Nafion® Coated Electropolymerised Flavanone-Based pH Sensor

*Monica Miranda[a], Clara Carvetta, Neel Sisodia[a], Luke Shirley, Cristina D. Day, Kay L. McGuinness[a], Jay D. Wadhawan[b], Nathan S. Lawrence[a]**

[a] ANB Sensors Ltd., 4 Penn Farm, Haslingfield Cambridge, CB23 1JZ, United Kingdom
[b] Department of Chemical Engineering, The University of Hull, Cottingham Road, HU6 7RX, United Kingdom
* Corresponding author

Received: ((will be filled in by the editorial sttaff))
Accepted: ((will be filled in by the editorial sttaff))

Abstract
This work summarizes the electrochemical response of flavanone carbon composite electrodes in comparison with Nafion®-coated flavanone carbon composite electrodes, for use as voltammetric pH sensors in both buffered and low-buffered media. Square wave voltammetric measurements suggest the peak potential achieved from the electrochemical polymerization after the electron-proton oxidation responds with accuracy to buffered pH solutions for both coated and non-coated electrodes, with a potential shift of 55.1 mV and 54.6 mV per pH unit respectively. However, a considerable improvement in stability, accuracy and sensitivity is provided by the proton-transfer Nafion® layer in CO_2 bubbled sea water. Furthermore, Nafion®-coated flavanone carbon composite electrodes predicted a pH of 8.04 for the commercial seawater, which is in excellent agreement with the measured pH 8.05 value.

Keywords: pH, electropolymerization, square wave voltammetry, Flavanone, Nafion®.

DOI: 10.1002/elan.((will be filled in by the editorial sttaff))

1. Introduction

The need to accurately sense pH in low ionic strength solutions and solutions where no natural buffer presides is extremely important in the water management industry, especially for water quality monitoring and treatment works, as well as in marine research [1,2]. However, despite this need, there are very few technologies that can operate successfully in these conditions [3,4]. Traditional glass electrodes require constant calibration due to reference electrode drift [5,6] and are fragile and difficult to deploy in remote conditions [7]. Ion-sensitive field-effect transistor (ISFET) based systems offer a solution for seawater applications [8,9] but often have to be deployed with salinity sensors to understand reference potentials [10]. Optical systems are also used in seawater, but they require deployment with optical dye bags which need to be replaced periodically [11,12].

Voltammetric pH sensors have been proposed as a solution, whereby a redox active/pH active molecule is combined with a redox active/pH inactive molecule to both determine the pH of the solution and the reference potential of the reference electrode in a single measurement [13,14]. However, the choice of a redox/pH active molecule is challenging, as the redox process consumes or releases protons at the surface perturbating the local pH of the solution [15].

Recent work has shown that the difficulty of measuring pH in unbuffered systems can be overcome by manipulating the structure of the compounds immobilized on the electrode surface, specifically through using those compounds with stable, intra-molecular hydrogen bonds, so that they can facilitate proton transfer between the water molecules and the redox active moiety without affecting the pH of the solution at the electrode surface [16,17]. However, issues around the solubility of the compound in aqueous media make them problematic for long term monitoring. In this paper, we present the chemical-coating effect of the pH measurement, for a novel type of voltammetric carbon-pH sensor based on a Nafion® coated electropolymerised pH sensitive 2'-hydroxyflavanone (see Scheme 1) based polymer [18].

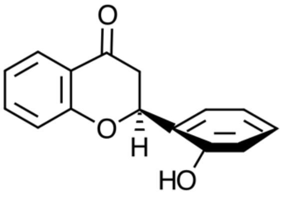
Flavanones are part of the flavonoid family, and they are often found in citrus fruits. Flavonoids are natural phenolic antioxidants. Their antioxidant activities are related to their chemical structure. 2'-hydroxyflavanone has strong antioxidant activity due to the substitution with the OH group at the position 2' of the B-ring. The functional groups are effective for free radical scavenging activity that leads to its antioxidant abilities [19]. Indeed, 2'-hydroxyflavanone is thought to exhibit anti-tumor effects in many different cancer types [20]. In this particular molecule, the carbon in the 2-position is a stereogenic center, with the *S*-enantiomer considered to

This is the peer reviewed version of the following article: Miranda, M., Carvetta, C., Sisodia, N., Shirley, L., Day, C., McGuinness, K., Wadhawan, j. and Lawrence, N. (2022), Nafion® Coated Electropolymerised Flavanone-Based pH Sensor. Electroanalysis., which has been published in final form at https://doi.org/10.1002/elan.202100652. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for self-archiving.

