7 changes adjacent to the electrode surface during a redox reaction. This approach can be applied to a
8 wide range of electrochemical systems.
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18 Experimental

19 (a) Apparatus

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23 A μ -Autolab-II computer controlled potentiostat (Metrohm-Autolab BV) was used to record
24 all voltammetric measurements. Experiments were performed using a standard three-electrode
25 system consisting of a saturated calomel reference electrode (SCE) (Hach Lange, UK), a platinum (Pt)
26 mesh counter electrode and a glassy carbon working electrode. The glassy carbon electrode, 3.0 mm
27 in diameter, was purchased from CH instruments, Austin, TX, USA.
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32 All independent pH measurements were conducted using a pH213 Microprocessor pH meter
33 (Hanna instruments, UK). Prior to the measurement of solutions, the pH meter was calibrated using
34 Duracal buffers of pH 4.01 ± 0.01 , pH 7.00 ± 0.01 and pH 10.01 ± 0.01 (Hamilton, CH). Using a 2 point
35 calibration, a working range of pH -2.0 to 16.0 could be achieved as stated in the manufacturer's
36 specifications at 298 K. pH measurements at the elevated temperature were made in accordance
37 with the recommendations of the manufacturers⁴¹.
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42 A thermostatted Faraday cage, made in-house, was used to house all the experiments
43 performed. Two temperatures were investigated and constant working temperatures of 298 K and
44 310 K were set within the Faraday cage whilst the temperature of the solutions were maintained at
45 298 ± 0.2 K and 310 ± 0.2 K, respectively. By placing the solutions within the Faraday cage for at least
46 two hours, thermal equilibrium could be ensured. A thermometer was used for measurement of the
47 solution during the experiment.
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52 (b) Reagents and solution

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3 All chemicals were of analytical grade and were used as received without further
4 purification. Solutions were prepared with deionized water with resistivity no less than 18.2 MΩ.cm
5 at 298 K (Millipore, UHQ, Vivendi, UK).
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9 The buffer solutions were prepared using HCl/ KCl for the pH range 0.0 – 2.5, citric acid/
10 sodium citrate for the pH range 2.5 – 5.0, monosodium phosphate/ disodium phosphate for the pH
11 range 5.0 – 9.0, sodium carbonate/ bicarbonate for the pH range 9.0 – 11.0, and sodium hydroxide
12 for the pH range 12.0 – 13.0. Supporting electrolyte of 100 mM KCl was added to all solutions, and
13 pH measurement was performed out on all solutions prior to experiments at their relevant
14 temperature.
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19 A degassed system was used throughout where solutions were purged with pure N₂ gas
20 (BOC, Guildford UK) prior to experiments for a minimum of 20 minutes in a seal tight environment to
21 ensure there is no reduction of oxygen seen within the results.
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27 (c) Experimental procedure

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30 Fresh buffer solutions were prepared daily, and their pH determined using a pH meter prior
31 to experiments. A small volume of each solution was transferred into an electrochemical cell where
32 thorough bubbling of pure N₂ into the vessel was performed to remove dissolved oxygen in solution
33 and a degassed system was established. A platinum mesh functioned as the counter electrode and
34 was flamed before the experiment to ensure a clean set-up. The system was thermostatted to
35 maintain temperature at 295 ± 0.2 K and 310 K ± 0.2 K, respectively.
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41 The glassy carbon electrodes were polished to a mirror finish by using an alumina slurry
42 (Buehler Ltd) on soft lapping pads of decreasing grades, from 1.0 μm to 0.3 μm and finally 0.05 μm,
43 followed by thorough sonication and rinsing using Millipore water. Since glassy carbon electrodes
44 are made up of interwoven ribbons of sp² carbons, mechanical polishing using alumina slurry can be
45 used to expose edge plane surface functionalities. After preparation of the GC electrode, cyclic
46 voltammograms were performed followed by square wave voltammetry using optimised
47 parameters. More sensitive results could be achieved using SWV, and by observing the reductive
48 cathodic scans, their peak potentials could be precisely determined and plotted against pH. The
49 optimised parameters for SWV were: frequency – 150 Hz, step potential – 2 mV, amplitude – 200
50 mV, over the entire pH range explored. The glassy carbon electrode was used to scan in the cathodic
51 direction, and the potential window was adjusted for different pHs to best observe the reduction
52 peak. Reported analysis of the reduction peaks were all carried in SWV.
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Results and discussion

Glassy carbon electrodes were polished to a mirror finish prior to each experiment. This is thought to provide surface quinone functional groups which were used to explore the electrode response to varying pH⁴². Surface renewal is essential to obtaining reproducible data. First, cyclic voltammograms (CVs) were performed on GC electrodes to characterise the surface quinones before SWV scans were taken. The optimised parameters for scanning in SWV are outlined in the experimental procedure above, and by scanning cathodically, this produced a single reduction SWV peak.

