

Scientific paper

Voltammetric Detection of Adenosine-5'-Diphosphate with a Carbon Paste Electrode Modified by a Hydroxyl Functionalized Imidazolium-Based Ionic Liquid

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Abstract

A hydroxyl functionalized ionic liquid (IL) 1-(3-chloro-2-hydroxy-propyl)-3-methylimidazolium tetrafluoroborate (PMIMBF₄) was used for the preparation of bulky-modified carbon paste electrode (IL-CPE), which was applied to the sensitive detection of adenosine-5'-diphosphate (ADP) in a pH 5.0 Britton-Robinson (B-R) buffer solution. IL-CPE is demonstrated to promote the oxidation of ADP with strong electrocatalytic ability. An irreversible oxidation peak appeared with adsorption-controlled process and enhanced electrochemical response on the IL-CPE. The electrode reaction parameters such as electron transfer coefficient (α) and electron transfer number (n) of ADP were calculated respectively. By using differential pulse voltammetry the oxidation peak current was linearly dependent on the ADP concentration in the range from 10.0 to 1000.0 $\mu\text{mol/L}$ with the detection limit as 3.23 $\mu\text{mol/L}$ (3σ). The proposed method showed good selectivity to the ADP detection without the interferences of coexisting substances, which could be further used for the synthetic sample detection.

Keywords: Carbon paste electrode; Adenosine-5'-diphosphate; Cyclic voltammetry; 1-(3-chloro-2-hydroxy-propyl)-3-methylimidazolium tetrafluoroborate

1. Introduction

As one of the most popularly used carbon electrode, carbon paste electrode (CPE) has been widely used in the field of electroanalytical chemistry and electrochemical biosensors with the advantages such as low cost, ease of fabrication, high sensitivity for detection and renewable surface.¹ Different kinds of modifiers can be mixed with graphite powder and binder to make the modified carbon paste electrodes, which greatly extend the applications in electrochemistry.² Recently ionic liquids (ILs) have been used as a new kind of modifier/binders in the preparation of carbon paste electrode.³ Due to their specific characteristics such as good chemical and thermal stability, almost negligible vapor pressure, good ionic conductivity and wide potential windows, ILs have been widely used

in the fields of electrochemistry.^{4,5} Liu et al. firstly introduced IL into the fabrication of carbon paste electrode, which exhibited excellent electrochemical performance.⁶ Then Maleki et al. widely studied the IL-based carbon paste electrode (IL-CPE) and applied to the electroactive substances detection.^{7,8} Our group also investigated the direct electrochemistry of redox proteins immobilized on the surface of IL-CPE or nanoparticle modified IL-CPE.^{9–11} Also the voltammetric determination of adenosine or guanosine were carried out on the N-hexylpyridinium hexafluorophosphate modified electrode¹² and multi-walled carbon nanotubes modified carbon ionic liquid electrode,¹³ respectively. Due to the presence of IL in the CPE, the modified electrode showed specific advantages such as higher ionic conductivity, wider potential windows, inherent catalytic ability and good anti-fouling capability.¹⁴

Adenosine-5'-diphosphate (ADP) is an ester of pyrophosphoric acid with the nucleoside adenosine, which is stored in dense bodies inside blood platelets and is released upon platelet activation. ADP can interact with a family of ADP receptors found on platelets and lead to further platelet activation.¹⁵ ADP in the blood can be converted to adenosine by the action of ceto-ADP synthases, which inhibits further platelet activation via adenosine receptors. ADP is also the end-product when ATP loses one of its phosphate groups located at the end of the molecule. The conversion of ATP and ADP plays a critical role in supplying energy for many processes of life. So it is important to establish sensitive method for the detection of the ADP concentration in the biological related samples.

