

Monitoring pH Using Alizarin-modified Commercial Screen-printed Electrodes

Achim Habekost*

Department of Chemistry, University of Education Ludwigsburg, Reuteallee 46, D-71634 Ludwigsburg, Germany

*Corresponding author: [A. Habekost@t-online.de](mailto:A.Habekost@t-online.de)

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Abstract A pH-sensor based on alizarin-modified screen-printed multiwalled carbon nanotubes (MWCNT-SPE, Orion High Technologies) imbedded in Nafion[®] shows a linear dependence between the oxidation potential and the pH from pH 0 to pH 10. This modified MWCNT-SPE is compared to a commercial alizarin SPE (DRP 110ALI, Metrohm - DropsSens). In addition to this technical application, these pH sensors seem to be a good didactic alternative to the widely used pH glass electrode, which many students find hard to understand.

Keywords: second-year undergraduate, demonstration, hands-on learning/manipulatives, electrochemistry, analytical chemistry

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1. Introduction

Determining pH is one of the most common analytical measurements in chemistry. While color-changing pH paper and conventional pH electrodes are standard features of student lessons, these methods suffer from inaccuracy and lack of transparency, respectively.

Because alizarin and alizarin red S have different pH-dependent redox-functionalities, this substance can be used as pH indicator.

Dai and Shiu¹ studied the electrochemical behavior of alizarin red S on glassy carbon electrodes via cyclic voltammetry. They found that the central quinone functionalities underwent a quasi-reversible reduction, forming dihydroxy moieties. The formal potential of this reaction varies linearly with pH, resulting in a Nernstian slope of -58 mV/pH. Figure 1 shows this redox couple: The reduction potential of the anthraquinone is around -0.4 V.

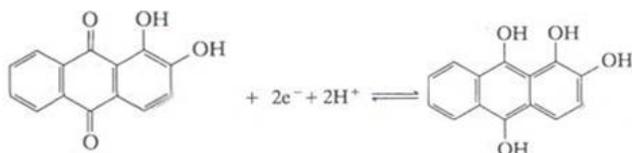


Figure 1. Redox of the anthraquinone moiety

Figure 2 shows the redox behavior of the catechol moiety. The dihydroxy groups oxidize irreversibly at more positive potentials. This potential is pH-dependent, too. The irreversibility results in the instability of the fully oxidized quinone derivate. [1,2] This oxidation product subsequently undergoes chemical transformation.

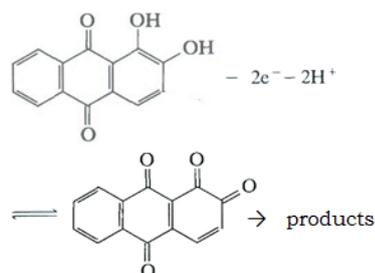


Figure 2. Redox of the catechol moiety

Compton *et al.* [3] used pH-dependent oxidation of an anthraquinone-diazonium salt which can derivatize carbon particles, the basic substance of the working electrode used.

Hydrophosphoric acid (H₃PO₂) removes the N₂ moiety from the diazonium salt, which can then electrophilically attack the pyrolytic graphite (Figure 1).

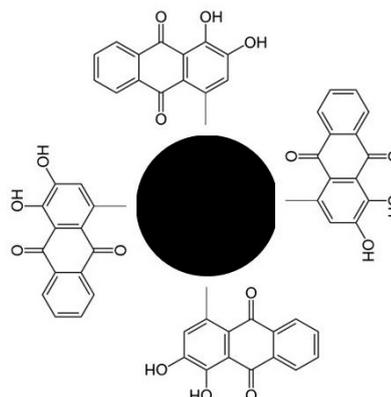


Figure 3. Schematic representation of the alizarin-modified pyrolytic graphite

The pH-dependence of the reduction potential of the anthraquinone was shown using square wave voltammetry (SWV). The more alkaline the solution, the more negative the reduction potential. In a further work, Compton *et al.* [4] investigate the pH probe based on the combination of anthraquinone and N,N' -diphenyl-*p*-phenyldiamine, which entails reduction of the former and oxidation of the latter. Both undergo a redox process with two electrons and two protons over a wide pH-range. Compton *et al.* [5] also derivatized carbon powder with anthracene, azobenzene, diphenylamine, 9,10-diphenylanthracene, methylene blue, 3-nitrofluoranthene, 6-nitrochrysene, 9-nitroanthracene, 9,10-phenanthraquinone (PAQ), thionine, and fast black K (2,5-dimethoxy-4-[(4-nitrophenyl)azo]benzenediazonium chloride). They found two different mechanisms: a reversible and an irreversible electrochemical behavior. This means that some substances can be used directly as pH-dependent species while others, such as diphenylamine, first form an electrochemically induced polymer which can then be used as the pH-dependent substance. Substances with nitro moieties first show an irreversible pH-dependent reduction to form an aryl nitro compound; after dehydration, an aryl nitroso compound is formed. It is this compound which reacts in a reversible pH-dependent oxidation reaction.