A range of 0.01 M pH buffer solutions at 298 K were used, and after scanning from a positive to a negative potential in SWV, a single reduction peak corresponding to the reduction of the surface quinone was produced for each buffer solution. With increasing pH of the buffer, the reduction peak was seen to shift in the cathodic direction to lower potential values. The potential window was adjusted accordingly to accommodate the shift in potential and observe the response of the reduction peak. In Figure 3, it can be clearly seen that the peak potential shifts with pH.

0.01 M buffer solutions were prepared as discussed in the experimental section. To reach a higher pH, a 0.1 M sodium hydroxide buffer was used to make up the pH 13.0 solution. 100 mM KCl of supporting electrolyte was added to all solutions. It can be seen that the reduction peak potential shifts from 0.263 V at pH 2.04 to -0.397 V at pH 13.0. The gradual decrease in peak current may be explained by the fact there are fewer free protons available (lower concentration) for the $2\text{H}^+/2\text{e}^-$ reduction process at high pH, and thus this may limit the extent of quinone reduction producing peaks of smaller current. The electrochemical properties of quinones have been studied extensively using experiments and modelling⁴³. A “scheme of squares” model for the 2 electron reduction of quinones provides mechanistic pathways for the reduced species by assuming the electron transfer is the rate limiting step in well buffered media, and suggesting the presence of semiquinone intermediates.

Analysis of the results was carried out after background correction and smoothing of the signals, which enhanced the peaks for clearer analysis. Both methods were performed using GPES software; the background correction involved subtracting a 2nd order polynomial baseline curve from the raw data, whilst background noise was smoothed using the Savitzky and Golay smoothing filter^{44, 45}. In Figure 4, a plot of reduction peak potential against pH at 298 K shows a linear response with

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3 a gradient of 59.0 mV per pH, which agrees well with the Nernstian equation with T at 298 K. The
4 linear slope reflects the sensitive nature of the quinone groups at the edge plane sites of the glassy
5 carbon electrode.
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9 A consistent gradient, corresponding to a $2\text{H}^+ / 2\text{e}^-$ process, was seen across the entire pH
10 range of pH 1.0 to pH 13.0. Literature values for the pK_a of free ortho-benzoquinone molecules in
11 aqueous solution were 9.25 and 13.0 for pK_{a1} and pK_{a2} , respectively. Lee et al.⁴⁶ reviewed the
12 change in pK_a for immobilised quinone groups compared to that in bulk solution. A significant
13 change in pK_a was seen, implying that significant differences in thermodynamic and chemical
14 behaviour exist between molecules in bulk solution and that immobilised at an interface. Given that
15 we do not see significant changes in pH at the two quoted pK_a values, we can infer that significant
16 differences in acidity exist between surface bound and bulk orthoquinone moieties, whereby the
17 deprotonation of surface hydro-orthoquinone groups is not seen below ca. pH 13.
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21 After observing a linear response between the peak potential and pH for the 0.01 M buffer
22 solutions, and seeing that the results agree well with the Nernst equation at 298 K, further
23 investigation into the effects of increasing the ionic concentration was explored. The concentration
24 of the solutions was increased ten-fold to 0.1 M, and a glassy carbon was used to see how the
25 reduction peak potential would change with pH. 0.1 M citrate, phosphate and carbonate buffer
26 solutions had pH values of 3.76, 6.11 and 9.31, respectively, at 298 K. Figure 5 shows the quinone
27 peak reduction in SWV at the above pHs. As with the 0.01 M solutions, the peaks can be seen to shift
28 towards more negative potentials at higher pH. By plotting peak potential against pH and
29 superimposing these results onto the previous calibration plot, we can see from Figure 6 that the
30 points lie well on the line of best fit.
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40 41 42 43 Investigating the GC electrode response to pH at higher temperatures 44

