Article

Fabrication of an All-Solid-State Carbonate Ion-Selective Electrode with Carbon Film as Transducer and Its Preliminary Application in Deep-Sea Hydrothermal Field Exploration

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Abstract: Real-time measurements of carbonate ion concentrations in the ocean are critical to advancing marine environmental monitoring and research into deep-sea hydrothermal activity. Herein, we report the first example of deep-sea hydrothermal field exploration using a carbonate ion-selective electrode (ISE). The novel carbonate ISE was composed of a Ni wire as substrate, carbon film as transducers and carbonate-selective membrane layers. This paper describes the preparation process of the electrode and characterises its performance via scanning electron microscopy (SEM) and electrochemical analysis. The detection limit of the electrode for CO_3^{2-} is 2.821×10^{-6} mol/L, the linear response range is 1.0×10^{-5} – 1.0×10^{-1} mol/L and the Nernst slope was -30.4 mV/decade. In April 2021, the carbonate ISE was mounted on multi-parameter sensors with pH and Eh (redox) electrodes for the search of hydrothermal activity at the Southwest Indian Ridge. The simultaneous potential anomalies appeared at this carbonate electrode with the pH and Eh electrodes when passing through the hydrothermal field. The study of the hydrothermal field was supported by the in situ camera video and the sulphide samples. Additionally, the carbonate electrode provides enhanced information of water chemistry for the study of the hydrothermal field.

Keywords: ion-selective electrode; carbonate determination; carbon film; hydrothermal field

1. Introduction

Carbon dioxide is one of the important greenhouse gases in the atmosphere, with around 28% of atmospheric CO_2 being dissolved in seawater [1]. In recent years, as atmospheric carbon dioxide levels have increased, the production of excess carbonate ions has led to the frequent acidification of seawater, and had a significant impact on marine ecosystems [2–4]. In addition, hydrothermal-associated CO_3^{2-} enrichment is a hallmark feature of hydrothermal fluid, where dissolved CO_2 concentrations may be tens of times higher than in seawater, with significant implications for the global carbon cycle and climate change [5–7]. Therefore, accurate knowledge of carbonate levels in seawater is necessary to maintain the balance of marine ecosystems, while the implementation of real-time monitoring of carbonate ion concentrations in hydrothermal fluids is a major advance in the detection of hydrothermal fields [2,3,8–10]. Most of the commonly used methods for determining carbonate concentrations rely on laboratory analytical instruments such as gravimetric methods, colour change, equilibrium pressure, gas chromatography, infrared spectrophotometry and coulometric titration [11–17]. These analytical methods require sample pre-treatment, which is a complex, time-consuming and insensitive process, cannot

meet the demands of long-term field monitoring. In contrast, all-solid-state ion-selective electrodes are of increasing interest due to their ease of manufacture, cost effectiveness, portability and high sensitivity [18].

Various researchers have made attempts to fabricate carbonate electrodes. Zhao et al. fabricated an all-solid carbonate electrode by using $\text{Ag}_2\text{CO}_3\text{-BaCO}_3$ as a sensitive layer and applied it to heat exchange water analysis [19]. Mendecki et al. altered the sensor's conditioning protocol to fabricate a carbonate sensor with an extremely low detection limit [20]. Mei et al. described the polymeric membrane ion-selective electrodes for determination of carbonate [21], while Li et al. developed a novel disposable all-solid-state carbonate-selective electrode based on a screen-printed carbon paste electrode [22]. Nevertheless, most of the electrodes prepared by these methods have a narrow linear range, are inherently expensive and are non-resistant to impurity ions in seawater. To our knowledge, no carbonate electrodes have been reported for application in long-term deep-sea environmental monitoring and deep-sea hydrothermal activity studies.

Herein we report the development of a novel all-solid-state carbonate ion-selective electrode (ISE) by using a Ni wire as the substrate, carbon film as the interlayer and polymeric membrane as sensitive layer. The ISE had a linear range of 10^{-5} M to 10^{-1} M, a response time of less than 1 s, were resistant to seawater interference and can be used in marine environments. The manufacturing process of the ISE is simple; the completed product was 0.5 mm in diameter and 6–12 mm in length and can be easily integrated into the same sensor device with other electrodes to monitor multiple ions simultaneously. The prepared electrodes enable real-time measurement of carbonate ion concentrations in hydrothermal fluid and long-term monitoring of carbonate ion concentrations in the ocean.

