

All-solid-state carbonate-selective electrode based on screen-printed carbon paste electrode

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Abstract. A novel disposable all-solid-state carbonate-selective electrode based on a screen-printed carbon paste electrode using poly(3-octylthiophene-2,5-diyl) (POT) as an ion-to-electron transducer has been developed. The POT was dropped on the reaction area of the carbon paste electrode covered by the poly(vinyl chloride) (PVC) membrane, which contains N,N-Dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide as a carbonate ionophore. The electrode showed a near-Nernstian slope of -27.5mV/decade with a detection limit of 3.6×10^{-5} mol/L. Generally, the detection time was 30s. Because these electrodes are fast, convenient and low in cost, they have the potential to be mass produced and used in on-site testing as disposable sensors. Furthermore, the repeatability, reproducibility and stability have been studied to evaluate the properties of the electrodes. Measurement of the carbonate was also conducted in human blood solution and achieved good performance.

Keywords: carbonate-selective electrode; all-solid-state; carbon paste electrode; poly(3-octylthiophene-2,5-diyl)

1. Introduction

Carbonate exists in many places such as ocean, industrial wastewater, and in environmental samples. Moreover, carbonate is an indispensability part of global carbon cycle and has a great influence on carbon dioxide emission and carbon balance. In particular, carbonate in blood helps maintain the balance of acid and base. Variations in the concentration of carbonate indicates abnormal conditions in human body. Therefore, the rapid and accurate detection of carbonate is of great importance [3,4].

Carbonate ions in water can have three forms: carbonate ion (CO_3^{2-}), hydrogen carbonate (HCO_3^-) and carbon dioxide (CO_2), and there is an equilibrium among them. Many methods have been proposed for detecting carbonate, for example optical sensors, titration, ion chromatography and others [5-7]. However, these methods are usually conducted in a laboratory and require expensive equipment, complex sample treatment and technical expertise. Furthermore, these methods are not suitable for in situ measurements.

As a reliable and quick type of technology, an ion-selective electrode (ISE) provides a method for the quantification of ions including carbonate. ISEs with neutral carrier-based polymeric membranes have been developing for decades [8, 9]. Many different ion sensors have been reported [10-12]. However, most carbonate-selective electrodes are of the traditional inner-liquid-electrolyte variety, and are inconvenient and non-portable. All-solid-state ISEs have been widely used in laboratories and industry because of their miniaturization and suitability for mass production. For example, they have been used in point-of-care devices and in other on-site testing [13, 14].

An ion-to-electron transducer layer is an important part for fabricating the all-solid-state ISE. The first proposed solid contact conductive polymer used polypyrrol(PPy) as the transducer for sodium detection [15]. Some other conductive polymers such as polythiophene (PT), polyaniline (PANI) and their derivatives have also been used as ion-to-electron transducers [16-18]. Among them, PEDOT(PSS) was the most popular one used in all-solid-state ISE. Its mechanism has been studied for cation detection [19, 20]. All-solid-state ISE for anion detection, on the other hand, are rarely mentioned. Poly(3-octylthiophene-2,5-diyl)(POT) is a conductive polymer that can be used both in cation and anion detection [21, 22].

Most ISEs were developed based on platinum, gold, or glass carbon, and are expensive and difficult to be applied widespread [23-25]. This paper first reports an all-solid-state screen-printed carbonate-selective electrode based on carbon paste electrode with POT as conducting polymer. Screen-printed technology was used to fabricate the carbon paste electrode substrate. POT is a solid-contact conducting polymer used as an ion-to-electrode transducer. It was coated on the reaction area of carbon paste electrode and covered by poly(vinylchloride) (PVC) membrane. Plasticized PVC was chosen as the membrane according to a common membrane matrix. The sensitive membranes were prepared with a molecular tweezer-type neutral carrier N,N-Dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide as the carbonate selective ionophore. Finally, the potential responses were tested and other performance characterizes were evaluated.

2. Experimental Section

2.1. Materials

N,N-Dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide (carbonate ion selective ionophore VII, CAS NO. 222310-82-9), high-molecular-weight poly(vinyl chloride) (PVC, CAS NO. 9002-86-2), Poly(3-octylthiophene-2,5-diyl) (POT, CAS NO. 104934-51-2), Bis(2-ethylhexyl) adipate (DOA, CAS NO. 103-23-1), Tridodecylmethylammonium chloride (TDMACl, CAS NO. 7173-54-8) were obtained from Sigma-Aldrich. NaHCO₃, NaCl, NaBr, Na₂SO₄, NaNO₃, NaNO₂, ethyl acetate and chloroform (CHCl₃) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. They were all analytical reagents. Cyclohexanone (CHA) was purchased from Aladdin reagent Co., Ltd, People's Republic of China.