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46 The experiment was repeated at an increased temperature of 310 K and the glassy carbon
47 electrode was investigated in different 0.01 M pH buffer solutions. The working temperature within
48 the Faraday cage was maintained at 310 K, whilst the solutions and experimental apparatus were
49 allowed to reach thermal equilibrium.
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53 A set of square wave peaks were produced for a range of 0.01 M buffer solutions and it
54 could be seen that with increasing pH, there was a corresponding reduction peak potential shift
55 towards more cathodic values, as expected. Taking the reduction peak potential values at 310 K and
56 plotting the pH against potential, a linear response could be seen in the calibration plot across the
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entire pH range. The theoretical value for the gradient ($2.303 RT/F$) was calculated to be 61.4 mV / pH, and the calibration produced from the results at 310 K agreed very well this, giving a gradient of 61.0 mV /pH.

Figure 7 shows a set of SWV reduction peaks in a range of 0.01 M buffer solutions, (with 0.1 M HCl/KCl and NaOH buffer solutions included for completeness across the entire pH range). The peak potential value shifts from 0.253 V at pH 1.09 to -0.449 at pH 13.07. Again, the peak heights can be seen to decrease with increasing pH. This is attributed to the concentration of free protons available for quinone reduction – with the number of H^+ ions being far less at high pH compared to low pH solutions. The effect of temperature on the size of currents is apparent by comparing Figure 7 with Figure 3. The peak heights are larger at higher temperature which may relate to faster diffusion of H^+ ions. The plot of the peak reduction against pH at 310 K gave a very linear correlation with a gradient of 61.0 mV / pH, as seen in Figure 8. From this, we can see that the plot highlights the temperature dependence of the Nernstian equation, and this can be exploited by observing the quinone reduction on carbon electrodes such as a GC electrode.

Using 0.1 M buffer solutions, investigation into the effects of higher ionic strength can be seen with respect to the reduction peak potentials seen. Buffer solutions of pH 3.98, pH 6.11 and pH 9.21 were made using citric acid/ sodium citrate, monosodium phosphate/ disodium phosphate and sodium carbonate/ bicarbonate, respectively. In Figure 9, it can be seen that all three solutions at higher concentration produced a single reduction peak which also shifted towards cathodic potentials with increasing pH. By plotting the reduction potentials and overlaying them with the 0.01 M buffer solution results at 310 K, we can see from Figure 10 that the results agree very well with the original calibration line.

It can therefore be concluded that a glassy carbon electrode works well as a pH sensor in aqueous solution across the entire pH range, at various ionic strength and at temperatures beyond room temperature of 298 K. By recording the reduction peaks in SWV, quantitative analysis of the signals can be used to plot a very linear peak potential versus pH calibration graph.

Conclusions

Glassy carbon electrodes have shown an analogous behaviour to unmodified edge plane pyrolytic graphite (EPPG) electrodes when their SWV peak potential for the reduction of surface quinones is plotted against pH. This behaviour can be explained due to the common intrinsic nature of edge-plane sites that contain quinone functional groups. By using SWV, and analysing the