Following Compton's research, Fisher and Lawrence *et al.* [6] investigated an alizarin-based homemade carbon SPE. Carbon ink and alizarin were mixed in a ball mill. The mixture was then screen-printed onto carbon paste which

was applied to an aluminum foil. SWV shows a Nernstian behavior with a sensitivity of about 56 mV per pH unit. At $\text{pH} > 7$, however, the SWV peaks become wider and the dependence of the current peak on the scan rate shows a deviation from the linear relationship. The authors attributed this to a nucleophilic attack by water on the carbonyl moiety of the oxidized alizarin followed by tautomerization of the resulting enol (Michael addition) (Figure 4).

In addition, the authors showed that this alizarin SPE can be coated very easily with Nafion (the most widely used proton exchange membrane, especially in hydrogen fuel cells). This modification prevents the nucleophilic attack on the alizarin by water and the dissolution of the alizarin. SWV shows no significant difference in pH-dependent potential with or without Nafion protective coating.

In our own work, we want to show that alizarin embedded into Nafion is physisorbed on commercial multiwalled carbon nanotube MWCNT-SPEs (Orion High Technologies). This modified electrode can fulfill all requirements of a stable pH sensor with reproducible results. The MWCNT-SPEs were modified by dropping an aqueous alizarin suspension onto them. After the water was evaporated, a drop of Nafion was used to coat the alizarin. This modified MWCNT-electrode was compared with a commercial screen-printed carbon SPE modified with alizarin (Metrohm-DropSens: DRP 110 ALI).