Electronic carbon paste(ED-423SS) and diluents (SBJ-5) were obtained from Kunshan Taixuan Electronic Technology Co, Ltd, People's Republic of China. Polypropylene sheets as the carbon paste substrate were purchased from Shanghai Bianlu Industrial Co, Ltd, People's Republic of China. Deionized water was always used in the experiments.

2.2. Apparatus

The potentiometric measurement was obtained with a CHI660 Electrochemical Work Station. The screen-printed carbon paste electrodes were obtained with an AT-60PD digital electric flat screen printer. The pH of solution was obtained with a Mettler-Toledo pH electrode. The reference electrode was the Ag/AgCl electrode obtained from Tianjin Aida Hengsheng Technology Developing Co, Ltd, People's Republic of China.

2.3. Fabrication of the electrode

The carbon paste electrodes were screen-printed on polypropylene sheets by a screen-printer. The carbon electrodes were printed with carbon ink and dried at 120°C for 90 minutes as described in [26-28]. The size of the electrode is 40mm*10mm, while the reaction area has a diameter of 3.2mm. Before fabricating the sensor, clean the electrode substrate with deionized water for removing loose carbon. After dried at room temperature, for each electrode, a POT layer was dropped on the reaction area of carbon paste electrode. CHCl₃ was used as solvent for POT. The concentration is 3.6mg/ml. Keep the electrode in dark at room temperature.

A cocktail of carbonate ionophore VII (5.1%, w/w), DOA (56.8%, w/w) as a plasticizer, PVC (36.9, w/w) as a membrane matrix and TDMACl (1.2%, w/w) as an anion exchanger was dissolved in CHA. Exactly 28.08mg PVC were dissolved in 0.3mL CHA. Then 0.14 ml ethyl acetate were added to the cocktail. Shake the cocktail to mix it evenly. Store the membrane solutions in 4°C refrigerator before use.

A 1.5uL quantity of POT was coated on the reaction area and then covered by 2uL PVC membrane after 2 hours of drying. The thickness of POT was about 10μm and PVC membrane was approximately 40μm. The electrode with the membrane was dried at room temperature for 24 hours without light to make sure that the membrane is dry and uniform. Finally, a transparent as an insulation layer was pasted on the top with a reaction area whose diameter is 2mm. The structure of the screen-printed carbonate electrode is shown in Fig.1.

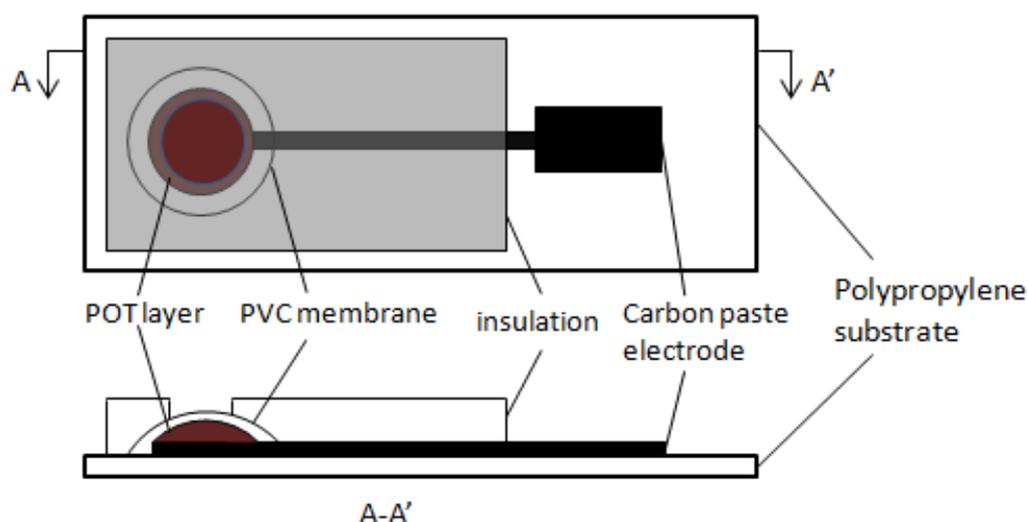


Fig.1. A schematic of screen-printed carbonate electrode.