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3 reduction peak in different pH buffer solutions, at different temperatures and ionic strengths, a
4 Nernstian response can be seen from the linear calibration plot. This suggests the presence of
5 surface quinone groups at glassy carbon electrodes which show electrochemically reversible
6 behaviour, and as such, by using SWV, lends itself to its use as a simple voltammetric pH sensor. In
7 particular, since GC electrodes are widely used for voltammetric electroanalysis, the possibility of
8 monitoring pH simultaneously with other electroanalytical measurements is viable.
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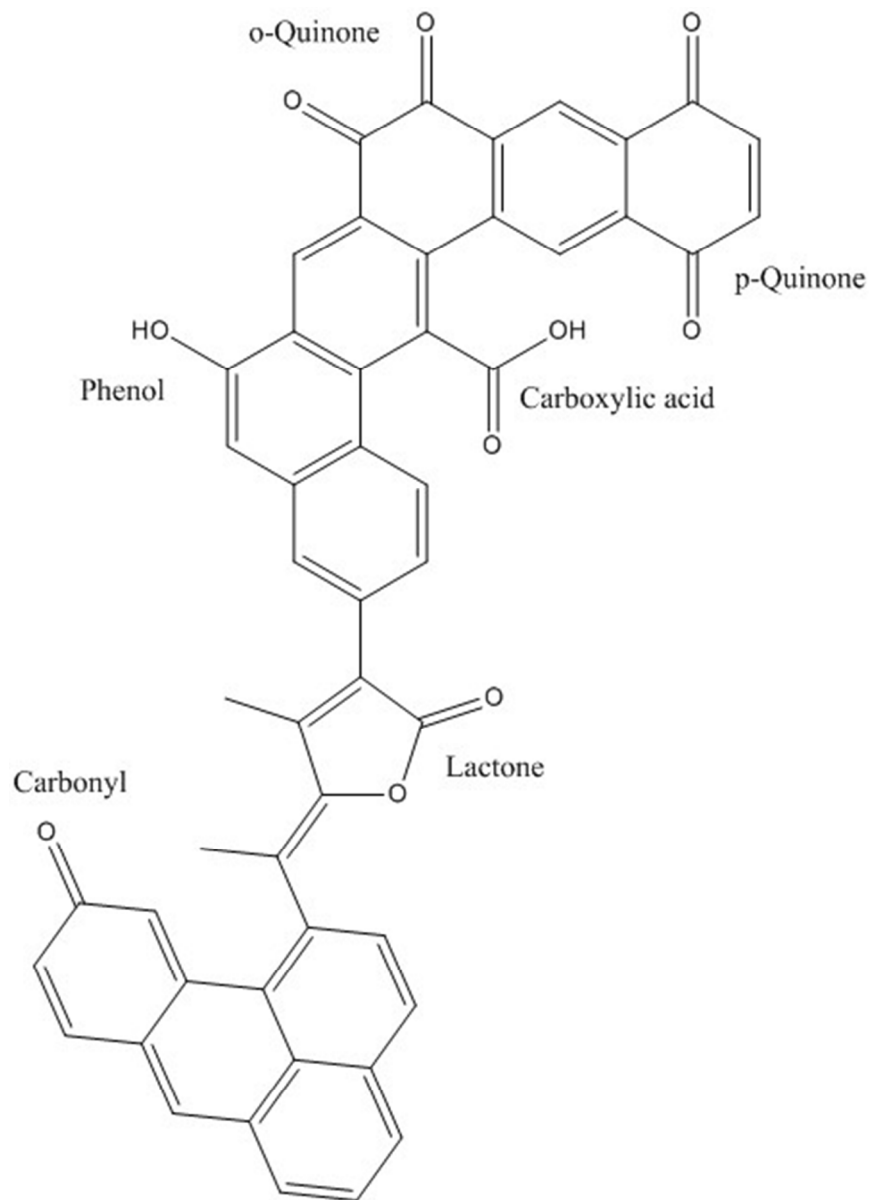


Fig 1. Representation of various functional groups present on graphitic carbon surfaces, adapted from reference [25]
119x165mm (96 x 96 DPI)