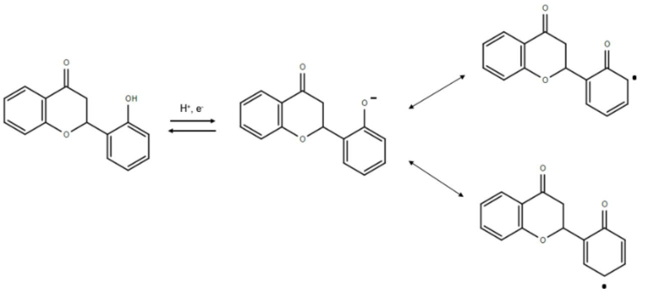
be slightly more stable (*ca.* 9.5 kJ mol^{-1}) than the *R*-form, at least in the gas phase and has the aromatic B-ring twisted from planarity (dihedral angle of *ca.* 24^{o}) [21], so that intra-molecular hydrogen bonding between the donor oxygen in the 1-position and the hydrogen of the 2'-hydroxyl moiety is not possible, at least in the solid state. In solution, however, this six-ring intra-molecular hydrogen bond is thought to exist [22,23], and this is compounded by the experimental pK_a of the 2'-hydroxyl functional group being 10.9 (in 40/60 vol.% methanol/water), compared with phenol (9.20 – 9.95).[24] It follows that this system should be a versatile molecule for a voltammetric pH sensor up to *ca.* pH 10, since above this value, the equilibrium starts to shift so that the flavanone starts to, slowly, ring-open [25] to afford the corresponding chalcone. [26].

Although the chemical oxidation of flavanones using oxygen usually occurs through hydroxyl substitution at the carbon at the 3-position on the C-ring, yielding the corresponding flavanonol [27], the electrochemical oxidation of flavanones tends to involve oxidation of the phenolic moieties on the A- and B-rings [28,29]. The electrochemical oxidation of the relative flavone derivatives typically involves a series of electron-proton transfers and fast hydroxylation [30,31]. In 2'-hydroxyflavanone, there is only one phenolic moiety – this can be electrochemically oxidized as illustrated in scheme 2, to form a phenoxy radical, which is likely to couple through the unblocked *para* position of the B-ring, ultimately to afford a polymeric species [32], which is likely to respond to pH.

In this article, we examine both the pH response of electropolymerised 2'-hydroxyflavanone and the effect of a Nafion® coating to the polymerized flavanone sensor, whereby the Nafion® is used as a proton-exchange membrane to facilitate proton transfer to and from the bulk solution to the underlying electropolymerised flavanone polymer. Nafion® is a well-known perfluoro ionomer, which has a polytetrafluoroethylene (PTFE) backbone and a perfluorinated side chain. Due to the presence of perfluoroalkyl backbones in Nafion®, it is highly hydrophobic. The combination of the stable PTFE backbone with the acidic sulfonic groups gives Nafion® its characteristics of being highly conductive to cations, making it suitable for use as a proton membrane [33,34].



Scheme 1: The structure of 2'-hydroxyflavanone, based on the solid-state crystal structure.



Scheme 2: Electrochemical formation of 2'-hydroxyflavanone radicals.

2. Experimental

2.1. Apparatus

Electrochemical measurements were conducted using an Ana Pot potentiostat (Zimmer & Peacock, UK) with a standard three-electrode configuration. A modified graphite electrode was the working electrode, with a carbon counter and Ag/AgCl (Part N° MF-2056, BASi, USA) acting as the reference electrode. Modification of the working electrode was achieved by abrasively immobilising the flavanone or the nafion coated flavanone material onto the surface of a graphite electrode. This was done by initially polishing the electrode on polishing paper (grit 120) for smoothness. The flavanone was then mechanically immobilised onto the graphite electrode by gently rubbing the electrode surface on a fine filter paper (Whatman) containing the 2'-hydroxyflavanone [35-37].

All square wave voltammetry (SWV) was conducted using the following parameters: frequency = 50 Hz, step potential = 1 mV, amplitude = 40 mV, no pre-treatment.

Absolute pH measurements were performed using a standard glass electrode (Sensorex, California, USA). Prior to the measurement of the solutions, the pH meter was calibrated using Reagecon buffers of pH 4.01 ± 0.01, pH 7.00 ± 0.01 and pH 10.01 ± 0.01 (Reagecon Diagnostics Ltd., Ireland). Measurement of the pH was carried out on each freshly made solution prior to experiments. All the experiments were carried out under thermostatic conditions at 20 ± 1 °C.

2.2. Reagents

All chemicals were purchased from Sigma–Aldrich and used without further purification (unless specified). Standard IUPAC buffer solutions (pH 4, 7, 9) were prepared as follows: pH 4.07 - potassium hydrogen phthalate (0.05 M); pH 6.86 - potassium dihydrogen phosphate (0.025 M) and sodium phosphate dibasic (0.025 M); pH 9.23 - sodium tetraborate (0.05 M), all in deionized water (Hexeal, UK). All buffers contained 0.1 M KCl as the supporting electrolyte.