In the present paper, a new hydroxyl functionalized IL 1-(3-chloro-2-hydroxy-propyl)-3-methylimidazolium tetrafluoroborate (PMIMBF₄) was synthesized and further used as the modifier for the preparation of IL-CPE. In general the physicochemical properties of ILs depend on the nature and size of both their anion and cation constituents. For example the solubility of ILs in the organic solvents depends on the dielectric constant of the solvent. However the solubility of ILs in water is highly dependent on the anion.¹⁶ The ILs with the hydrophilic anions such as Cl⁻, Br⁻, BF₄⁻, CF₃SO₃⁻ are often miscible with water. While the increase of alkyl side chain of the cation will result in the decrease of the solubility in water.¹⁷ Freire et al had discussed the mutual solubilities of water with imidazolium-based ILs systems,¹⁸ which indicated that both the cation and anion could affect the mutual solubilities of water and ILs. The anion plays the major role on their phase behavior and the cation alkyl side chain length and the number of hydrogen substitutions in the imidazolium cation have impacts in the mutual solubilities. The ILs synthesized in this paper contains short chain with a hydroxyl group and a hydrophilic anion of BF₄⁻, so it can be miscible with water. By mixing small amounts of PMIMBF₄ in the traditional carbon paste electrode, the IL-CPE was fabricated with the IL acted as the modifier to increase the whole properties of the CPE. The IL-CPE was characterized by different methods including scanning electron microscopy (SEM), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). A well-defined anodic oxidation peak of ADP at +1.36 V appeared on the IL-CPE and the electrochemical behaviors of ADP were carefully investigated. Under the selected conditions a new and sensitive differential pulse voltammetric (DPV) method for ADP detection was further established.

2. Experimental

2.1. Reagents

The 10.0 mmol/L stock solution of adenosine-5'-diphosphate (ADP, Shanghai Kayon Biological Tech. Co.

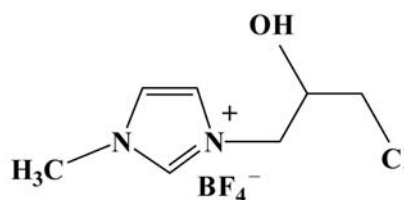
Ltd.) was prepared just before use and stored in 4 °C refrigerator. Graphite powder (average particle size of 30 μm) was obtained from Shanghai Colloid Chemical Company. 0.2 mol/L Britton-Robinson (B-R) buffer solutions with various pH values were used as the supporting electrolytes for the electrochemical measurements. All solutions were prepared with double-distilled water and all the other reagents were of analytical grade.

2.2. Apparatus

All the electrochemical experiments including cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS) were carried out using a CHI 750B electrochemical workstation (Shanghai CH Instruments, China). The traditional three-electrode system employed was composed of an IL-CPE (Φ = 4 mm) as working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum wire as auxiliary electrode. All the electrochemical experiments were carried out at 25 °C.

2.3. Synthesis of PMIMBF₄

Ionic liquid 1-(3-chloro-2-hydroxy-propyl)-3-methylimidazolium tetrafluoroborate (PMIMBF₄) was synthesized according to the reference.¹⁹ To a stirred solution of 1-methylimidazolium (0.25 mol) in ethanol (25 mL) at room temperature was carefully added fluoboric acid (0.25 mol, 45 wt% solution in water). After the addition of acid, the reaction mixture was cooled to room temperature and 3-chloro-propylene oxide (0.25 mol) was added dropwise with stirring. Then the reaction vessel equipped with a drying tube was irradiated in the water bath of the laboratory ultrasonic cleaning (ultrasonic power 100 W, frequency 40 kHz) at 30 °C for 2.5 h. The reactant was disappeared by TLC detection, and the solvent was removed under reduced pressure with heating at 60 °C followed by heating under high vacuum to yield a colorless liquid. The molecular structure of the final product was shown in scheme 1.



Scheme 1: The molecular structure of PMIMBF₄.

2.4. Fabrication of Modified Electrodes

The PMIMBF₄ modified CPE (IL-CPE) was prepared by mixing 0.27 g of PMIMBF₄, 3.2 g of graphite powder and 1.0 mL of liquid paraffin in a mortar. The homo-

geneous paste was packed into a cavity of glass tube with the diameter of 4.0 mm. The electrical contact was got with a copper wire connected to the paste in the tube and the surface of the prepared electrode was polished on a weighing paper just before use.