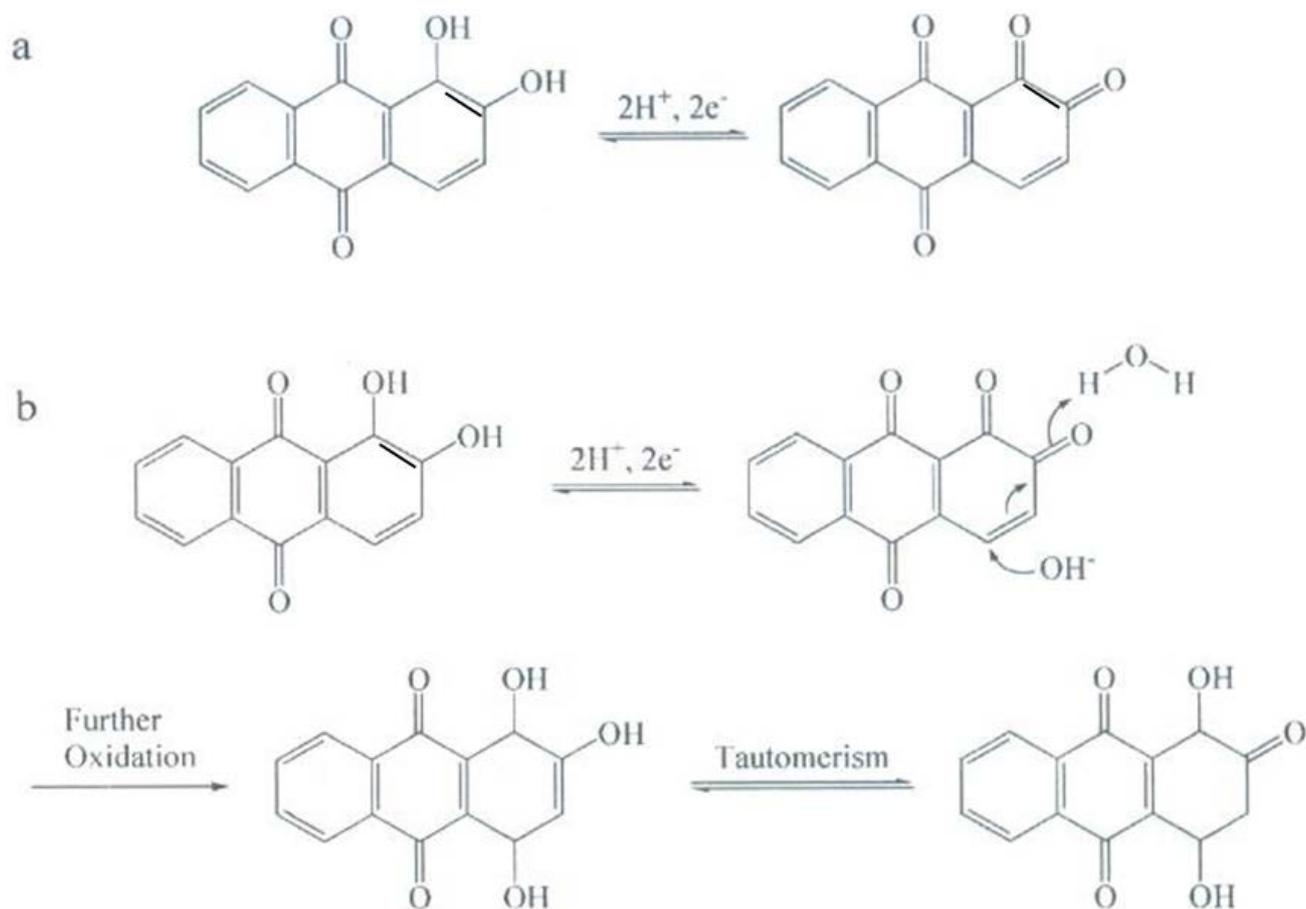


Figure 4. a: Reversible oxidation of alizarin: 2-electron, 2-proton process, b: Nucleophilic attack by water followed by further oxidation and tautomerism [6]

HAZARDS

Alizarin, CAS number 72-48-0, purchased from Sigma Aldrich (122777), has no known toxicity.

Diethyl ether, CAS number 60-29-7, purchased from Sigma Aldrich (296082), flammable liquid, acute toxicity upon oral intake, damage to the central nervous system upon single exposure.

Nafion, perfluorinated resin solution, 5 wt. % in mixture of lower aliphatic alcohols and water, CAS Number: 31175-20-9, purchased from Sigma Aldrich (527084).

2. Experimental Procedure

2.1. Reagents and Instrumentation

We used 10^{-3} mol/L aqueous solution of alizarin in a 0.1 mol/L solution of KCl. Ultrapure water was obtained from tap water with additional cleaning in a reversed osmosis system, leading to an electric conductivity of about $0.2 \mu\text{S}/\text{cm}$.

To thicken the alizarin layer, alizarin was dissolved in diethyl ether and the solution was dropped onto the working electrode. The ether evaporated immediately. Nafion was then dropped onto the electrode. The evaporation time of the alcoholic solvent is about 1 minute.

Cyclic voltammetry (CV) and SWV [7,8] measurements

were carried out with a μStat 400 potentiostat from DropSens that was controlled by DropView software (SWV parameters: frequency: 2 Hz, step potential: 5 mV, amplitude potential: 50 mV). pH measurements were taken using the CASSY data system with pH insertion.

We used commercial SPE, either MWCNT-SPE from Orion High Technologies, Madrid, Spain or a carbon-SPE modified with alizarin (DRP 110 ALI) from Metrohm, DropSens, Oviedo, Spain. Only $60 \mu\text{L}$ of the investigated solutions are required. However, SPEs have the disadvantage that they cannot be cleaned by polishing or in an ultrasonic bath because the coating would be damaged.

3. Results and Discussion

Figure 5 shows the CV of alizarin with DRP 110 ALI SPE pure and MWCNT-SPE with alizarin imbedded in Nafion at pH 1 the latter at two different scan rates.

The numbers at the oxidation peaks refer to the reaction scheme above. Additional alizarin in Nafion increases the current but does not shift the formal potential. At faster scan rates, the current peaks drift apart, which is typical for quasi-reversible electron transfers. The star in Figure 5 shows the reaction product for the dicarbonyl oxidation product.

