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Redox Properties of Poly (aniline boronic acid) in Aqueous Environment with Glucose and Table Sugar Addition

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Abstract

Polyaniline boronic acid, a conducting polymer with unique properties, has gained attention for its potential applications in flow batteries, sensors, drug delivery systems, and electrochemical devices. Understanding the redox behavior of this polymer in the presence of sugars is of particular interest due to the potential implications for its functionality in various applications. Cyclic voltammetry is employed to analyze the redox behavior of the polymer in aqueous solutions with glucose and table sugar. Preliminary results suggest that the presence of glucose increase and table sugar decrease the peak values. The diffusion coefficient of the polymer is found as 2.6×10^{-9} cm^2/s. The choice of supporting electrolyte, exemplified by potassium carbonate and potassium chloride, also exhibited an influence on redox behavior of polyaniline boronic acid, and peak potential and peak values are higher in potassium chloride solutions.

Keywords: Redox, Cyclic voltammetry, Flow batteries, Polyaniline boronic acid, Glucose, Table sugar

1. Introduction

Redox active materials are significant due to their pivotal role in many electrochemical processes, enabling efficient electron exchange and facilitating redox reactions. These materials are essential elements in various applications, such as energy storage systems, catalysis, sensors, and electronic devices [1, 2]. Their ability to undergo reversible changes in oxidation states makes them valuable for storing and releasing energy, enabling the development of high-performance batteries and supercapacitors. Moreover, redox active materials find significance in the design of catalysts for promoting chemical transformations and in the creation of sensors for detecting analytes in various fields. The fundamental redox properties of these materials contribute to their versatility and make them indispensable in advancing technologies that rely on efficient electron transfer mechanisms [3, 4].

The ability of conductive polymers to transfer electrons, driven by their redox properties [5, 6] remains a hot debate among researches. These materials have a conjugated backbone with alternate single and double bonds. There are many examples of these types of conductive polymers such as polyaniline (PANI), polypyrrole (PPY) and poly (3,4-ethylenedioxythiophene) (PEDOT). It is this group of conductive polymers that can control the surface charge on the basis of their high conductivity. They are used in many applications including redox flow batteries, skin tissue engineering, wound treatment, high-performance supercapacitors besides antibacterial and antioxidant uses. This implies that they have diverse applications where changing the electrical charge on their surfaces is necessary [7].

Polyaniline boronic acid (PABA) is a conductive polymer that exhibits a distinctive blend of electrical conductivity and redox responsiveness [8–10]. This characteristic renders it a highly attractive option for novel technologies and multipurpose devices. PABA has attractive uses in a variety of industries, such as electrochemical devices, drug delivery systems, and sensors. One of PABA's most interesting features is its redox behavior, which is essential to its operation. Gaining insight into PABA's interactions with redox-active species—especially those found in aqueous environments—is essential to realizing its potential in a range of biological and technological applications [7, 11–17].

PABA's potential applications range from glucose biosensors to drug delivery systems for controlled release, highlighting the importance of understanding its redox behavior in the context of these applications [18]. PABA can also serve as electroactive components in energy storage devices, such as supercapacitors and batteries, where their redox processes are instrumental in storing and delivering electrical energy. An in-depth understanding of the redox behavior of PABA can thus have implications beyond the realms of sensors and drug delivery systems, extending into the domain of sustainable energy storage and conversion [19].

In previous studies, electrochemical tests of PABA polymer in various environments were performed [7, 12, 13, 15, 20, 21]. However, since the studies were generally related to sensors, the graphite electrode was coated with PABA, and then their performance was tested with different salt structures in acidic environments [21].

There were no CV tests performed with PABA in aqueous solutions according to the literature. Hence, in this study, it was aimed to prepare the solution of PABA polymer in aqueous media and subject it to CV tests and to guide

future studies based on its behavior. Additionally, in order to increase solubility, the CV behavior of PABA was tested with additives such as glucose and table sugar [19, 21, 22, 16], which were previously used in the literature. It was observed that the solubility of PABA is high in a basic environment and its half-wave peak potential is very low, while in an acidic environment, both solubility and peak potential are low. Therefore, the solution was prepared in a neutral environment.