2. 5. Detection of ADP

The three-electrode system was immersed in a 10 mL electrochemical cell containing proper amount of ADP and 0.2 mol/L pH 5.0 B-R buffer solutions. After accumulation at 0.2 V in a still solution for 50 s, cyclic voltammetric experiments were performed in the potential range from 1.0 to 1.8 V with the scan rate as 100 mV/s. As for the differential pulse voltammetric (DPV) experiments, the optimal conditions were selected as sampling width (0.017) and pulse amplitude (0.05 V). After electrochemical measurements the IL-CPE can be regenerated by three cyclic sweeps between 1.0 V and 1.8 V at the scan rate of 100 mV/s in a blank B-R buffer solution to give a fresh electrode surface.

3. Results and Discussion

3. 1. Electrochemical Characteristics of the IL Modified Electrode

Electrochemical performances of CPE and IL-CPE were compared by recording the cyclic voltammograms in a 1.0 mmol/L $K_3[Fe(CN)_6]$ solution containing 0.5 mol/L KCl. As shown in Figure 1A, on the IL-CPE a pair of well-defined symmetric redox peaks appeared with the peak-to-peak separation (ΔE) of 103 mV (curve a). While on the CPE the ΔE value was 332 mV (curve b) with smaller redox peak currents. So the increased electrochemical response and better reversibility was got on IL-CPE, which was due to the present of good ionic conductivity of IL in the carbon paste. The influence of scan rate on the faradic current (I_p) of ferricyanide with IL-CPE was investigated and a good linear relationship between I_p with the square root of scan rate ($v^{1/2}$) was plotted in the range from 10.0 to 500.0 mV/s. So the electrode process was a semi-infinite linear diffusional-controlled process. By exploring the relationship of I_p with scan rate, the electrochemical effective area of IL-CPE was calculated as 0.24 cm² by the Randles-Sevcik equation.

Electrochemical impedance spectroscopy (EIS) was further used to investigate the interfacial properties of CPE and IL-CPE, which was performed in 0.01 mol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl solution with the frequency changed from 10⁵ to 0.1 Hz and the AC excitation amplitude as 5 mV. As shown in Figure 1B, the electron transfer resistance (Ret), which was derived from the semi-circle domains of impedance spectra, was got as 412.7 Ω on the CPE. This value was bigger than that of the reported va-

lue in the reference²⁰. The reason may be due to the different size of graphite powder used in the experiment. As indicated in the reference,²⁰ the larger and rougher graphite particles in the CPE will increase the resistances. In this paper graphite powder with the average particle size of 30 μ m was used, which was bigger than that of 5–10 μ m in the reference. Then the bigger Ret value was got. After mixing IL in the carbon paste, the Ret value decreased greatly to 4.51 Ω , so the presence of high ionic conductive ILs in carbon paste promoted the electron transfer of redox probe greatly.

The interface capacitance of the electrode was further calculated by using the equation of $C^{app} = I/Sv$, where I is the average of the positive and the negative charging current obtained from the cyclic voltammetric curves at 0.4 V that were performed in the phosphate buffer solution (0.05 mol/L, pH 7.4) between 0 and 0.6 V, S is the area of the electrode, v is the scan rate.²¹ The capacitance value of the IL-CPE was calculated as 403.02 μ F/cm², and that of the CPE was got as 7.53 μ F/cm². So the increase of the capacitance reflected the presence of IL film on the electrode surface, which acted as the double layer with increasing charge currents.