Sea water, H2Ocean Natural Reef Salt, was purchased from Maidenhead Aquatics (UK) in which 1 kg of this salt was dissolved in 25 L of water. For the sea water calibrations, different concentrations of CO_2 (BOC) were bubbled into a stirred sea water solution, and the corresponding pH measured using the standard glass electrode.

Nafion coated flavanone was achieved by dissolving 5 mg of flavanone in 2mL of Nafion solution. The solution was allowed to dry and the resulting solid removed. The solid was then crushed in a pestle and mortar to produce a fine solid, which could be mechanically immobilised to the graphite electrode.

3. Results and discussion

The electrochemical response of the flavanone carbon composite electrode (Flav) was first tested using square wave voltammetry (SWV) in sea water. It has been shown previously that substituted phenol species such as salicylic acid can be electropolymerized to generate the new redox active species [16,17]. Electropolymerisation involves the initial formation of oligomers followed by nucleation and growth, leading to polymeric materials. By oxidizing the flavanone, the hydroxy group loses a proton, leading to a radical, as presented in scheme 2. This propagating radical will react with other radicals, forming the polymer. The polymer growth is reflected in Figure 1. Figure 1A shows the SWV of the oxidative polymerization. Scan 1 exhibited a small oxidative wave at +0.215V, with an increase in oxidative current at the higher potentials. The second and subsequent scans showed a large increase in this oxidative peak current due to the growth in the polymeric chain, meaning that the oligomer is propagating, concurrent with a decrease in the oxidative current at +0.50 V, where the oxidation of the monomeric flavanone species occurs. As the polymer is formed the peak potential shifts to +0.275 V, where it stabilizes after five scans. This corresponds to the polymer phenolic oxidation potential, leading to a phenoxy radical, after proton loss. This phenoxy radical is long-lived and stable – its reduction can be observed through sweeping the electrode potential in a negative direction after its formation, as illustrated in Figure 1B. In this case a single reductive wave is observed, corresponding to the phenoxy radical reduction with proton uptake, whereby, on multiple repeats, the peak potential moves from +0.197 V to +0.187 V whence it stabilizes. Of the two processes (oxidation or reduction), the lower degree of drift in the peak potential of the reductive wave, encouraged the use of this process as the marker for subsequent experiments.

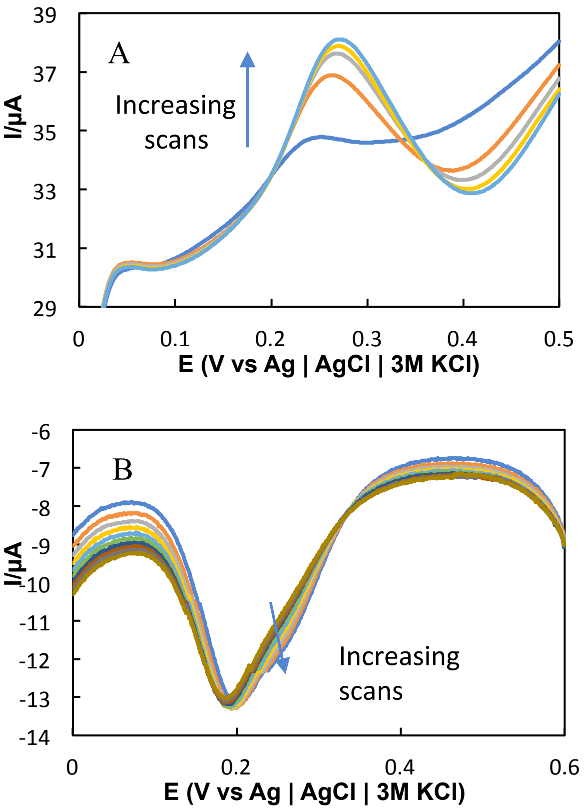


Fig. 1. Repetitive square wave voltammetric (frequency = 50 Hz, step potential = 1 mV, amplitude = 40 mV) response of flavanone electrode in sea water in (A) oxidative and (B) reductive conditions.

Next, the response to pH was studied. Figure 2 details the reductive square wave voltametric response of the polymerised Flav in IUPAC buffers and sea water. A clear response to pH is observed with the peak potential shifting to higher potentials as the solution pH decreases, as expected for a reduction process that consumes protons. Pleasingly, the response to sea water (pH 8.02) is located between the responses for the buffered systems at pH 7 and pH 9. The observed current changes with the nature of the electrolyte solution; this is expected, since the identity of the ions present also varies in each case, and different composite electrodes are used. Nevertheless, a linear plot of peak potential with pH was observed. The sensitivity to pH of 55.1 mV/pH unit is consistent with previous data of 59.2 mV per pH unit at 25 °C for electropolymerized phenol species [17].