2. Materials and Methods

The process of preparing an all-solid carbonate electrode is briefly described as follows. Firstly, a carbon film is plated on the surface of the nickel wire by electrochemical methods, then a carbonate-sensitive film is applied to the surface of the carbon plated nickel wire using the dipping method. The schematic diagram is shown in Figure 1.

Figure 1. Diagram of the electrode preparation process.

2.1. Reagents and Apparatus

A Ni wire (99.9%, 0.5 mm in diameter) was obtained from the Precious Materials Company of Changzhou, China. Carbonate ionophore VII (93206 Merck, Darmstadt, Germany) for the ISE were supplied by Merck. Dimethyl sulfoxide (DMSO), dibutyl phthalate, tetraoctyl ammonium chloride, ammonium thiocyanate, polyvinyl chloride (PVC) and imidazole were obtained from Aladdin (Shanghai, China). The sodium carbonate anhydrous, magnesium chloride, analytical-grade sodium chloride and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of the Electrode

2.2.1. Carbon Film Coating

The carbon film was prepared by cyclic voltammetry (CV) method. The process is described below. The carbon film was coated on the Ni wire, using a three-electrode system by a CHI760D electrochemical workstation (Chenhua Company, Shanghai, China). The working electrode was a Ni wire, the reference electrode was a commercial Ag/AgCl electrode and the auxiliary electrode was a Pt electrode. In a classic process, the plating was carried out in a self-prepared electrolyte solution, scanning 260 segments from 0 to 1.3 V at a rate of 100 mV/s.

The electrolyte solution was synthesised as follows: 13.2 g imidazole (0.09 mol) was added into a 50 mL beaker with 4.29 g magnesium chloride anhydrous (0.045 mol), heated at 70 degrees until completely dissolved to solution *a*. Then, 13.71 g ammonium thiocyanate (0.18 mol) was added into 15 g dimethyl sulfoxide in a 50 mL beaker, stirred to dissolve to solution *b*. Next, the mixture of solution *a* and solution *b* was stirred and centrifuged, and its supernatant was used as the electrolyte solution for reserve.

During the preparation of the carbon film coating, the imidazole cations were aggregated towards the negative Ni wire in the presence of an applied electric field. Following this, they were catalytically degraded on the surface of the Ni to form monomeric carbon. This method enabled a metallurgical bond between the carbon coating and the metal substrate, showing a strong bonding capacity.

2.2.2. Carbonate-Sensitive Film Coating

The carbonate-sensitive film solution was made by dissolving a total of 100 mg of carbonate ionophore VII (93206 Merck), dibutyl phthalate, tetraoctyl ammonium chloride, polyvinyl chloride ether in 1 mL of N,N-Dimethyl formamide (DMF), with a mass fraction of 5.2%, 47.1%, 0.6% and 92.4%, respectively, as suggested by Merck, and stored at 2–8 °C. The electrode, which had been covered with a carbon film coating, was immersed in the carbonate-sensitive film solution for 2 s at room temperature, then dried in a vacuum desiccator for 4 h at 35 °C.

DMF is highly volatile and small amounts of DMF on the electrode surface can evaporate rapidly, thus forming a polymeric carbonate-sensitive film on the electrode surface. The process did not require high temperatures for drying, avoiding different degrees of thermal expansion and contraction that can lead to flaking of the coating. The carbonate-sensitive film formed a surface with a certain curvature due to gravity during the evaporation of DMF. The structure of the membrane shortened the electrical signal transmission distance and reduced the electrode response time compared with flat shaped sensitive film.

After the course described above, the all-solid-state carbonate ion-selective electrode was carbon black and the gloss of the polymer film was visible, with a diameter of 0.5 mm and a length of 6–12 mm. The dense carbon film was approximately 500–600 nm thick and the carbonate-sensitive film was no more than 500 nm thick. They were coated in Ni filaments, and were close in length to the electrode.