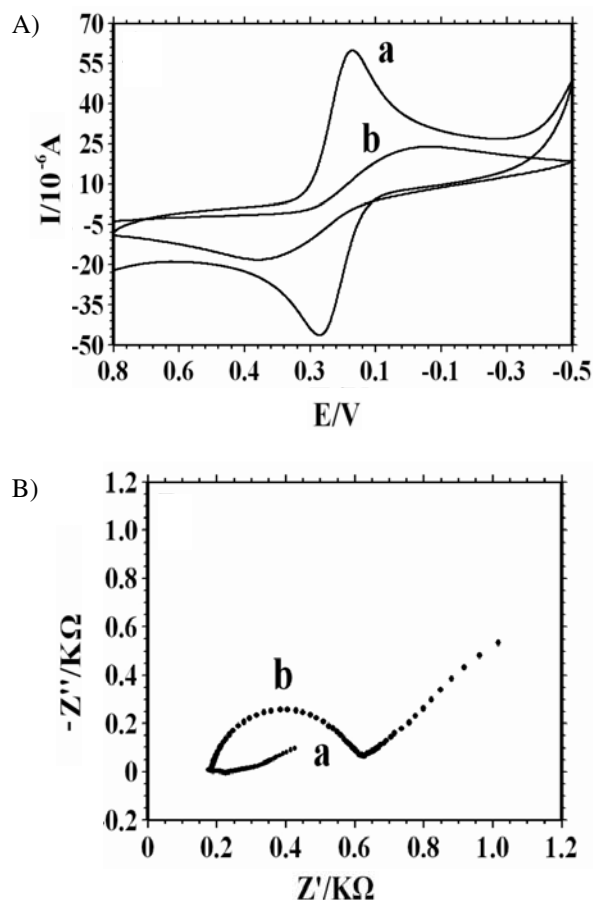


Figure 1: (A) Cyclic voltammograms of IL-CPE (a) and CPE (b) in solution of 1.0 mmol/L $K_3[Fe(CN)_6]$ and 0.5 mol/L KCl at the scan rate of 100 mV/s, (B) Electrochemical impedance spectra for IL-CPE (a) and CPE (b) in a solution of 10.0 mmol/L $[Fe(CN)_6]^{3-/4-}$ and 0.1 mol/L KCl with the frequencies swept from 10⁵ to 0.1 Hz.

3. 2. Cyclic Voltammetric Behavior of ADP on CPE and IL-CPE

Figure 2 showed the cyclic voltammograms of background solution (pH 5.0 B-R buffer) and 500.0 $\mu\text{mol/L}$ ADP in pH 5.0 B-R solution on CPE and IL-CPE, respectively. In pH 5.0 B-R solution no electrochemical responses appeared on the IL-CPE (curve a) and CPE (curve c). On the CPE a smaller oxidation peak of ADP appeared at +1.37 V (curve d). Under the same conditions a bigger oxidation peak appeared at +1.36 V (curve b) on the IL-CPE with the oxidation peak current increased for about 1.9 times. The enhancement of oxidation peak current proved the redox catalysis activity of IL-CPE. Based on the references,^{3,6} IL-CPE had exhibited the advantages including higher conductivity and inherent catalytic ability. So the use of IL as a modifier in the carbon paste facilitated the electron transfer rate between ADP and electrode. Multi-cyclic voltammetric results showed that the oxidation peak current decreased gradually with the increase of scan cycles, indicating the adsorption of ADP on the electrode surface.

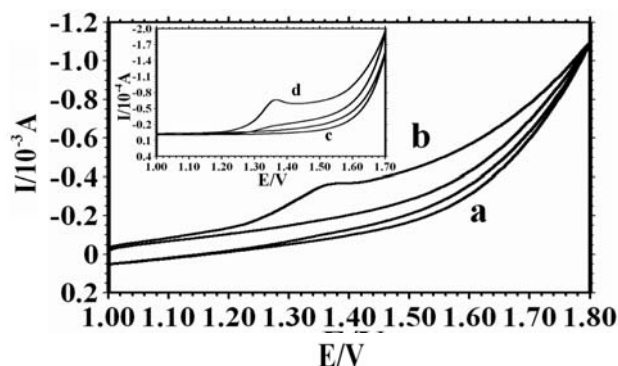


Figure 2: Cyclic voltammograms of pH 5.0 B-R buffer solution on IL-CPE (a) and CPE (c) and 500.0 $\mu\text{mol/L}$ ADP on IL-CPE (b) and CPE (d) after pre-concentration at 0.20 V for 50 s with the scan rate of 100 mV/s.