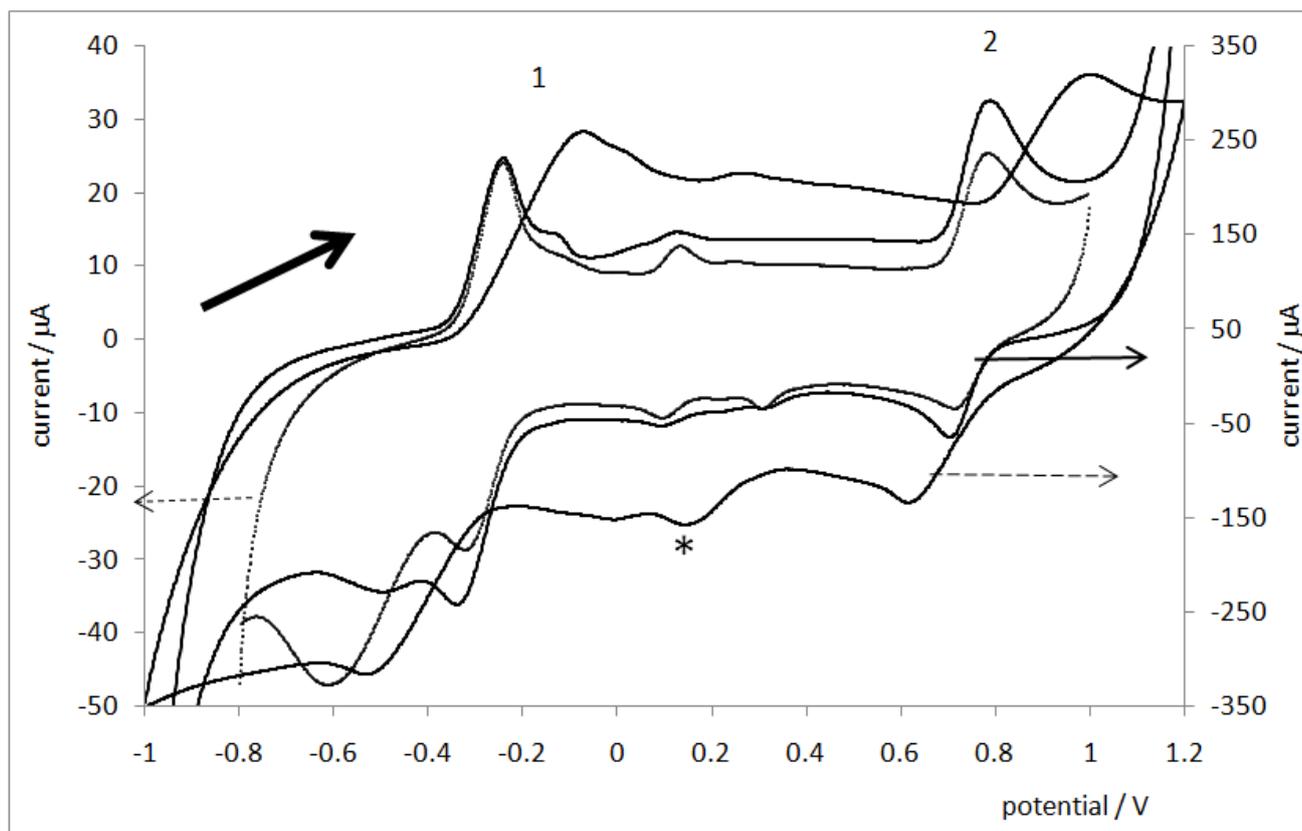


Figure 5. CV of alizarin (DRP 110ALI unmodified) and MWCNT-SPE with alizarin / Nafion modified with Nafion). Dotted line: Sampling rate 0.02 V/s, unmodified DRP 110ALI-SPE. Black solid line: Scan rate 0.02 V/s, MWCNT/alizarin/Nafion-SPE. Dashed line: scan rate 0.2 V/s MWCNT/alizarin/Nafion-SPE (see the different current scales). Numbers refer to the above reaction scheme. The star symbolizes the reaction product of the dicarbonyl, see reaction (2). Wide arrow: scan direction