2.4. Evaluation of the potentiometric response

The potentiometric responses were obtained with a two-electrode system. The working electrode

was the carbonate electrode made as described above. The reference electrode was the Ag/AgCl commercial reference electrode. The potential was tested by electrochemical work station. The response time was 30 s and the test solution was 5mL. All measurements were obtained at room temperature of about 25°C. The selectivity experiments were performed with the fixed interferential ion method.

3. Results and discussion

3.1. Potentiometric characterization

The potential response curve of the carbonate-selective electrode in test solutions is recorded. The response time of the sensor is 30 s until the output of the sensor reached equilibrium. A fast response is one of the main advantages of this sensor.

The test solution has different concentrations of NaHCO₃ in 0.1 mol/L Tris-H₂SO₄ as background electrolyte with a pH of 8.6. The dissolving of atmospheric CO₂ in solution was not considered because the experiment was performed within 30 minutes. The electrodes with the trifluoroacetophenone derivatives detecting carbonate only used under alkaline pH conditions [29]. When measured with serum sample (pH=7.4), the electrode should be diluted with a high-pH buffer.

The calculation curve of the electrode is shown in Fig. 2. The slope is about -27.5mV/decade which is slightly lower than the theoretical Nernstian response. The electrode exhibited a working concentration range of 3.6x10⁻⁵ to 2.5x10⁻³mol/L. With other plasticizers, such as dioctyl subacate (DOS) and 2-nitrophenyl octyl ether (NPOE), the slopes of the electrodes are similar and close to the theoretical values.

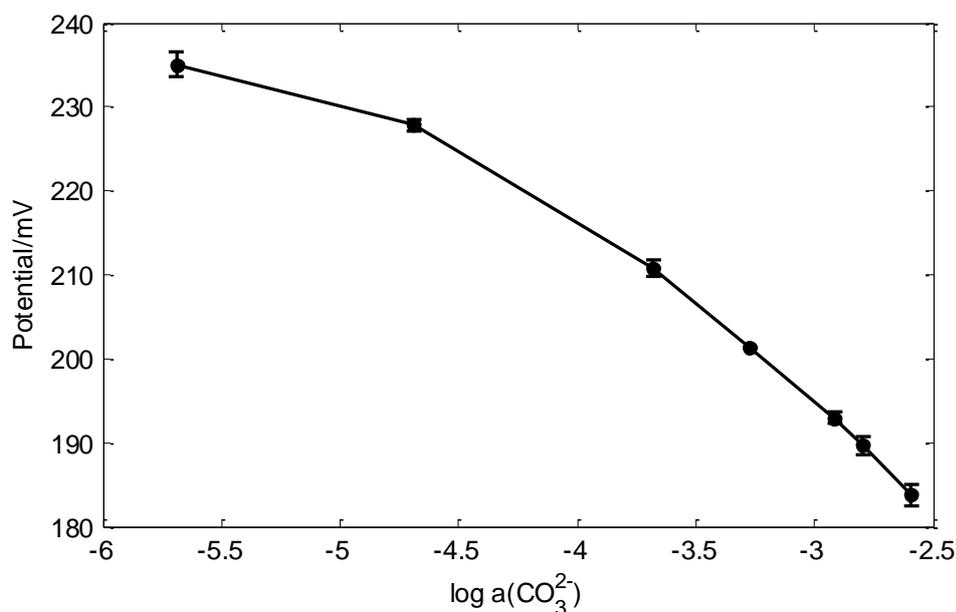


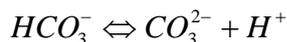
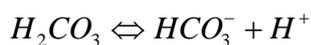
Fig. 2. The calculation curve of the screen-printed carbonate electrode in carbonate solution with Tris-H₂SO₄ as background.