3. 3. Effect of pH

The influence of pH on the electrochemical response of ADP was investigated by cyclic voltammetry. A

stable and well-defined irreversible oxidation peak can be obtained in the pH range of 4.0–8.5. Figure 3 showed the relationships of the oxidation peak current and potential with buffer pH. It can be seen that the oxidation peak potential (E_{pa}) of ADP shifted to a negative direction with the increase of pH, indicating that protons took part in the electrode reaction. The E_{pa} value was linearly dependent on the buffer pH with the linear regression equation as $E_{\text{pa}}(\text{V}) = -0.052\text{pH} + 1.63$ ($\delta = 0.995$). The slope value of 52.0 mV/pH was close to the theoretical value of 59.0 mV/pH, indicating that equal amounts of protons and electrons transfer involved in the electrode reaction.²² The biggest oxidation peak currents appeared at pH 5.0, then the peak currents decreased gradually with the further increase of pH value. So pH 5.0 B-R buffer was used as the supporting electrolyte in the following experiments.

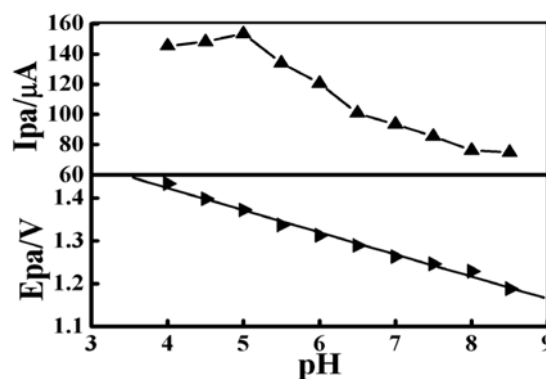
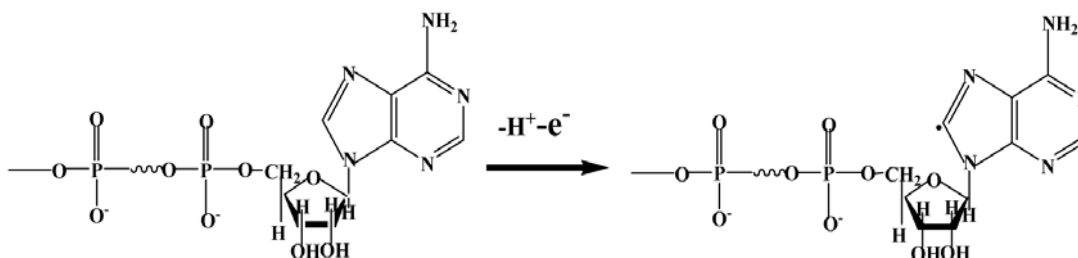


Figure 3: The relationships of the oxidation peak current (I_{pa}) and the oxidation peak potential (E_{pa}) with pH.

3. 4. Effect of Scan Rate

The influence of scan rate on the oxidation peak current and potential were investigated in the range from 10 to 500 mV/s. The oxidation peak current of ADP was proportional to the scan rate with the linear regression equation as $I_{\text{pa}}(\mu\text{A}) = 133.7 v(\text{V/s}) + 16.1$ ($\delta = 0.992$), indicating an adsorption-controlled electrode reaction process. Based on the following equation:²³



Scheme 2. Electro-oxidation process of ADP.

$$I_p = \frac{nFQv}{4RT} = \frac{n^2F^2A\Gamma_T v}{4RT}$$

where A is the effective area of the electrode, Q is the charge involved in the reaction, v is scan rate, Γ_T is the amount of the adsorbed analyte, and n , R , F and T have their common meanings. The value of n was estimated as 1.33, suggesting that totally one electron was involved in the oxidation reaction, which was in accordance with a reported result.²⁴ Also the surface coverage (Γ_T) of ADP was calculated to be 2.3×10^{-9} mol/cm². With the increase of scan rate the oxidation peak potential moved to a positive direction. The relationship of E_{pa} with $\ln v$ was further constructed as $E_{pa}(\text{V}) = 0.001 \ln v (\text{V/s}) + 1.16$ ($\delta = 0.991$). According to the Laviron's equation for a totally irreversible electrode process,²⁵ the values of the charge transfer coefficient (α) and the electrode reaction standard rate constant (k_s) were calculated to be 0.27 and 4.5×10^{-6} s⁻¹, respectively.

Based on the above results and according to the reference,²⁴ the electrode oxidation process of ADP can be proposed with the equation shown in scheme 2.