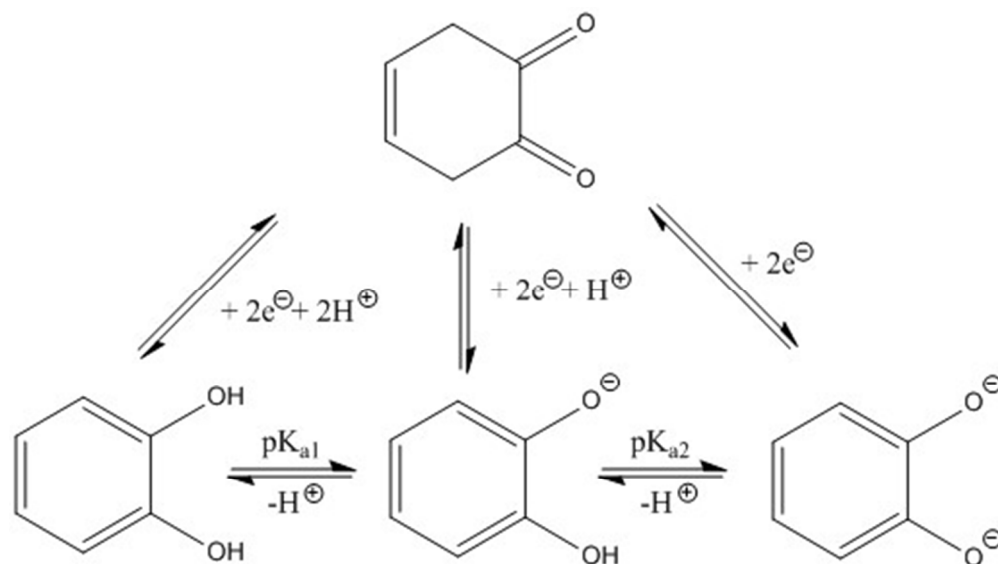


Fig 2. Schematic showing 3 pathways in which an orthoquinone molecule can be reduced in a $2e^-$ fashion with $m = 2, 1$ or 0
136x77mm (96 x 96 DPI)

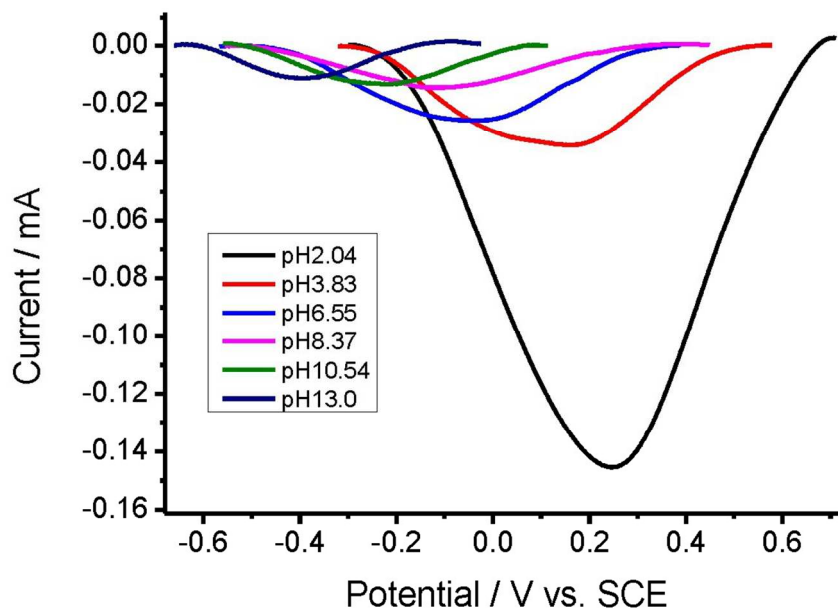


Fig 3. Quinone reduction peaks in square wave (SWV) on glassy carbon electrode at 298 K. Reduction peaks were obtained in different media (HCl/KCl buffer, citrate buffer, phosphate buffer, carbonate buffer at 0.01 M and NaOH buffer at 0.1 M), ranging in pH from 2.04 to 13.0. SWV performed under optimised conditions: frequency - 150 Hz, step potential - 2 mV, amplitude - 200 mV
115x80mm (300 x 300 DPI)