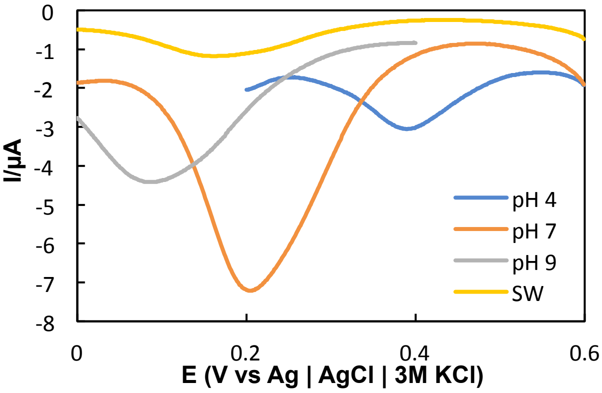


Fig. 2. Square Wave Voltammograms of flavanone electrode in IUPAC standard buffers (pH 4, 7 and 9) and sea water (SW). (frequency = 50 Hz, step potential = 1 mV, amplitude = 40 mV)

For the Flav-based polymeric system to be used in the sensing of pH, the system has to possess stability when undergoing multiple electrochemical measurements without any manual maintenance. This means that the sensor has to possess signal stability, calibration, and accuracy across the duration of its deployment. The electrochemical stability of the sensor was studied by continuously cycling. It is envisaged that the sensor response would deteriorate faster with continuous cycling, due to the energy that is applied to the molecules during the electrochemical process. Figure 3A details the continuous reductive SWV signals of the electropolymerized Flav electrode when placed in a sea water solution. The first ten scans are consistent with the data shown in Figure 1 as explained above. Upon further scanning, the peak current begins to decay and shift to lower redox potentials until after 170 scans when no discernible signal is observed over the baseline response. This is highlighted further in Figures 3B and C. Figure 3B shows the peak current variation during scans and Figure 3C the peak potential with scanning. A comparison of the data shows that the peak current starts to decrease after 10 scans whilst the peak potential requires 40 scans to stabilize, with the potential decreasing from +0.20 V to +0.18 V over the 40 scans. This behavior is consistent with first polymerisation of the flavanone species, followed by the system reaching a local environment steady state; it is expected that the reduction of the polymerised flavanone species involves proton and electron transfer (*vide supra*), on continuous cycling, the concentration of hydrogen ions in the vicinity of the electrode will decrease and the pH will increase as the weak buffer concentration of the sea water cannot maintain constant pH across the electrode surface. The increase in pH is consistent with a shift to lowering in potentials of the flavanone redox couple.

Although the response of the polymerised flavanone electrode is promising as an electrochemical pH sensor, the stability is not sufficient for prolonged monitoring in aqueous environments where the sensor could be deployed for periods of weeks or months. To overcome the issue of stability the impact of polymer coating with the flavanone compound prior to incorporation into the carbon composite electrode was studied. Nafion® has shown to be a good candidate polymer for electrochemical coating systems due to its ability to enhance the stability through its excellent film-forming ability and owing to its hydrophobic backbone, which provides excellent mechanical and chemical stability.

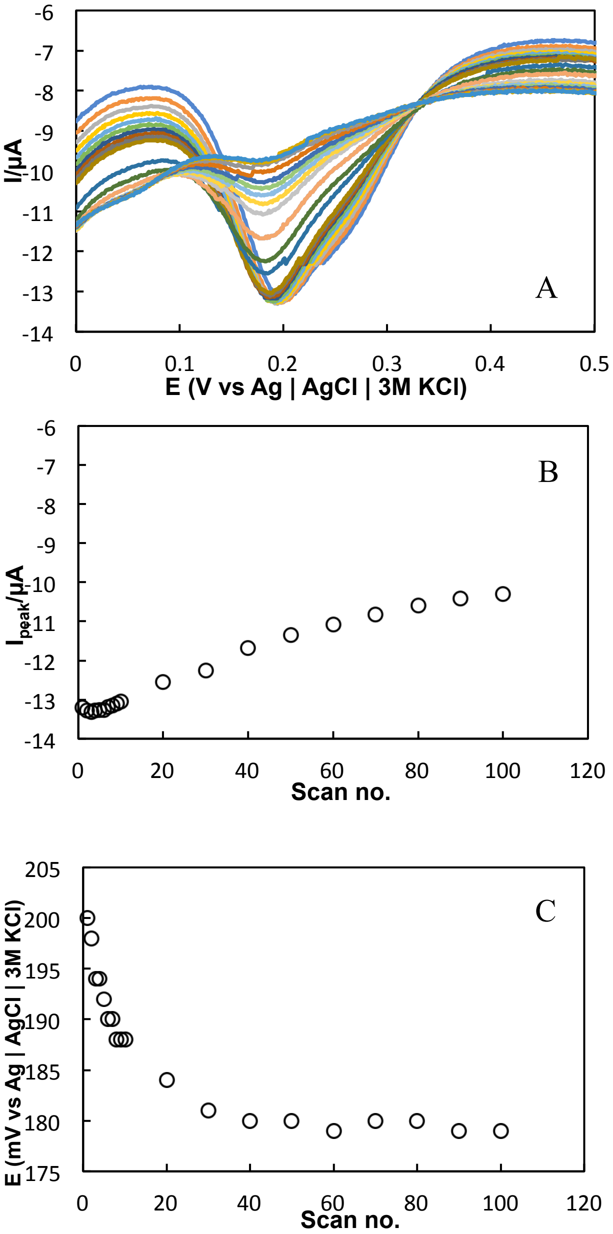


Fig. 3. Lifetime studies for flavanone pH electrodes by (A) continuously SWV (frequency = 50 Hz, step potential = 1 mV,