3. 5. Optimization of Experimental Conditions

Because PMIMBF₄ is a kind of hydrophilic ionic liquid, so the optimal amount of IL added in the carbon paste electrode was selected. By changing the ratio of IL with liquid paraffin and compared the electrochemical response in the ferricyanide solution, a final amount of 0.27 g was optimized in the preparation of IL-CPE. At this ratio IL-CPE exhibited a good stability in this solution with the electrochemical response did not changed after scanning in the ferricyanide solution for 40 circles at the scan rate of 100 mV/s.

Accumulation is a commonly used effective way in electroanalysis with increased sensitivity. When the accumulation potential was changed from 0.0 V to 0.9 V, the biggest oxidation peak current appeared 0.2 V, then the peak currents decreased gradually with the further increase of potential value. Hence 0.2 V was chosen as the accumulation potential. The oxidation peak current of ADP increased with the increase of accumulation time. When the accumulation time was above 50 s, the peak current turned to level off, indicating the accumulation of ADP on the surface of IL-CPE reached saturation, so the accumulation time was selected as 50 s in the experiment.

3. 6. Calibration Curve

The proposed electrode was further used for the ADP detection with the typical differential pulse voltammograms shown in Figure 4. Under the optimized conditions, the oxidation peak current of ADP increased linearly with its concentration in the range from 10.0 to

100.0 $\mu\text{mol/L}$ and from 100.0 to 1000.0 $\mu\text{mol/L}$, respectively. Two linear regression equations were calculated as $I_{pa}(\mu\text{A}) = -0.44C(\mu\text{mol/L}) + 0.23$ ($n = 5$, $\delta = 0.926$) and $I_{pa}(\mu\text{A}) = -0.06C(\mu\text{mol/L}) + 16.73$ ($n = 4$, $\delta = 0.997$). The detection limit was estimated to be 3.23 $\mu\text{mol/L}$ (3σ). The relative standard deviation (RSD) for six parallel measurements of 10.0 $\mu\text{mol/L}$ ADP was 3.6%, indicating the good reproducibility of the detection.

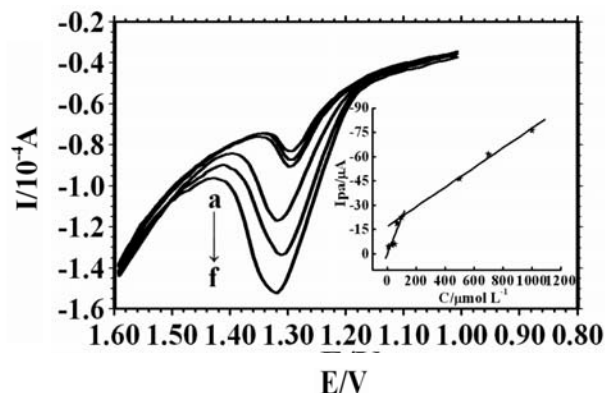


Figure 4: Differential pulse voltammograms of ADP at different concentrations (from a to f: 70.0, 100.0, 300.0, 500.0, 700.0, 1000.0 $\mu\text{mol/L}$); Inset is the calibration curve of the oxidation peak current (I_{pa}) with the ADP concentration.

3. 7. Selectivity of the IL-CPE

The influence of interferences on the detection of ADP was investigated. Table 1 showed the changes of the electrochemical responses of 500.0 $\mu\text{mol/L}$ ADP in the presence of the same concentrations of different coexisting substances in pH 5.0 B-R buffer solution. Most of interferences did not interfere with the current response of ADP. Hence, there is negligible interferences from other electro-active components.

Table 1. Influence of coexisting substances on the determination of 500.0 $\mu\text{mol/L}$ ADP ($n = 3$)

Coexisting Substance	Concentration ($\mu\text{mol/L}$)	Relative error (%)
L-cysteine	500.0	2.3
Arginine	500.0	3.7
Tyrosine	500.0	6.3
Tryptophan	500.0	1.0
Glutamic acid	500.0	-1.0
Leucine	500.0	0.2
Glycin	500.0	4.7
Valine	500.0	-0.5
Cytosine	500.0	0.7
Uracil	500.0	1.8
Thymine	500.0	-0.4
Mg ²⁺	500.0	-0.3
Zn ²⁺	500.0	0.1