2.3. Evaluation of the Electrode

SEM analysis was performed to analyse the microstructure involved in the carbon film for the electrode performance. The potentiometric properties of electrodes were evaluated at room temperature on the CHI760D electrochemical workstation. The electrode detection system is a two-electrode system with open circuit technology, with the prepared all-solid carbonate electrode as the indicator electrode and an Ag/AgCl electrode as the external reference electrode. The dynamic response curves were obtained by measuring the potential in Na₂CO₃ solutions of different concentrations, while 1.0×10^{-1} – 10^{-8} M Na₂CO₃ solutions were prepared by serial dilutions with deionized water.

3. Results and Discussion

3.1. SEM Analyses

For the all-solid-state ion-selective electrodes, the electrical signals from the different solid layers tend to pass along each layer rather than across the interface, which is due to the interfacial impedance between the layers of the all-solid electrodes [23]. The carbon film coating on the surface of the nickel wire had good electrical conductivity and is tightly bonded to the polymer film, eliminating interfacial impedance with an effect similar to that of the internal electrolyte solution in conventional ion-selective electrodes [24–27].

Under scanning electron microscopy (SEM), Figure 2a presented a dense carbon film that was generated on the surface of the Ni wire by cyclic voltammetry. The physically broken surface of the carbon film was observed at high magnification (Figure 2b) and its composition remained comprised of carbon particles. The EDS analysis of the broken surface showed the element mass fraction of 76.58% for C, which was solid evidence for its composition. The SEM results proved that the prepared carbon film had a certain thickness and completely wrapped the Ni substrate, which meets the requirements as an ion-to-electron transducer in the electrode. In subsequent experiments and applications, the carbon film never peeled off from the nickel wire over a period of 5 months, confirming the excellent adhesion and stability of the carbon film prepared by this method. The traditional methods of carbon film coating preparation include chemical vapor deposition [26], plasma spraying [28] and multi-arc ion plating [29]. The bonding between the carbon coating and the substrate prepared by the above methods relies on organic bonding or Van der Waals forces, and the adhesion performance is poor. The cyclic voltammetry is simple, low cost and environmentally friendly [30]. Coating the surface of metallic materials using cyclic voltammetry increased the penetration process of the deposited carbon on the surface of the metal substrate as well as the adhesion between coating and substrate [24,30–33]. The carbon film prepared by electrochemical methods can effectively eliminate the interfacial impedance between the Ni substrate and the polymer film, solving the inherent problem of all-solid-state electrodes [24,25,34].

(a)

Figure 2. Cont.

Figure 2. SEM images of the carbon film coating. (a) The Ni wire with carbon film coating viewed at $97\times$ magnification, (b) the carbon film viewed at $4000\times$ magnification.

The carbon film prepared by this method is a graphite carbon film, which has many excellent properties in addition to its application as an electrode substrate. The graphite carbon film effectively improves the lubricity, corrosion resistance and hardness of the metal substrate. In addition, metal–graphite coating has good resistance to high temperature molten salt corrosion, making it an ideal material for lithium-ion battery anodes [25,35,36].

3.2. Potentiometric Performance of the Electrode

In this work, the carbonate ionophore VII (93206 Merck) with the chemical component bis (TFAB)CAs (N,N-dioctyl-7R-acetoxy-3R,12R-bis(4-trifluoroacetylbenzoxy)-5 α -cholan-24-amide) was used to prepare carbonate-sensitive films for ISE. The bis (TFAB)CAs recognize the incoming carbonate ion by forming both covalent and hydrogen bonding between the hydrated and unhydrated TFAB (trifluoroacetylbenzoxy) groups according to Merck [37]. The principle is the theoretical basis for the ability of this carbonate electrode to characteristically identify carbonate ions and determine CO_3^{2-} concentrations. The voltage produced by the electrode is linearly related to the activity or concentration of the carbonate ion, in accordance with the Nernst equation [38]. In the following, the potential measurement properties of the electrodes were described by the slope of the calibration graph, the detection limit, selectivity factor, response time and life span.