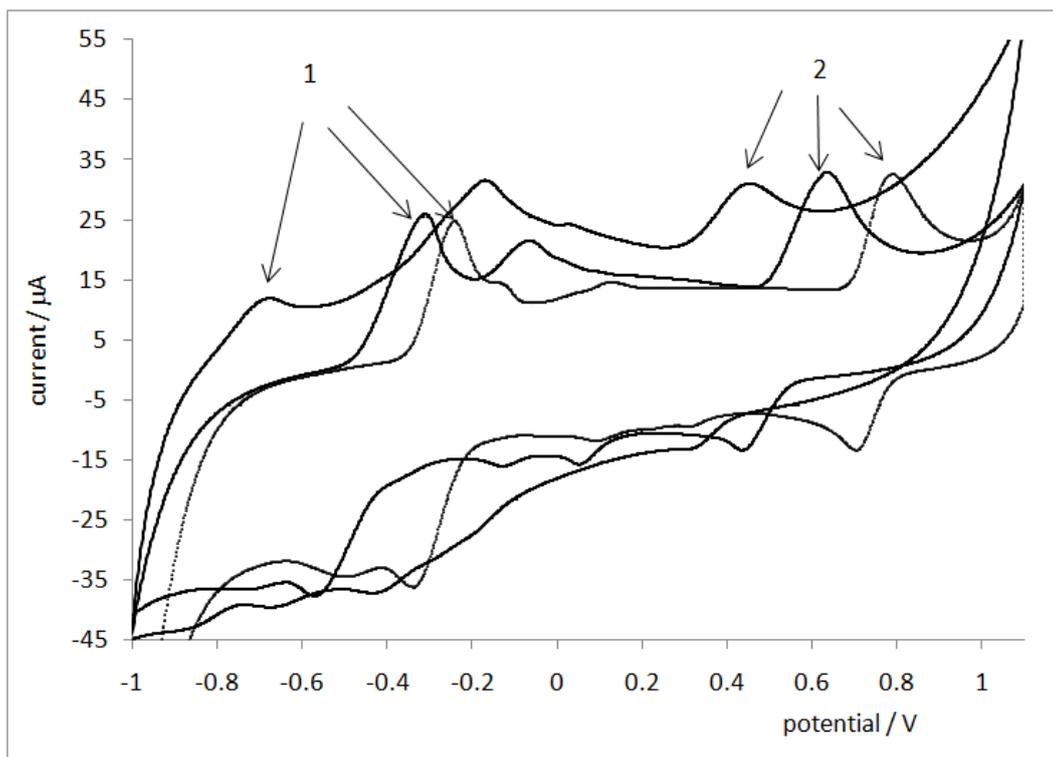


Figure 6. pH dependence of MWCNT/alizarin/Nafion-SPE. Solid line: pH 7; dashed line: pH 4; dotted line: pH 1. Numbers refer to the above reaction scheme. The arrows indicate the two oxidation reactions (1) and (2)

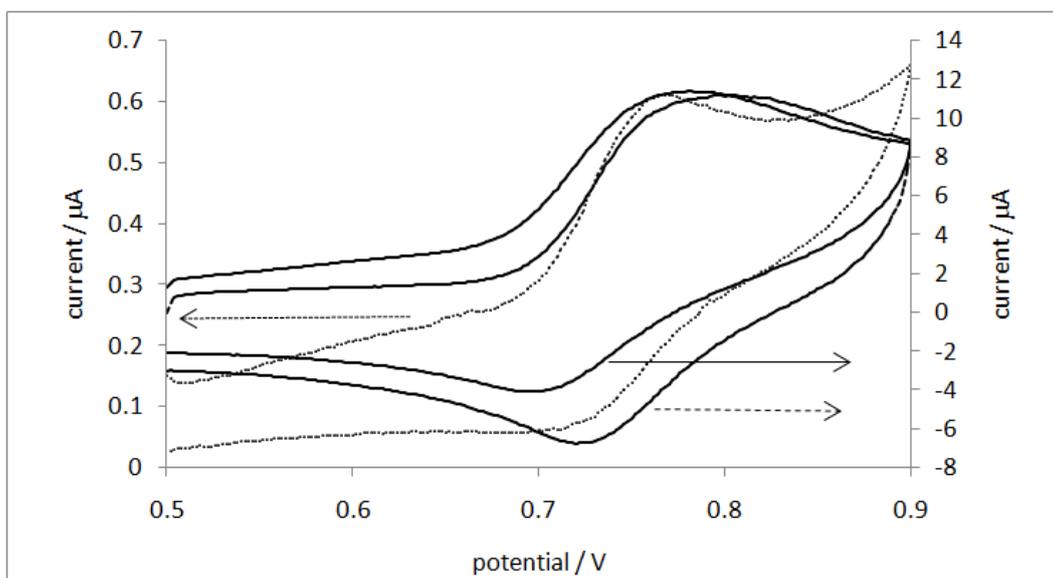


Figure 7. Comparison of unmodified DRP 110 ALI (dotted line) and modified DRP 110 ALI with less (solid line) and more alizarin (dashed line). Scan rate: 0.05 V/s

Figure 6 shows three pH-dependent CVs with MWCNT/alizarin/Nafion-SPE. The more acidic the solution, the more the potential shifts to higher values. This applies to both reactions (1) and (2).