3. 8. Repeatability and Stability of the Electrode

The repeatability and stability of the IL-CPE were also evaluated. The relative standard deviation (RSD) for the detection of 500.0 $\mu\text{mol/L}$ ADP was 3.5% for five electrodes prepared individually, confirming that the preparation of electrode had highly repeatability. The modified electrode was stored at room temperature for a period of time to evaluate its storage stability. After 5 days the modified electrode remained 97.5% of its initial current value and 25 days with 93.4% of the initial responses, which indicated the IL-CPE had good storage stability. The response of 500.0 $\mu\text{mol/L}$ ADP was determined every 4 days. The results showed that the oxidation peak current only decreased by 3.2% of the initial value after 25 days, which indicated a reliable cyclic voltammetric response with almost constant sensitivity for the whole period of experiments.

3. 9. Determination of Artificial Samples

This method was applied to the determination of two artificial samples, which were prepared by mixing different kinds of foreign substances with ADP. The results of the determination were listed in Table 2 with the recoveries of ADP ranged from 97.2 to 99.8%, demonstrating the accuracy of the proposed method.

Table 2. Determination results of ADP in artificial samples (n = 3)

Sample	Added ($\mu\text{mol/L}$)	Found ($\mu\text{mol/L}$)	Recovery (%)	Relative error (%)
1	200.0	194.3	97.2	-2.9
2	400.0	398.5	99.6	-0.4
3	600.0	598.6	99.8	-0.2
4	800.0	796.4	99.6	-0.5

Sample contains 0.1 mmol/L L-leucine, L-tryptophan, thymine and 1.0 mmol/L Na^+ , K^+

4. Conclusion

IL 1-(3-chloro-2-hydroxy-propyl)-3-methylimidazolium tetrafluoroborate (PMIMBF_4) was mixed in the carbon paste to get a new IL-CPE. Compared with the former used ILs in the electrode preparation such as N-hexylpyridinium hexafluorophosphate (HPPF_6)¹² or 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF_4)¹³ the IL used in this paper was a functionalized IL with hydroxyl group and the fabricated CILE also exhibited good electrochemical performances. Due to the specific characteristics of IL such as high ionic conductivity and strong adsorption ability, IL-CPE showed remarkable redox catalysis effect on the oxidation of ADP. The electrochemi-

cal oxidation of ADP was promoted with an adsorption-controlled irreversible process. Under the selected conditions a good linearity was observed between the DPV oxidation peak current and the ADP concentration in the range from 10.0 to 1000.0 $\mu\text{mol/L}$ with a detection limit of 3.23 $\mu\text{mol/L}$ (3σ). The prepared IL-CPE showed wider linear range and lower detection limit for the ADP detection with excellent reproducibility and easy preparation procedure.

5. Acknowledgement

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Povzetek

Ionsko tekočino (IL) s hidroksilno funkcionalno skupino 1-(3-kloro-2-hidroksi-propil)-3-metilimidazolijev tetrafluoroborat (PMIMBF₄) smo uporabili za pripravo modificirane elektrode iz ogljikove paste (IL-CPE), s katero smo z visoko občutljivostjo detektirali adenzin-5'-difosfat (ADP) v pH 5.0 Britton-Robinson (B-R) puferski raztopini. IL-CPE pospešuje oksidacijo ADP z močno elektrokatalitsko sposobnostjo. Pojavil se je ireverzibilni oksidacijski vrh z adsorpcijsko kontroliranim procesom in povečanim elektrokemijskim odzivom na IL-CPE. Izračunali smo parametra elektrodne reakcije: koeficient elektronskega prenosa (α) in število prenesenih elektronov (n). Z uporabo diferenčne pulzne voltometrije smo pokazali, da je oksidacijski tok vrha linerano odvisen od ADP koncentracije v območju 10,0 do 1000,0 $\mu\text{mol/L}$ z mejo zaznave pri 3,23 $\mu\text{mol/L}$ (3σ). Predlagana metoda je pokazala dobro selektivnost za detekcijo ADP brez vpliva interferenc prisotnih spojin, kar bi se lahko uporabljalo tudi pri detekciji sintetičnih vzorcev.