3.2. Dynamic effect

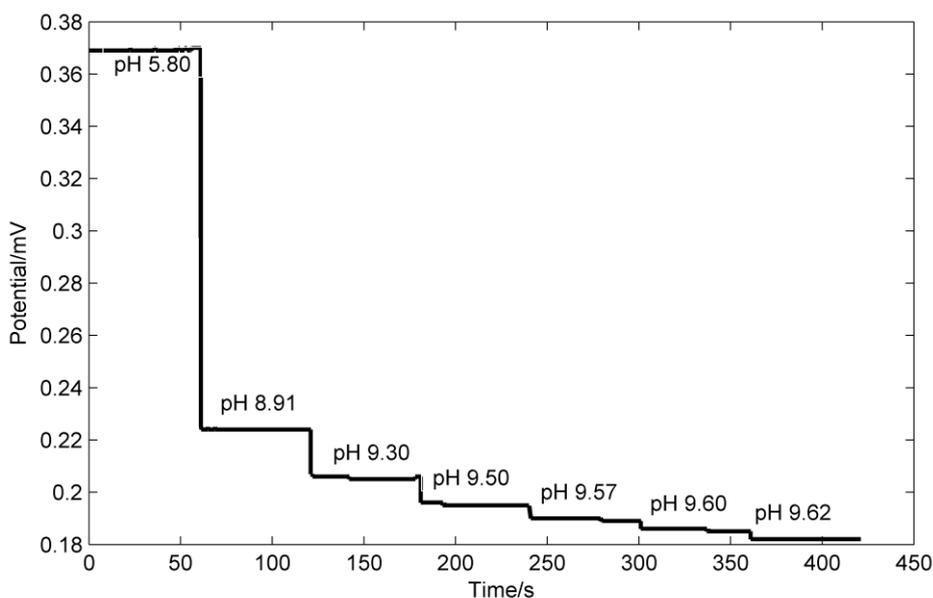
The potentiometric response was performed by adding 100 μ L 1mol/L NaHCO₃ stepwise to 100mL deionized water. The step responses to varying NaHCO₃ lead to the changes in the carbonate concentration. By adding of NaHCO₃, the pH of the sample changed. The pH also had a direct effect on the actual concentration of the carbonate. An independent pH meter was used to monitor the variation. The EMF and pH of the solution should be detected at the same time.

The dynamic response curve and the corresponding calibration curve are presented in Fig.3.

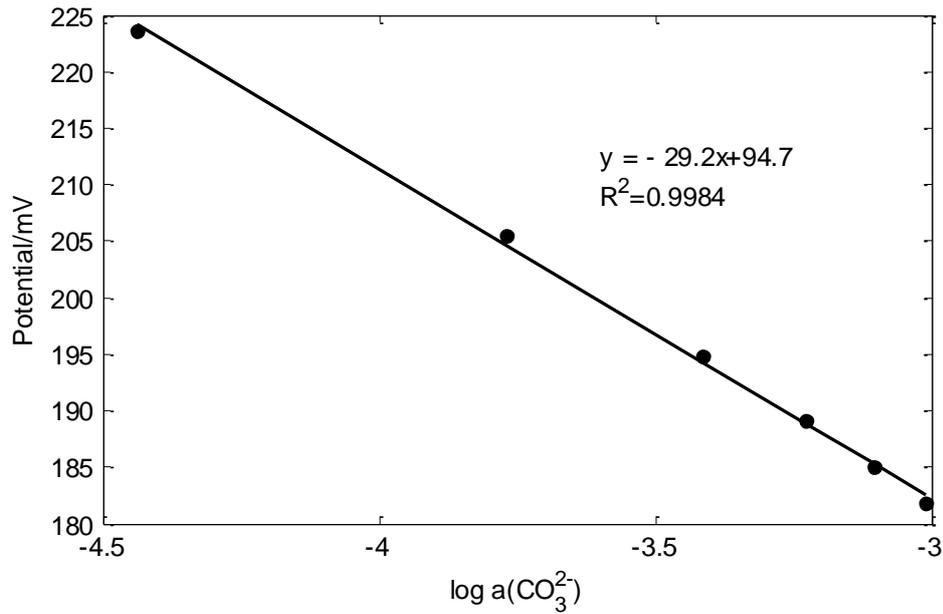
The actual activity of the carbonate can be obtained according to the following equilibrium:



When the system is in equilibrium, in principle, any component of the carbonate system (CO₂, HCO₃⁻, CO₃²⁻) can be calculated given the pH and the other component. The dissociation constants of carbonic acid K₁ and K₂ are equal to 10^{-6.35} and 10^{-10.33}, respectively at 25°C [30].



(a)



(b)

Fig. 3. Dynamic response curve (a) and corresponding calibration curve (b) of the carbonate electrode to different NaHCO₃ concentrations in deionized water.