2. Materials and Methods

2.1. Materials

3-Aminophenylboronic acid monohydrate (98 %) and Potassium Iodate (KIO_3) were obtained from Thermo Fisher Scientific Chemicals. Hydrochloric Acid (37 %, ACS reagent) was obtained from Fluka. Nitrogen gas was obtained from Asalgaz company. All electrodes were obtained from CH Instruments Inc. (Austin, Texas, USA). Glucose powder (chemical grade) was obtained from Sigma Aldrich. Typical market sugar is used as sugar addition. Potassium Carbonate (K_2CO_3) was obtained from AGC chemicals. Potassium chloride was obtained from Sigma Aldrich.

2.2. Electrochemical Studies

The main electrochemical method used to examine the redox characteristics of polyaniline boronic acid (PABA) in an aqueous environment was cyclic voltammetry (CV), with particular focus on how PABA interacts with glucose and table sugar solutions. Three electrode systems were used with a CHI608E model from CH Instruments, and CHI608E Electrochemical Analyzer software was used for the electrochemical tests. A schematic representation of three-electrode system is shown in Figure 1. The EIS and CV methodologies were applied. At scan rates from 5 to 500 mV/s, the electrodes' cyclic voltammetric behaviors were examined in aqueous solutions of 1 M KCl, and 1 M K_2CO_3 to establish the intended ionic environment. Potential range of the cell was between -1.2 to +0.8 V. Ag/AgCl and Platinium electrodes served as the reference and counter electrodes, while glassy carbon electrodes with a surface area of 0.7069 cm^2 served as the working electrodes. The CV testing involved the purging of N_2 gas. We conducted the experiments at room temperature. PABA, glucose, and table sugar were carefully dissolved in high-purity deionized water (DI water) to create solutions. Current-voltage profiles that showed PABA's redox activity in the presence of glucose and sugar solutions were the data gathered during the CV tests. By analyzing these profiles, peak potentials, peak currents, and electrochemical pathways were found, which shed light on how the addition of sugar affected the redox characteristics of PABA.
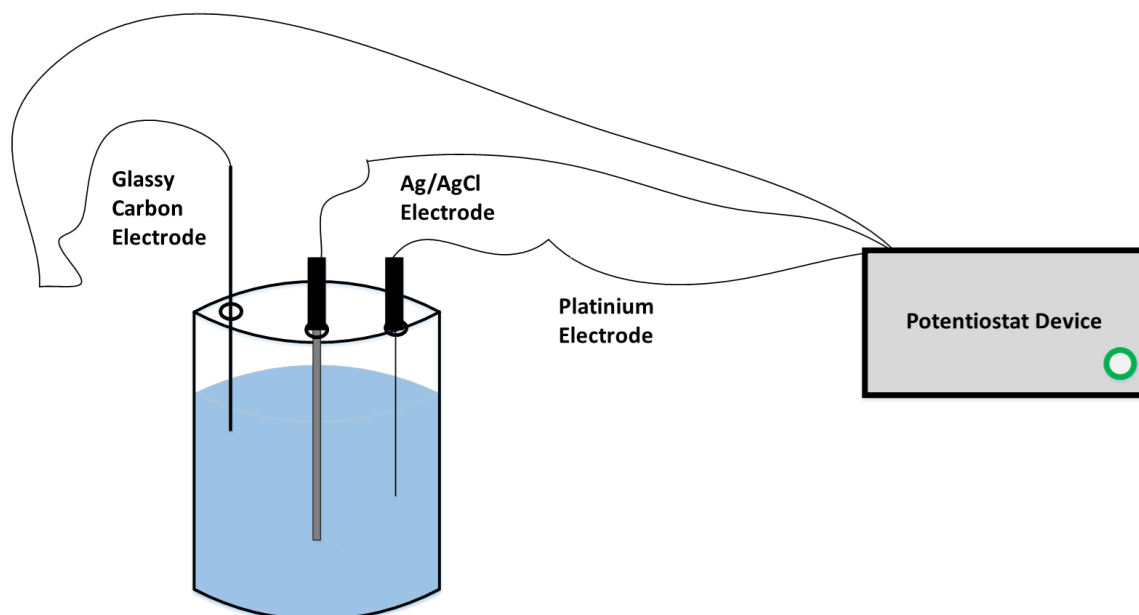
Figure 1. 3-electrode electrochemical cell system setup is schematically shown. Working electrode is glassy carbon electrode, reference electrode is Ag/AgCl electrode and counter electrode is Platinium electrode.