amplitude = 40 mV) testing and analysis of (B) peak current and (C) peak potential over scans.

The electrode properties are clearly improved after the addition of Nafion®: Figure 4A shows the continuously tested reductive SWV of a Nafion®-coated flavanone electrode (Flav-Naf). As the polymer is formed, the peak potential shifts to +0.250 V, where it stabilises after ten scans. This corresponds to the reduction potential of the polymer. This potential is 25 mV lower than the potential of the Flav electrode without the coating (Figure 1B). This potential shift is due to the rapid proton transfer provided from the Nafion®. This coated electrode showed almost six times longer lifetime than the Flav electrode (presented in Figure 3A). Indeed, Flav-Naf exhibited a 1,000 scans lifetime, as highlighted in Figure 4B, which shows the variation in peak current as a function of scan number compared with the Flav alone electrode. Analysis of the peak potential over scans 10 - 1000 shows that this is stable over the entire period, indicating the Flav-Naf redox reaction does not perturb the environment local to the electrode surface, in contrast to the flav electrode (Figure 3C).

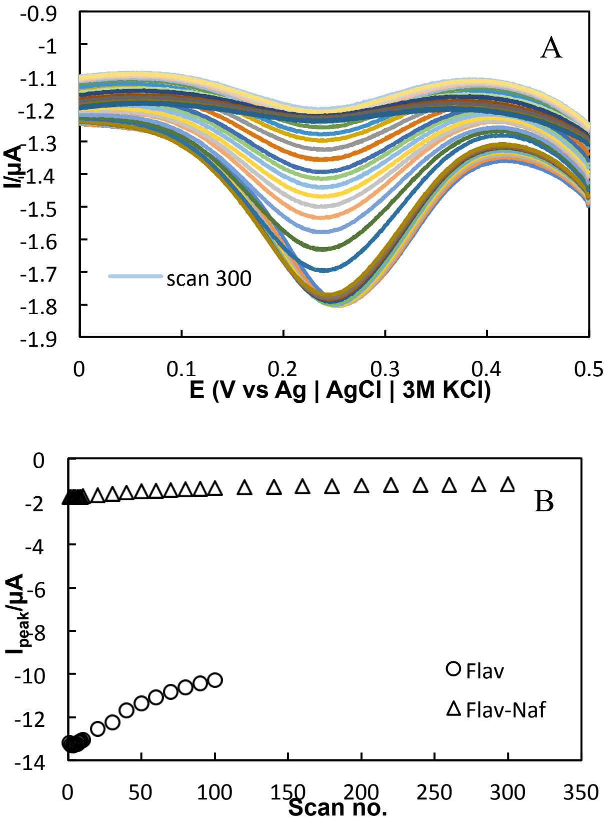


Fig. 4: Lifetime studies for Nafion®-coated flavanone (Flav-Naf) pH electrodes by (A) continuously SWV (frequency = 50 Hz, step potential = 1 mV, amplitude = 40 mV) testing and (B) peak current change comparison with non-coated electrodes (Flav).

The impact of the Nafion® layer on the performance of the electrode as a pH sensor was next studied. The SWV of the Flav-Naf electrode in IUPAC standard buffers and in various sea water samples with different pH values obtained from the addition of different concentrations of CO_2 are shown in Figures 5A and 5B respectively. In all cases, well defined redox waves are observed, indicating that the Nafion® layer is effectively facilitating proton transfer from the bulk solution to the flavanone molecules. As shown in Figure 5C, the peak potential decreases linearly with increasing pH, with a sensitivity to pH of 54.6 mV/pH unit in both the buffered and sea water solutions.