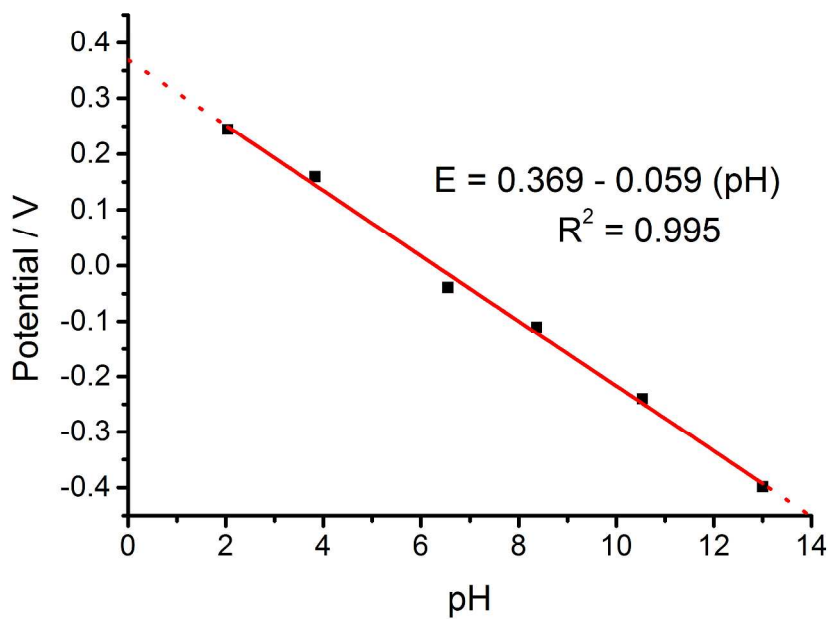


Fig 4. Calibration plot of SWV peak potential against pH for a glassy carbon electrode in 0.01 M buffer solutions (with 0.1 M NaOH buffer solution at pH 13.0), showing a linear response with gradient of 59.0 mV / pH corresponding to a Nernstian behaviour at $T = 298$ K. At least 3 experimental points were averaged for each data set.

288x201mm (300 x 300 DPI)

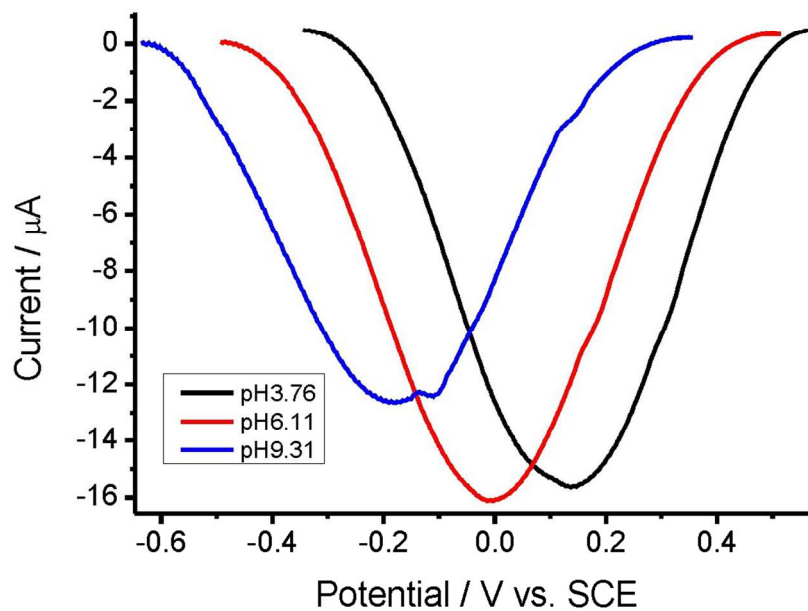


Fig 5. Reduction peaks at GC electrode in 0.1 M buffer solutions at 298 K (pH 3.76 citrate buffer solution, pH 6.11 phosphate buffer solution, pH 9.31 carbonate buffer solution)
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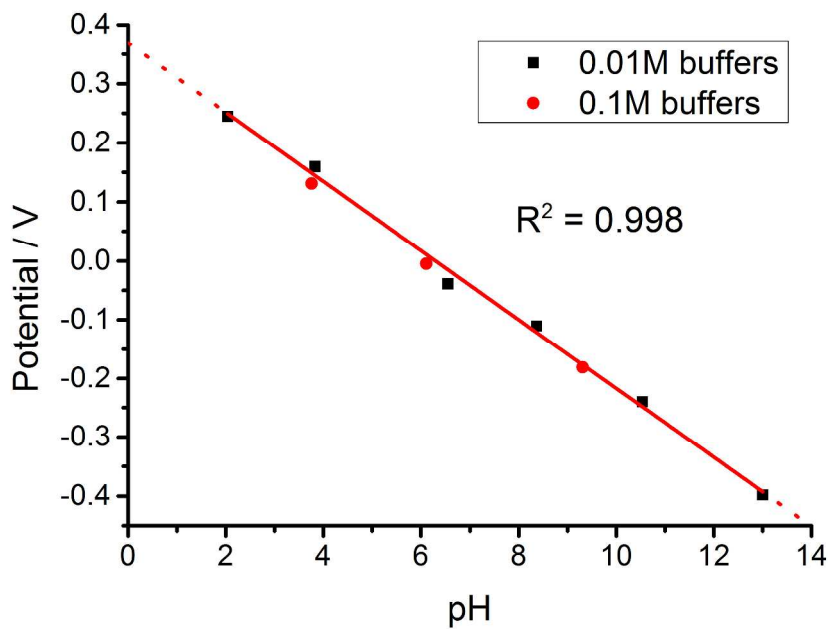