2.3. Synthesis of PABA

The synthesis procedure utilized in our study had been employed in a prior investigation [23]. KIO_3 was used to start the synthesis of polyaniline boronic acid (PABA). Hydrochloric acid (HCl) was used as the dopant to improve solubility and aid in the polymerization process. A nitrogen atmosphere was used to for the polymerization process. The reaction mixture was kept in an ice bath for a full day while the polymerization was taking place. During this time, there was a noticeable shift in color—the solution became a shade of purple. The successful polymerization of ABA into polyaniline boronic acid (PABA) is characterized by this color change. Following the completion of the polymerization procedure, contaminants and unreacted ABA were removed from PABA by precipitation and subsequent filtration. PABA was acquired with a substantial yield of 80% and to eliminate any remaining solvents, the purified PABA was vacuum-dried, producing a high-purity polymer. The chemical structure and purity of the synthesized PABA were verified via analytical technique: Fourier-transform infrared spectroscopy (FTIR). These investigations confirmed that PABA was successfully formed and guaranteed that it would be suitable for further electrochemical experiments.

3. Results

FTIR results for the monomers aniline boronic acid (ABA) and its polymer, PABA, are presented in Figures 2a and 2b. In the FTIR spectrum of PABA, a broad absorption at 3263 cm^{-1} indicates O-H stretching, and a peak at 1180 cm^{-1} suggests C-O stretching. Additionally, absorptions at 3460 cm^{-1} and 3380 cm^{-1} correspond to -NH stretching vibrations of ABA. During polymerization, we see absorption peaks, which move to higher wavenumbers, indicating that PABA has formed as expected, just like previous studies have shown [19, 24, 23].
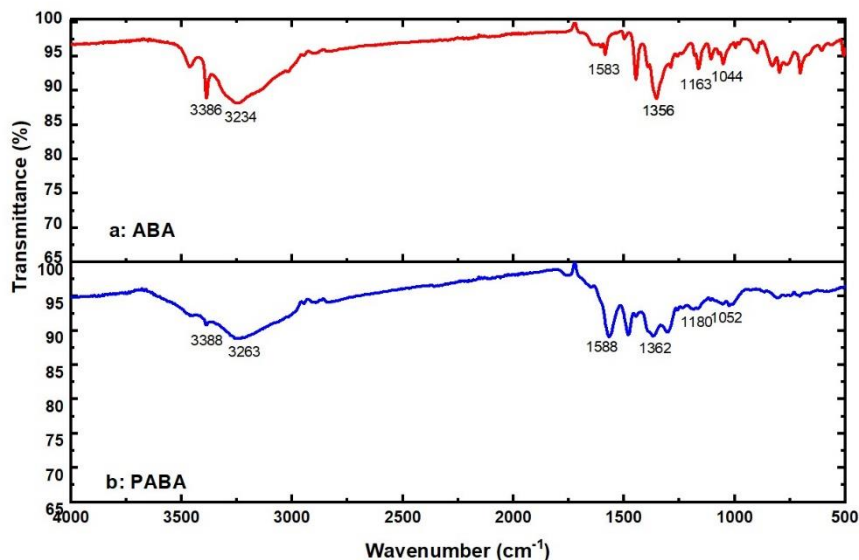
Figure 2. FTIR results of (a) ABA and (b) PABA polymers.

The electrochemical studies conducted to examine the redox characteristics of PABA in an aqueous solution with the addition of glucose, and table sugar solutions offer important insights into how PABA behaves when these redox-active species are present.

The redox activity of PABA was shown by CV experiments. In the absence of glucose and sugar solutions in Figure 3, two redox peaks—which represent the PABA oxidation and reduction processes—were seen in 1 M K_2CO_3. The standard hydrogen electrode (S.H.E.) is used as a potential parameter in this study. The oxidation peak voltage is -0.112 V, and the reduction peak voltage is -0.625 V for 500 mV/s scanning rate and half-wave potential is -0.368.5 V. The oxidation of PABA (0) to PABA(I) and the reduction of PABA(I) to PABA (0) were represented by the anodic and cathodic peaks that were obtained in the cyclic voltammograms, respectively. In Figure 4, oxidation and reduction peak points of each scan rate (5 mV/s, 20 mV/s, 100 mV/, 250 mV/s, and 500 mV/s) of Figure 3 were used. It shows the CV peak current versus square root of scan rate linear fit graph. According to this graph and using the Randles-Ševčík equation,