3.3. Selectivity coefficients

The selectivity coefficients for common ions were determined by the fixed interference ion method. The test solution was in the range of 10^{-7} to 10^{-1} NaHCO₃ without Tris-H₂SO₄. The pH was also recorded to calculate the actual activity of the carbonate. The experiment was carried out under 25°C. The results of potentiometric log selectivity coefficients for different ions respectively are: $\log K_{CO_3^{2-}, Cl^-} = -4.7$, $\log K_{CO_3^{2-}, Br^-} = -4.6$, $\log K_{CO_3^{2-}, NO_3^-} = -3.2$, $\log K_{CO_3^{2-}, NO_2^-} = -2.7$, and $\log K_{CO_3^{2-}, SO_4^{2-}} = -5.2$.

The results are slightly lower than those of the liquid-contact electrodes [3]. It can be seen that the selectivity was reduced when the structure of the ISE altered from a liquid-contact to a solid-contact. However, the selectivity is good enough for carbonate detecting, especially in human blood. Furthermore, the all-solid-contact ISE has advantages over the liquid-contact one in terms of convenience and applicability.

3.4. Repeatability, reproducibility and stability

To evaluate the repeatability of the carbonate ISE, three sensors were prepared. Each sensor was measured three times in three different standard solutions (i.e. 25, 50 and 100 mM) with Tris-H₂SO₄ as the background. The testing results, along with their mean values and the relative standard deviations (RSD), are shown in Table 1.

The reproducibility was measured with 10 carbonate ISEs in four different concentrations with Tris-H₂SO₄ of pH=8.6 as background electrolyte. The slope of every electrode (nos. 1-10) is shown in Table 2. The mean value of slope is 28.0mV/decade and the standard deviation is 1.8mmol/L. In

order to get a better result, the layer thickness of the relevant materials and the measured area exposed by insulation should be fixed while fabricating.

The long-term stability of the carbonate electrode was evaluated with the testing solutions as mentioned above. The electrodes were stored in a dark, dry place at room temperature. The slopes of the carbonate electrode within three weeks are shown in Fig. 4. It can be seen that the carbonate electrode has a fairly good stability and can be stored before use.

Table 1. Repeatability of the carbonate electrode.

c (NaHCO ₃) (mM)	No. 1		No. 2		No. 3	
	Mean (mM)	RSD (mM)	Mean (mM)	RSD (mM)	Mean (mM)	RSD (mM)
25	25	0.8	25	0.8	25	1.4
50	48	1.1	49	0.2	52	0.9
100	108	4.6	97	1.3	101	4.3

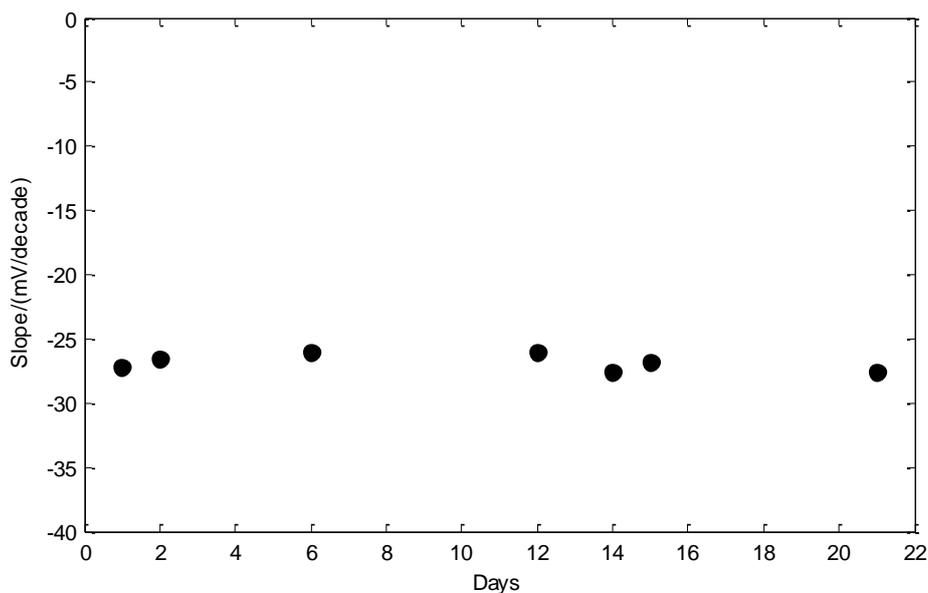


Fig. 4. The long-term stability of carbonate electrode.