3.2.1. Linear Slope, Detection Limits and Calibration Curve

The electrodes were activated in a 10^{-3} mol/L Na_2CO_3 solution for 3 h at room temperature before measurement. A range of Na_2CO_3 solutions at concentrations of 10^{-1} M, 10^{-2} M, 10^{-3} M, 10^{-4} M, 10^{-5} M, 10^{-6} M, 10^{-7} M, 10^{-8} M were prepared for calibrating the ISE. The positive curve of the electrode obtained by plotting the electrode potential E against the logarithm of the ion concentration in a given solution was shown in Figure 3. The detection limit was defined as the intersection of straight line and tangent part of the calibration curve. The linear range of the calibration curves was 10^{-1} – 10^{-5} M with detection limit was determined as 2.821×10^{-6} M and the line of fit of $y = -30.40 \times -94.035$ ($R^2 = 0.9996$). The slope in the calibration curve was -30.4 mV/decade closing to the Nernst theoretical slope (-29.6 mV/decade) [38]. In addition, the determination coefficient R^2 was 0.9996, indicating that the preparation method was reproducible. These data in-

indicate that the carbonate electrode has a wide linear range (10^{-5} to 10^{-1} M) for Na_2CO_3 solutions and low detection limits.

Figure 3. Electrode performance in 1×10^{-8} – 10^{-1} M Na_2CO_3 solution.

3.2.2. Repeatability, Stability, Lifespan and Response Time

Figure 4 shows the response curve of the carbonate ion-selective electrode in Na_2CO_3 solutions, with concentrations ranging from 10^{-5} M to 10^{-1} M. The potentials were 57.23 mV, 28.96 mV, -3.01 mV, -34.17 mV and -63.2 mV from 10^{-5} M to 10^{-1} M, then increased to -34.21 mV, -3.06 mV, 28.89 mV and 57.31 mV from 10^{-2} M to 10^{-5} M. The potential curve showed that the carbonate electrode demonstrated a stable and consistent response to all concentrations of Na_2CO_3 in the test. Meanwhile, the potential difference in the concentration of the Na_2CO_3 solution, first from low to high, then from high to low, did not exceed 1 mV at the same concentration, indicating the good repeatability of the carbonate ion-selective electrode.

In this work, the immersion method was used to determine the response time of this electrode, meaning the time it takes for the carbonate electrode to reach a stable value (1 mV from the steady state value) to the time of contact with the sample solution [39]. Figure 4 shows that once the electrodes were in contact with the solution, a constant potential signal is obtained within 1 s and remains constant during the measurement. The response time of less than 1 s means this electrode is practical when used for in situ measurements compared to the 60–120 s response time of other reported carbonate electrodes in recent years [19–22]. The rapid response of this carbonate electrode is related to its construction. As discussed in Section 3.1, there was the carbon layer as the transducer between carbonate-sensitive film and Ni wire. The dense carbon film, prepared by cyclic voltammetry, is tightly bonded to the nickel wire and polymer carbonate-sensitive film and its high conductivity also ensures the speed of electrical signal transmission. Due to this microstructure and its electrical conductivity, the cross-border resistance between the sensitive film coating, the carbon film and the metal wire is quite low and the electrical signal was conducted rapidly.

Figure 4. The calibration curve of the carbonate electrode for Na_2CO_3 solutions with concentrations ranging from 10^{-5} M to 10^{-1} M.

To determine the life span of the electrode, the performance of the electrode was evaluated several times over a period of 60 days with a series of Na_2CO_3 solutions at room temperature [39]. The potential values of the electrodes, the slope and correlation coefficient of the calibration curve are displayed in Table 1. The slope was stable between -30 ± 0.5 mV over 60 days, with a determination coefficient R^2 value greater than 0.98. This indicates the electrode has a lifetime of more than 60 days and its lifetime meets the requirements for long-term monitoring of the marine environment.

Table 1. Performance of the ISE (mV) in the range of 10^{-5} – 10^{-1} M Na_2CO_3 over 60 days.