$$i_p = (2.69 \times 10^5)n^{3/2}AC(Dv)^{0.5} \tag{1}$$

the peak current (i_P) is determined by various factors, such as the number of moles of electrons transported in the reaction (n), the electrode's surface area (A), the concentration of the analyte in units of mol/cm^3 (C), the diffusion coefficient (D), and the scan rate of the applied voltage (v). The n value is taken as 1 for the number of electron transfer, A is taken as 0.07 cm^2, and concentration is taken as 0.000001 M, and the slope of the reduction side is 0.00217 which is equal to $\frac{i_p}{v^{0.5}}$. After calculations, the diffusion coefficient of 1 mM PABA in 1 M K_2CO_3 is found as 2.6x10^{-9} cm^2/s. The observed value appears to be relatively low when compared to other polymers that exhibit good solubility in aqueous environments. For instance, Poly(N-vinylbenzyl phthalimide-co-TEGSt) demonstrates a value of 2.33x10^{-7} cm^2/s [25]. Nevertheless, the low diffusible nature of polymers makes PABA a viable candidate for such experiments.
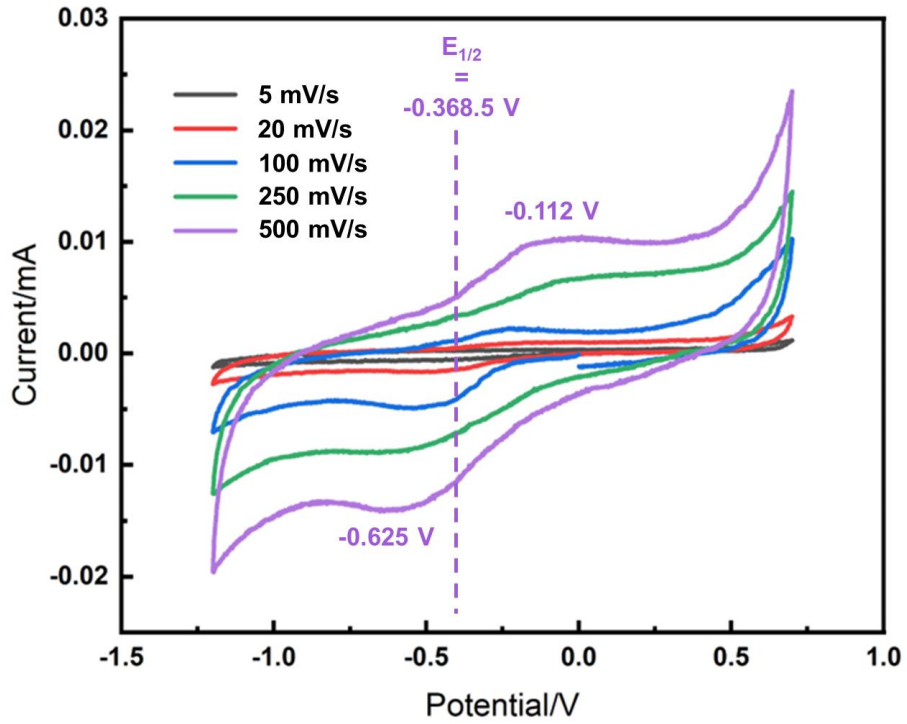
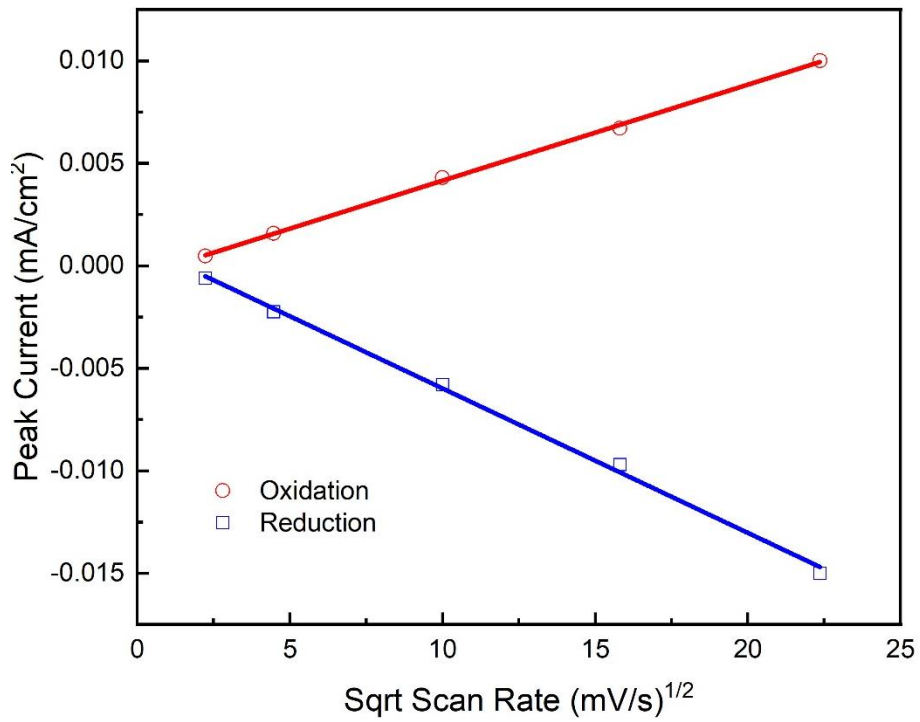**Figure 3.** Cyclic voltammetry of 1 mM PABA with 1 M K$_2$CO$_3$.