Interestingly, not only does the current intensity increase with additional alizarin, but the ratio between cathodic and anodic current peaks shifts to 1 with both additional alizarin and with the scan rate (see Figure 8). This means that the back reaction (2) increasingly takes place with additional alizarin and the reaction under formation of the products (see (2)) is increasingly suppressed with increasing scan rate.

Figure 9 shows the pH dependence of the oxidation peak (2), which shows a linear relationship between pH and the peak potential according to the Nernstian equation

$$E_p = E_0 - 2.303 \frac{R \cdot T \cdot m}{n \cdot F} \cdot \text{pH} \quad (3)$$

where E_p : peak potential (V), E_0 : standard potential (V) at pH=0, R: universal gas constant (J/(K·mol)), T: temperature (K), F: Faraday constant (C/mol) and n: number of transferred electrons, m: number of transferred protons. Here $n = m = 2$. This results in a gradient of about 58 mV/pH.

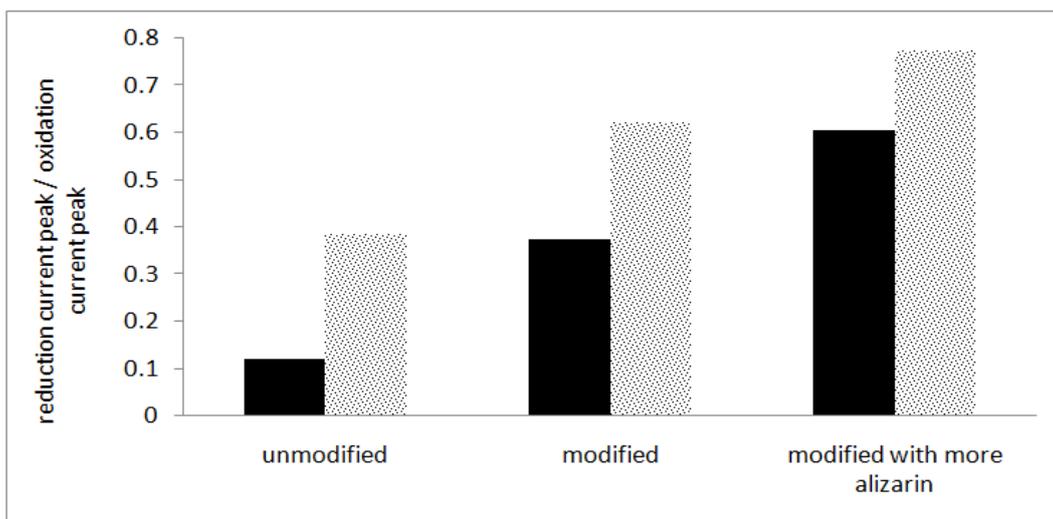


Figure 8. Ratio between cathodic and anodic current peaks. Black: scan rate 0.05 V/s; dotted: scan rate 0.5 V/s