Fig 6. Calibration plot of the original reduction points in 0.01 M buffer solutions (black squares), with reduction points of 0.1 M buffer solutions (red circles), at 298 K, added for comparison
288x201mm (300 x 300 DPI)

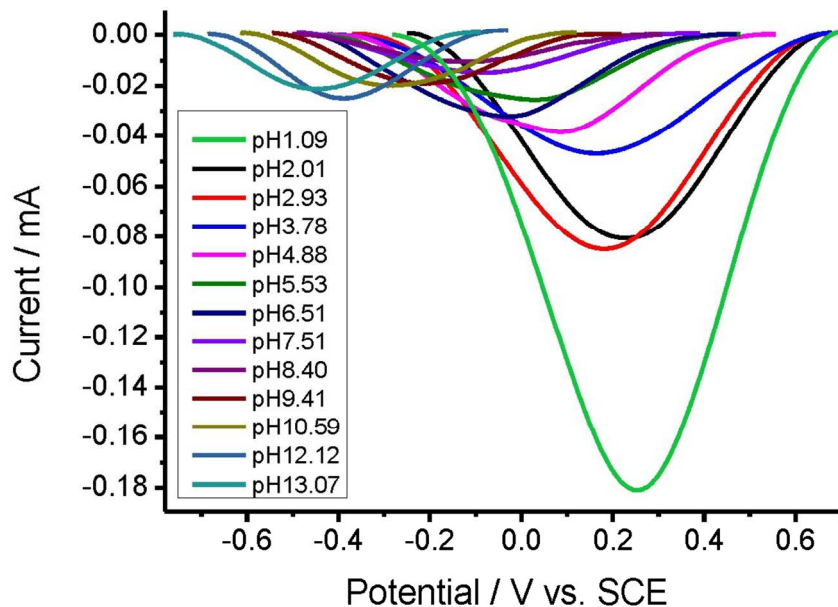


Fig 7. Quinone reduction peaks in square wave (SWV) on glassy carbon electrode at 310 K. Reduction peaks were obtained in different media (HCl/KCl buffer, citrate buffer, phosphate buffer, carbonate buffer at 0.01 M, 0.1 M HCl/KCl and NaOH buffers were included for completeness), ranging in pH from 1.09 to 13.07. SWV performed under optimised conditions: frequency – 150 Hz, step potential – 2 mV, amplitude – 200 mV 115x80mm (300 x 300 DPI)

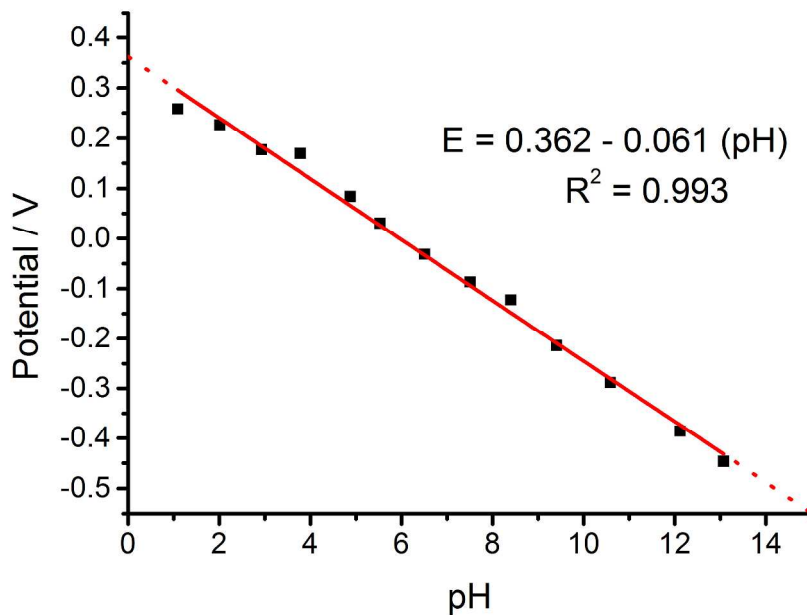


Fig 8. Calibration plot of SWV peak potential against pH for a glassy carbon electrode in 0.01 M buffer solutions (with 0.1 M HCl/ KCl and NaOH buffer solutions at pH 1.09 and pH 13.0, respectively), showing a linear response with gradient of 61.0 mV / pH corresponding to a Nernstian behaviour at T = 310 K. At least 3 experimental points were averaged for each data set.