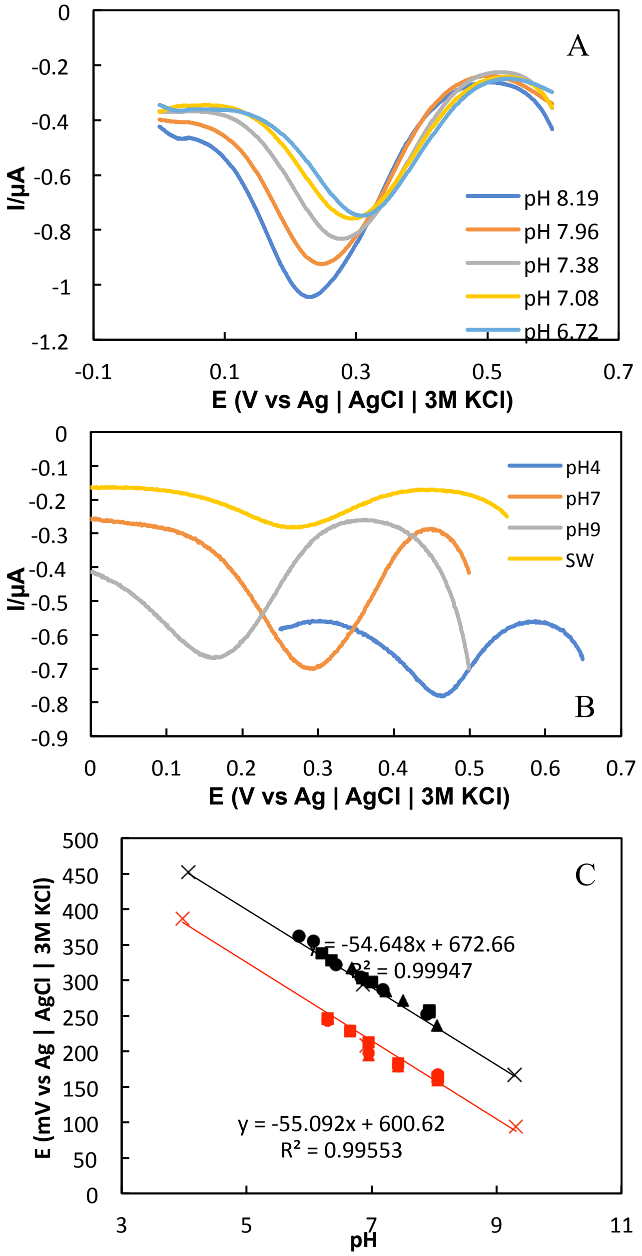


Fig. 5. SWV (frequency = 50 Hz, step potential = 1 mV, amplitude = 40 mV) of Flav-Naf electrodes in (A) standard

IUPAC buffers and (B) sea water calibration. (C) Overall calibration of three different Flav (red line) and three different Flav-Naf electrodes (black line) in standard buffers and CO_2-bubbled sea water (SW).

Figure 5C compares the response of the Flav and Flav-Naf electrodes with IUPAC buffers and when the pH of sea water was varied by injection of CO_2 into the solution. In this case, the corresponding plots of pH as a function of potential for three Flav and three Flav-Naf electrodes in pH 4, 7, 9 IUPAC buffer solutions (long line) and different concentrations of CO_2 purged sea water solutions (dots) are shown. Both formulations exhibit the same sensitivity to pH for the IUPAC buffer solutions calibration. However, there is a significant difference in peak potential values (around 70 mV), with the Flav-Naf coated electrodes having a higher peak potential than the Flav electrodes. This increase in redox potential can be attributed to the Nafion® coating making the oxidation of the underlying flavanone species harder.

The Nafion® has a profound influence on the response on the sea water/CO_2 calibration. In the case of the Flav electrode, the pH trend in the sea water solution deviates from the linear buffer trend, whilst the Flav-Naf electrode follows the trend line exactly. This is a consequence of the rapid proton transfer from the bulk solution to the flavanone layer provided by the Nafion®. This results in a linear response in the sea water/CO_2 calibration system compared to a non-coated Flav system and overcomes the solution buffering issues [38]. This is highlighted further in Table 1 which compares how the sensitivity and the linearity to pH and lifetime improves as the Flav-Naf ratio is increased in the sea water/CO_2 solutions. No significant improvement in the sensitivity between the Flav (1:0) and Flav-Naf (1:1) electrodes is observed. However, there was an increase in the intercept, and noticeable increase in the lifetime of the sensor, indicating that there was at least partial Nafion® coverage of the flavanone. Increasing the Nafion® further to Flav-Naf (1:2) had little impact on the lifetime, but the sensitivity to pH highly improved, and again an increase in the intercept was observed. Furthermore, there was a lowering in the standard deviation compared to the two previous formulations, indicating a higher degree of reproducibility across the electrodes. Increasing the Nafion® concentration further to 1:3 had little improvement with both ratios showing good sensitivity and high degrees of reproducibility, albeit slightly worse than 1:2 ratio, and a decrease in the regression line was observed. Increasing the Nafion® further to Flav-Naf (1:5) resulted in poor voltammetric responses indicating too much Nafion® had been applied to the flavanone layers. Therefore, the limit in Nafion® amount was established. As 1:2 showed the best sensitivity and reproducibility, this was chosen as the optimum formulation.