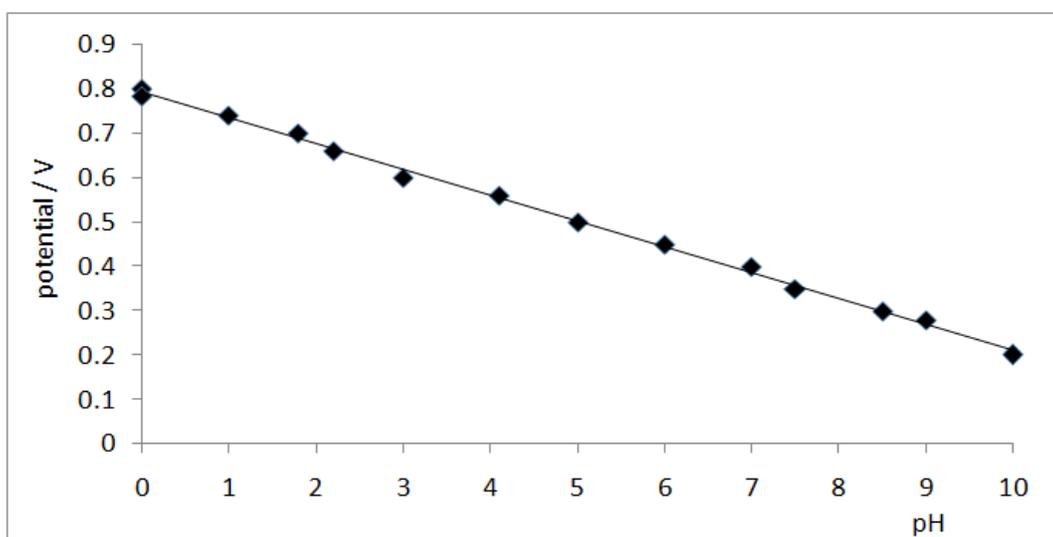


Figure 9. pH dependence of the oxidation potential: $E_p = -58 \text{ mV/pH} + 0,8 \text{ V}$

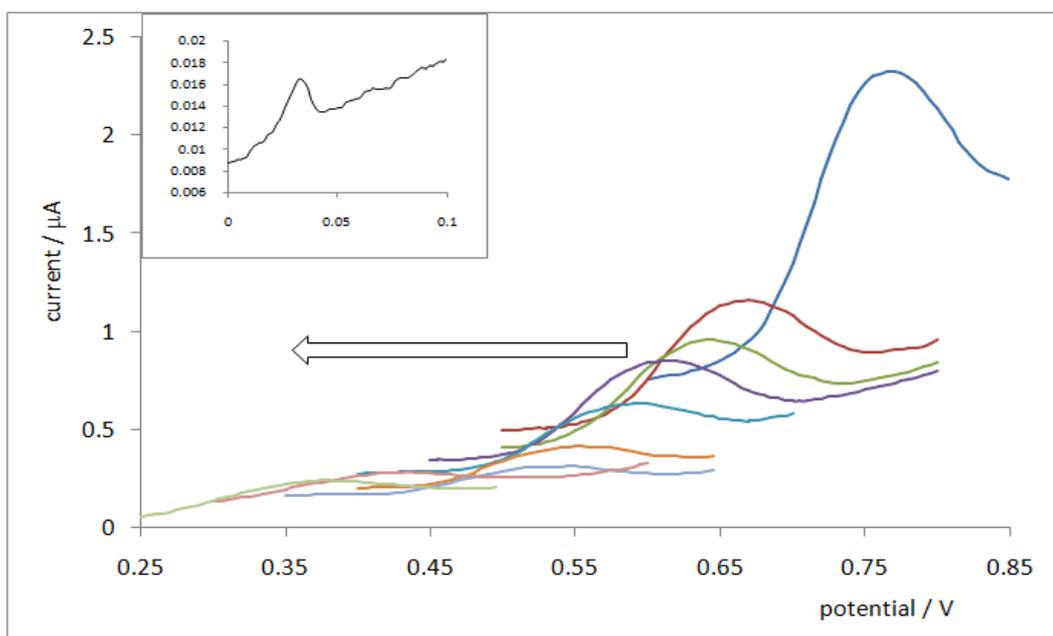


Figure 10. Anodic current peaks as a function of pH. Arrow indicates increasing pH. Insert: Current peak at pH 11. Electrochemical method SWV