Table 2 Reproducibility of the carbonate electrode

No	1	2	3	4	5	6	7	8	9	10
Slope	-29.8	-26.6	-30.2	-28.6	-26.1	-26.9	-27.6	-30.9	-27.2	-26.2

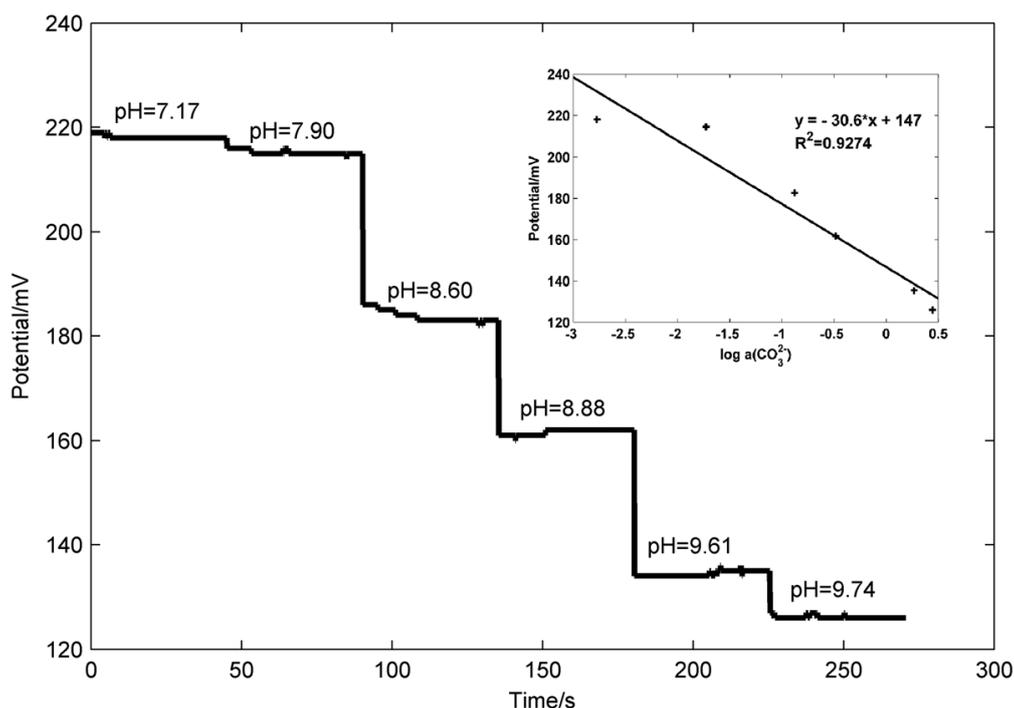


Fig. 5. The detection of carbonate in human blood solution.

3.5. Application in human blood solution

The evaluation of applicability of the carbonate ISE was based on human blood. The experiment was done in the dynamic effect mode described in section 3.2. The pure blood solution was tested first. After that, 100 μ l NaHCO_3 (100 mmol l^{-1}) was added each time to the solution. The potential of the carbonate sensor and the pH of the solution were measured at the same time, and the procedure was repeated four times. The response and calibration curves (upper-right-hand corner) are shown in Fig. 5. The calibration curve in the figure shows a linear trend, and this result indicates the potential that this electrode has for measuring carbonate in human blood.

4. Conclusion

An all-solid-state carbonate-selective electrode was designed and developed in this paper, with POT used as conducting polymer and a PVC membrane as membrane matrix. Screen-printed technology was applied and a carbon paste electrode was selected due to its low cost and suitability of mass production. The POT was used as the ion-to-electron transducer and showed excellent conductivity. A near-Nernstian response with the slope of 27.5mV/decade in the working range from $10^{-4.44}$ to $10^{-2.5}$ mol/L was obtained. The repeatability and reproducibility were evaluated to demonstrate the excellent property of the disposable carbonate electrode. The carbonate was also measured with the electrode in a human blood solution, and the results indicate the electrode's potential for the measurement of carbonate in human blood.

The screen-printed carbonate electrode has low-cost and can be mass produced. In addition, it is fast and easy to test. Therefore, the electrode can be commercialized as a disposable sensor for on-site testing, in areas such as point of care test and oceanic carbon detection. In the future, screen-printed reference electrodes can be made based on the carbonate electrodes. Both electrodes

could be used for making miniature sensors and fast measurements.

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