288x201mm (300 x 300 DPI)

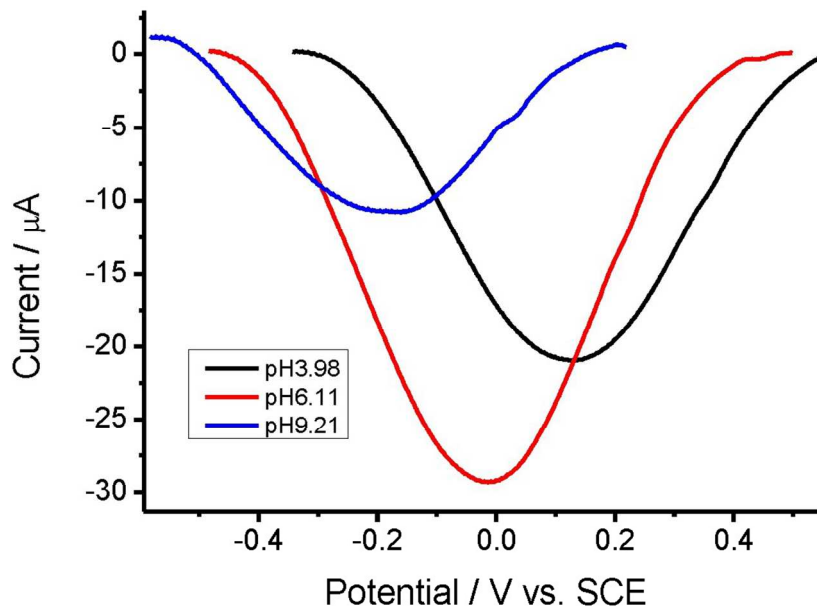


Fig 9. Reduction peaks at GC electrode in 0.1 M buffer solutions at 310 K (pH 3.98 citrate buffer solution, pH 6.11 phosphate buffer solution, pH 9.21 carbonate buffer solution)
115x80mm (300 x 300 DPI)

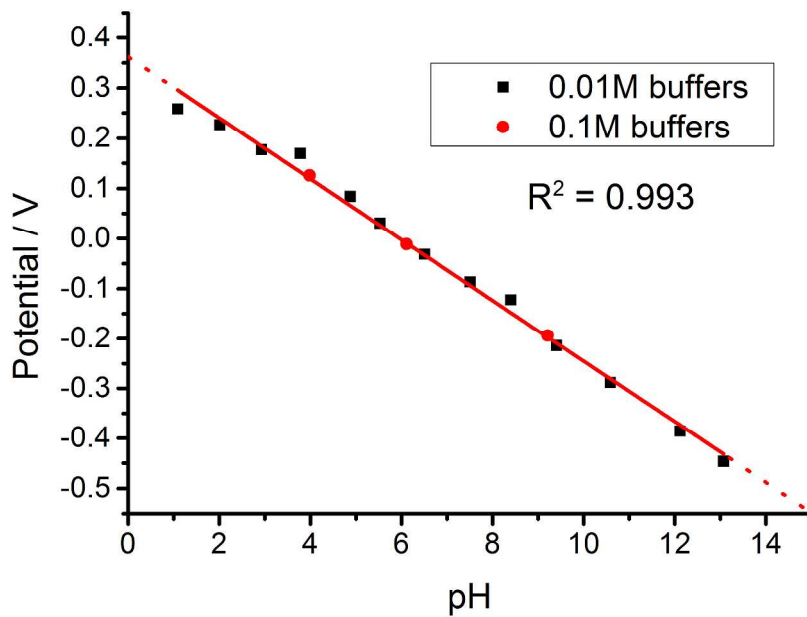


Fig 10. Calibration plot of the original reduction points in 0.01 M buffer solutions (black squares), with reduction points of new 0.1 M buffer solutions (red circles), at 310 K, added for comparison
288x201mm (300 x 300 DPI)