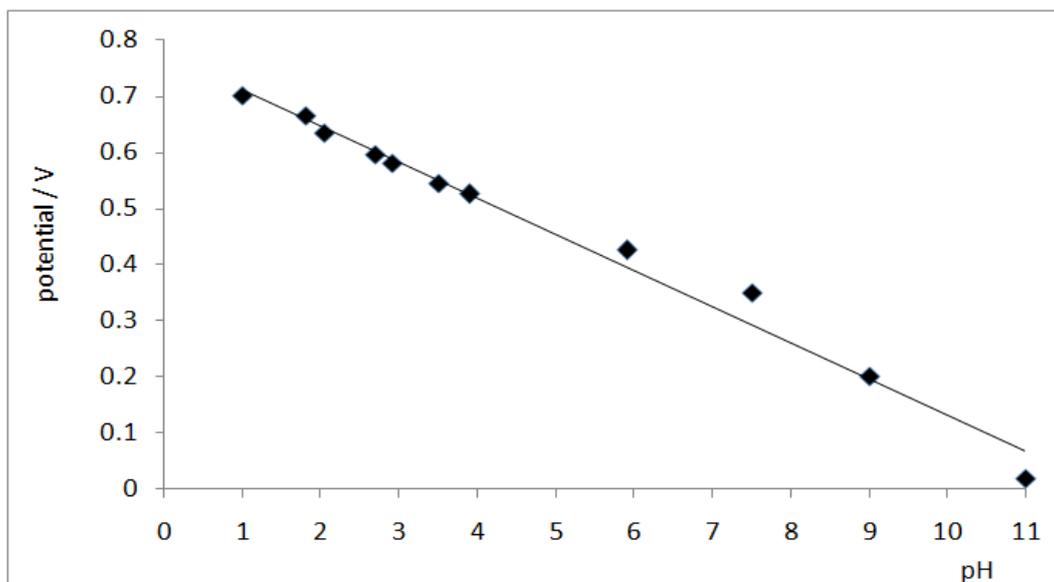


Figure 11. pH dependence of the oxidation potential: $E_p = -64 \text{ mV/pH} + 0,77 \text{ V}$

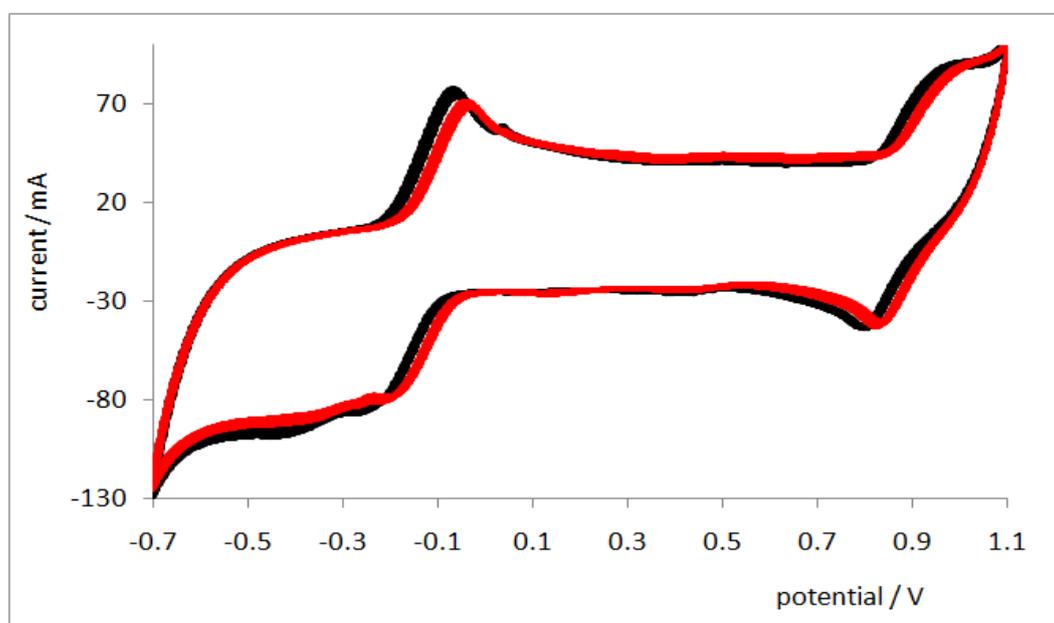


Figure 12. CV recorded twenty times in a row (black lines). After one week, the same SPE was used for the same procedure (red lines). Scan rate 0.05 V/s

When using the commercial DRP 110 ALI, the current peaks decreased with increasing pH, but the relationship between anodic peak and the oxidation potential was also linear, with a gradient of -64 mV/pH (see Figure 10 and Figure 11).

The stability of the MWCNT/alizarin/Nafion-SPE was tested in two ways: Figure 12 shows the CVs recorded twenty times in a row (black lines). After one week, the same SPE was used for the same procedure (red lines). The deviation between the CVs was very small. Therefore, the modified SPEs can be used with sufficient accuracy.

4. Conclusion

The experiments are based on two physicochemical principles: cyclic voltammetry and square wave voltammetry. The availability of alizarin-modified carbon SPEs as a

powerful pH sensor was investigated. For this purpose we used the pH-dependent oxidation of the catechol moiety to dicarbonyl. A linear dependence between the oxidation potential and the pH value was found.

In order to increase the sensitivity and longevity of the sensor, alizarin was additionally dropped onto the working electrode. This was then embedded in Nafion to protect the SPE from alkaline or aerobic damage.

The didactic advantage of the described electrodes is their simple manufacture and handling. In addition, this pH sensor can be an interesting alternative to the difficult to understand pH glass electrode, since knowledge of only one reaction scheme is necessary to understand the sensor.

Notes

The author declares no competing financial interest.

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