Figure 4. CV peak current versus square root of scan rate linear fit graph for oxidation and reduction peak currents of Figure 3, which shows 1 mM PABA with 1 M K$_2$CO$_3$.
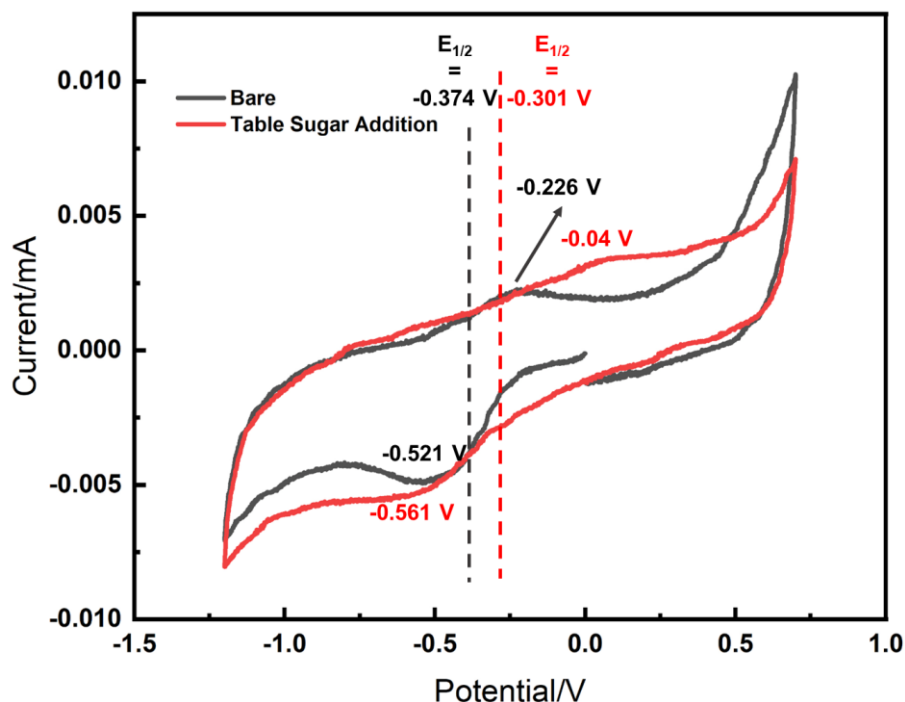
Figure 5. Cyclic voltammetry of 1 mM PABA with 1 M K_2CO_3 with addition of 1 mM table sugar, scan rate is 100 mV/s.