Using the Flav-Naf 1:2 ratio the experimental pH of the sea water based on the average equation obtained in Table 1 was calculated and compared to that measured with the standard glass electrode. The calculated pH for the obtained peak potential was pH 8.04 ± 0.1 pH unit, which is in excellent agreement with the measured value of pH 8.05.

Table 1. A comparison of the sensitivity, redox potential at pH 0 and lifetimes of different amounts of Nafion® in Flav pH sensors, based on sea water calibrations using CO_2.

Flav/ Naf Ratio	Sensitivity (mV/pH)	Redox Potential at pH 0 (mV)	R^2	Lifetime/ No. of scans
1:0	-47.72 ± 2.22	541.66 ± 15.97	0.943 ± 0.031	~300
1:1	-44.45 ± 1.48	608.18 ± 10.88	0.996 ± 0.004	~850
1:2	-53.14 ± 0.20	673.46 ± 3.57	0.997 ± 0.002	~900
1:3	-55.15 ± 0.76	683.39 ± 5.73	0.988 ± 0.001	~1100

4. Conclusions

A novel pH sensing system utilizing flavanone-carbon-composite-based electrodes has been successfully developed. The electropolymerisation of flavanone embedded within the carbon composite electrode in sea water produces an electro-active polymer with a redox potential of ca. +0.20 V. The resulting polymer was found to provide a Nernstian response in buffered pH solutions, however when moving to lower buffered systems a deviation from the Nernstian response was observed, with the proton transfer in the vicinity of the electrode controlling the local pH rather than the bulk solution. Combining this with a low electrochemical stability means that the sensor would not be suitable for deployment as a pH sensor.

To overcome this issue, a Nafion® polymer coating was successfully incorporated to the flavanone carbon composite electrode. A great improvement was shown regarding stability, sensitivity and lifetime. In these electrodes, the redox reaction was not perturbing the environment local to the electrode surface due to the rapid proton transfer provided by Nafion®, so the potential was stable over the entire testing period. It has been demonstrated that Nafion® coatings help the pH sensing behaviour by improving their calibration in IUPAC standard buffers and in CO_2 bubbled sea water. The CO_2/sea water system calibration line overlays the standard buffers calibration whilst also increasing electrode to electrode reproducibility. Furthermore, a six-fold improvement of lifetime was observed with the Nafion® coated electrodes compared with the Flav electrodes.

Different Flav-Naf ratios were studied and the 1:2 ratio showed the best sensitivity, accuracy, reproducibility and lifetime properties. Finally, experimental pHs were successfully calculated based on the average equation obtained from the calibration plots.

5. Acknowledgements

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 82297.

ANB Sensors gratefully acknowledges funding this work through Innovate UK grant funding, Grant no. 133171. Innovate UK is the UK's innovation agency. It works with people, companies and partner organisations to find and drive the science and technology innovations that will grow the UK-economy.

6. References

[1] J. C. Orr, V. J. Fabry, O. Aumont, L. Bopp, S. C. Noney, R. A. Feely, A. Gnanadesikan, N. Gruber, A. Ishida, F. Joos, R. M. Key, K. Lindsay, E. Maier-Reimer, R. Matear, P. Monfay, A. Mouchet, R. G. Najjar, G. K. Plattner, K. B. Rodgers, C. L. Sabine, J. L. Sarmiento, R. Schlitzer, R. D. Slater, I. J. Totterdell, M. F. Weirig, Y. Yamanaka, A. Yool, *Nature*, **2005**, 437, 7059

[2] A. R. Sastri, J. R. Christian, E. P. Achterberg, D. Atamanchuk, J. J. H. Buck, P. Bresnahan, P. J. Duke, W. Evans, S. F. Gonski, B. Johnson, S. K. Juniper, S. Mihaly, L. A. Miller, M. Morley, D. Murphy, S. Nakaoka, T. Ono, G. Parker, K. Simpson, T. Tsunoda, *Front. Marine Sci.*, **2019**, 6, 653

[3] J. Virmani, P. M. E. Bunje, *Marine Technol. Sci. J.*, **2015**, 49, 27

[4] R. R. Okazaki, A. J. Sutton, R. A. Feely, A. G. Dickson, A. R. Alin, C. L. Sabine, P. M. E. Bunje, J. I. Virmani, *Limnol. Oceanol. Methods*, **2017**, 15, 586

[5] T. J. Smith, K. J. Stevenson in *Handbook of Electrochemistry, 1st ed.,* (Ed.: C. G. Zoski), Elsevier, **2007**.

[6] M. Sophocleous, J. K. Atkinson, *Sens. Acts. A: Phys.*, **2017**, 267, 106

[7] D. J. Graham, B. Jaselskis, C. E. Moore, *J. Chem. Educ.* **2013**, 90, 345-351.

[8] Y. Takeshita, T. R. Martz, K. S. Johnson, A. G. Dickson, *Anal. Chem.*, **2014**, 86, 11189-11195.

[9] K. McLaughlin, A. Dickson, S. B. Weisberg, K. Coale, V. Elrod, C. Hunter, K. S. Johnson, S. Kram, R. Kudela, T. Martz, K. Negrey, U. Passow, F. Shaughnessy, J. E. Smith, D. Tadesse, L. Washburn, K. R. Weis, *Regional Studies in Marine Science*, **2017**, 12, 11-18.

[10] T. R. Martz, J. G. Connery, K. S. Johnson, *Liminol. Oceanogr.: Methods*, **2010**, 8, 172-184.

[11] K. Newhall, R. Krishfield, D. Peters, J. Kemp in *Deployment Operation Procedures for the WHOI Ice-Tethered Profiler*, Woods Hole Oceanographic Institution, Massachusetts, **2007**.

[12] S. R. Laney, R. A. Krishfield, J. M. Toole, T. R. Hammar, C. J. Ashjian, M. L. Timmermans, *Polar Science*, **2014**, 8, 73-85.

[13] M. Lu, R. G. Compton, *Analyst,* **2014**, 39, 4599-4605.

[14] M. Lu, R. G. Compton, *Analyst*, **2014**, 139, 2397-2403.

[15] C. B. McAuley, B. R. Kozub, D. Menshykau, R. G. Compton, *Phys. Chem*., **2011**, 115, 714-718.

[16] C. Dai, L. P. Crawford, P. Song, A. C. Fisher, N. S. Lawrence, *RSC Adv.,* **2015**, 5, 104048-104053.

[17] C. Dai, P. Song, J. D. Wadhawan, A. C. Fisher, N. S. Lawrence, *Electroanalysis*, **2015**, 27, 917-923.

[18] M. Shoja, K. Samuel, *Z. Kristallogr. NCS*, **1999**, 214, 239.

[19] J. Kocábová, J. Fiedler, I. Degano, R. Sokolová, *Electrochim. Acta*, **2015**, 187, 358-363.

[20] K. Wu, Z. Ning, J. Zhou, B. Wang, J. Fan, J. Zhu, Y. Gao, X. Wang, J.-T. Hsieh, D. He, *Oncol. Reports*, **2014**, 32, 131.

[21] E. Łodyga-Chruścińska, A. Kowalska-Baron, P. Błazińska, M. Pilo, A. Zucca, V. M. Korolevich, V. T. Cheshchevik, *Molecules*, **2019**, 24, 3049.

[22] N. Narasimhachari, D. Rajagopalan, T. R. Seshadri, *Proc. Ind. Acad. Sci.*, **1952**, 36, 231.

[23] H. Wang, Y. Shuang, L. Li, *Anal. Sci.*, **2020**, 36, 687.

[24] P. Sykes in *A Guidebook to Mechanism in Organic Chemistry, 6th ed.,* Longman, Harlow, **1986**.

[25] J. Tirouflet, A. Corvaisier, *Bull. Soc. Chim. Fr.*, **1962**, 640.

[26] A. Cisak, C. Mielczarek, *J. Chem. Soc., Perkin Trans. II*, **1992**, 1603.

[27] J. Mann in *Secondary Metabolism*, Oxford University Press, Oxford, **1978**.

[28] E. S. Gil, R. O. Couto, *Brazil. J. Pharmacol.*, **2013**, 23, 542.

[29] J. Kocábová, J. Fiedler, I. Degano, R. Sokolová, *Electrochim. Acta*, **2016**, 187, 358.

[30] R. Sokolová, I. Degano, S. Ramesová, J. Bulícková, M. Hromadová, M. Gál, J. Fiedler, M. Valásek, *Electrochim. Acta*, **2011**, 56, 7421-7427.

[31] E. S. Gil, R. O. Couto, *Brazil. J. Pharmacol.*, **2013**, 23, 542.

[32] H. Schafer in *Organic Electrochemistry: Revised and expanded, 4th ed.* (Eds.: H. Lund, O. Hammerich), Marcel Dekker, New York, **2001**, p.883.

[33] Q. Tang, Z. Shan, L. Wang, X. Qin, K. Zhu, J. Tian, X. Li u, *Journal of Power Resources*, **2014**, 246, 253-259.

[34] Z. Jin, K. Xie, X. Hong, Z. Hu, X. Liu, *Journal of Power Resources*, **2012**, 218, 163-167.

[35] F. Scholz, B. Meyer, *Chem. Soc. Reviews*, **1994**, 23, 341-347.

[36] A. M. Bond, R. Colton, *Coord. Chem. Reviews*, **1997**, 166, 161-180.

[37] M. Pandurangappa, N. S. Lawrence, L. Jiang, T. G. J. Jones, R. G. Compton, *Analyst*, **2003**, 128, 473-479.

[38] L. Chen, C. Lin, R. G. Compton, *Phys. Chem. Chem. Phys.*, **2019**, 21, 607-616.