The effect of table sugar is shown in Figure 5. The redox behavior of PABA was negatively affected by the addition of table sugar to the aqueous environment in 1 M K_2CO_3. The redox peaks become lower, and the half-wave potential decreases after addition. However, the area between the peaks increases, so the area between peaks in a CV curve can be related to the overall capacity. The influence of table sugar on the redox behavior of PABA in a 1 M K_2CO_3 aqueous environment was negative, as evidenced by a reduction in redox peaks and a decrease in the half-wave potential upon addition. Despite these changes, the area between the peaks in a cyclic voltammetry (CV) curve increased, suggesting a potential relationship to the overall capacity.

In some instances, the addition of glucose led to an increase in peak currents and a slight shift in peak potentials (Figure 6(a)). This enhancement in redox activity is attributed to the interaction between glucose and PABA, which can facilitate electron transfer processes and promote the conversion between the leucoemeraldine and emeraldine oxidation states. The degree of enhancement varied with glucose concentration, with higher concentrations generally resulting in more pronounced effects [12, 26, 27].

On the contrary, specific sugar additions, notably sucrose and lactose, demonstrated a contrasting impact by diminishing peak currents and modifying peak potentials. The inclusion of these sugars introduced steric hindrance, influencing the kinetics of electron transfer, and resulting in the suppression of the redox activity of PABA. The extent of this suppression was found to be directly related to the concentration of sugars [28, 29].
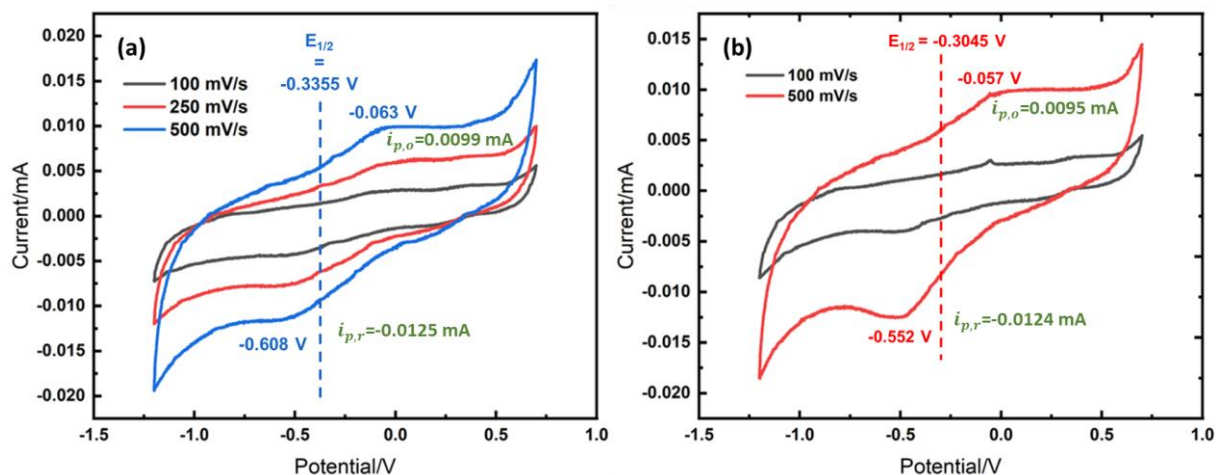
Figure 6. Cyclic voltammetry of 1 mM PABA with (a) 1 M KCl, (b) 1 M KCl and 1 M K_2CO_3 with the addition of 1 mM glucose.

To determine the impact of K_2CO_3 on PABA in comparison to KCl, an investigation was conducted, and the results are presented in Figure 6(b). The solution of Figure 6(b) was carefully prepared by mixing 1 M KCl and 1 M K_2CO_3 in distilled water as the solvent. To observe the clear difference between these solutions, Figure 7 shows the 100 mV/s scan rate CV comparison. PABA polymer can dissolve in basic solutions easily, but the reduction and oxidation points become invisible. Visible peaks can be observed in acidic conditions mostly, but in acidic conditions there were no solubility. Hence, neutral conditions would mostly be ideal for aqueous PABA solutions. In this study, to increase the pH value of KCl solution, 1 M K_2CO_3 solution had been added as drops (2 drops equal to 0.1 mL) to observe the effect of pH. There is a visible drop in both peak voltage and peak current, as evidenced by the significant difference in the half-wave potential. This variation indicates a distinct influence of the choice of supporting electrolyte on the redox behavior of PABA. The shift in peak potential and reduction in peak current suggest altered electrochemical kinetics and charge transfer processes, presenting the sensitivity of PABA to the nature of the supporting electrolyte. Further analyses and comparisons with alternative electrolytes will contribute to a comprehensive understanding of the factors influencing the redox behavior of PABA in different environments, aiding in the design and customization of PABA-based materials for specific electrochemical applications.
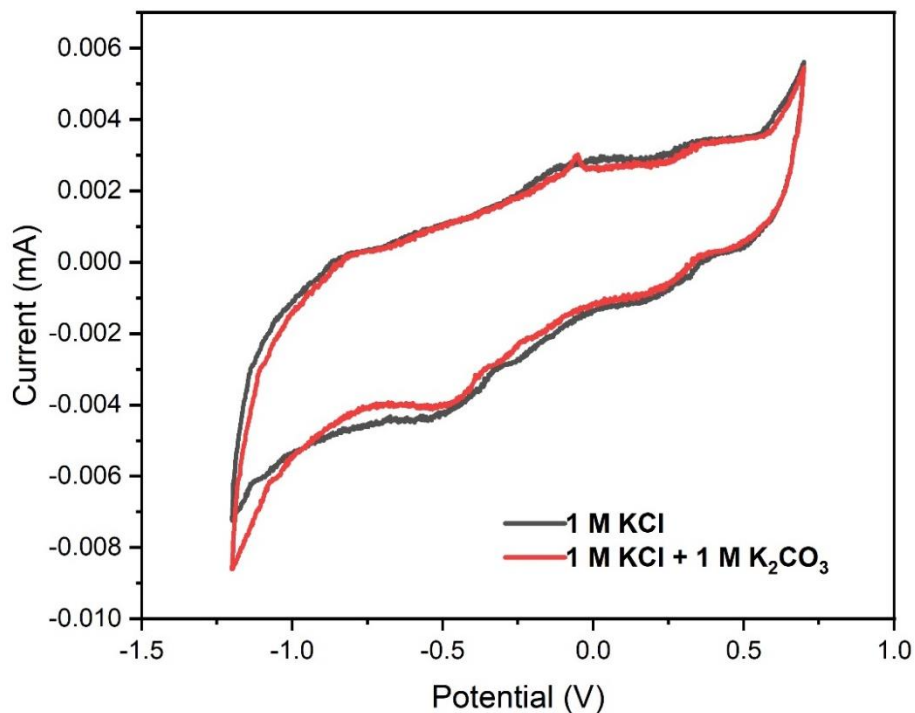
Figure 7. Cyclic voltammetry of 1 mM PABA with 1 M KCl, 1 M KCl and 1 M K$_2$CO$_3$ with the addition of 1 mM glucose, scan rate is 100 mV/s.

4. Conclusion

In conclusion, this study investigated the redox properties of polyaniline boronic acid (PABA) in an aqueous environment with a focus on its interaction with glucose and table sugar additions. Cyclic voltammetry experiments provided valuable insights into the electrochemical behavior of PABA, shedding light on its potential applications in batteries, sensors, drug delivery systems, and other electrochemical devices. The research revealed that the redox behavior of PABA was influenced by the addition of sugar species. The presence of glucose led to an enhancement in redox activity, manifested by increased peak currents and a slight shift in peak potentials. This enhancement was attributed to the facilitation of electron transfer processes and the promotion of conversion between the leucoemeraldine and emeraldine oxidation states of PABA. The degree of enhancement varied with glucose concentration, emphasizing the importance of understanding the concentration-dependent effects on PABA's redox behavior.

In contrast, the addition of particular sugars, had an inhibitory impact on the redox activity of PABA. The suppression observed was marked by reduced peak currents and altered peak potentials, which can be attributed to steric hindrance affecting the kinetics of electron transfer. Furthermore, the choice of supporting electrolyte was found to significantly impact the redox behavior of PABA. A notable drop in both peak voltage and peak current was observed when using K$_2$CO$_3$ compared to KCl, indicating the sensitivity of PABA to the nature of the supporting electrolyte. These findings provide a foundation for tailoring PABA's redox behavior for specific applications, including biosensors, drug delivery systems, and energy storage devices. Further investigations into the effects of different electrolytes and concentrations will enhance the versatility of PABA-based materials in diverse electrochemical applications.

5. Acknowledgements

6. References

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