Day	10^{-5} M	10^{-4} M	10^{-3} M	10^{-2} M	10^{-1} M	Slope	R^2
1	57.23	28.96	−3.01	−34.17	−63.20	−30.40	>0.99
3	56.68	29.04	−2.96	−33.86	−62.03	−30.03	>0.99
9	56.86	27.85	−2.01	−34.56	−62.77	−30.17	>0.99
17	55.45	26.11	−0.12	−36.93	−65.54	−30.50	>0.99
31	52.33	21.12	−1.66	−38.66	−69.24	−30.29	>0.99
43	55.39	19.34	1.26	−39.23	−63.21	−29.58	>0.98
60	51.14	18.37	0.11	−34.22	−70.75	−29.64	>0.98

3.2.3. Selectivity

The sensitive membrane of an ion-selective electrode has a specific response to the measured ion and the response of the electrode will be disturbed in the presence of other ions in solution [40]. The carbonate electrodes were intended to be applied to actual in situ measurements in the water containing a variety of interfering ions, compared with a pure Na_2CO_3 solution. Experiments on the selectivity of electrodes for some of the common interfering anions prevalent in the ocean are indispensable tests before application to the marine environment. The selection factor (K_{ij}) is calculated from the potential response of the electrode to the ion to be measured and the interfering ion. In this study, the selectivity coefficient of this carbonate electrode was calculated the fixed interference method (IFM).

According to reports in the literature, the $\log K_{i,j} < 0$ means the test electrode has good resistance to this interfering ion j [41].

The response of the electrode to interfering ions was determined by mixing a fixed concentration of interfering ions in a series of Na_2CO_3 solutions of different concentrations (10^{-1} – 10^{-5} mol/L). In this procedure, the following interferences were used: SO_4^{2-} , Cl^- , Br^- , NO_2^- , NO_3^- , CH_3COO^- and OH^- with a fixed interfering ions concentration of 10^{-2} M. The results of the measurements are shown in Table 2. The constructed electrode showed little response to the major interfering ions present in seawater such as Cl^- , SO_4^{2-} , Br^- and NO_3^- (selectivity coefficients of -4.24 , -3.16 , -2.21 and -2.58 , respectively). Additionally, hydrolysis of carbonate ions may change the pH of the solution, the selection factor of $\text{OH}^- < 0$ (-3.44) indicating the electrode is responding to the carbonate rather than to the OH^- from carbonate hydrolysis. The potential response of the prepared carbonate electrode was hardly affected by the pH of the solution. The findings showed that this carbonate electrode was highly resistant to seawater, had high selectivity for carbonate and can be used for resource exploration and environmental testing in the ocean.

Table 2. Selectivity factor measured for the carbonate electrode by the IFM.

Interfering Ions	Slope	R^2	$\log K_{i,j}$
SO_4^{2-}	-30.62	>0.99	-3.16
Cl^-	-30.99	>0.99	-4.24
Br^-	-29.87	>0.99	-2.21
NO_2^-	-31.22	>0.98	-3.36
NO_3^-	-30.65	>0.99	-2.58
CH_3COO^-	-31.87	>0.98	-1.96
OH^-	-29.94	>0.99	-3.44

3.3. Application at Southwest Indian Ocean Ridge

The Southwest Indian Ridge (SWIR) extends from the Rodrigues Triple Junction (RTJ) in the east to the Bouvet Triple Junction (BTJ) in the west is the important boundary between the Antarctic and African plates [42]. Since the first confirmation of the high temperature active hydrothermal field ‘Long qi’ at the ultra-slow spreading oceanic ridge SWIR in 2007 [43], China Ocean Mineral Resources R&D Association has carried out a series of sulphide exploration cruises at SWIR, discovering multiple hydrothermal fields [44–48].

Near-bottom detection of hydrothermal fields is currently the most widely used technique for seafloor hydrothermal activity investigations [10]. The development of in situ chemical sensors made it possible to monitor the spatial and instantaneous changes of hydrothermal fields [49,50]. The lack of oxygen supply to the deep-sea hydrothermal field and the anaerobic decomposition of the sulphide surface layer by bacteria produce large amounts of reducing components, resulting in a dramatic decrease in pH and CO_3^{2-} concentration and an overall reductive water column [51–55]. The pH, redox potential values and the carbonate concentration are important indicators for measuring and detecting hydrothermal field environment. However, carbonate sensors for deep-sea applications have not yet been reported. To remedy this deficiency, we integrated the carbonate electrode prepared in this paper with Eh (redox) and pH electrodes in a multi-parameter chemical sensor (MPCS) for hydrothermal field identification and detection at the SWIR where water depths of over 1400 m. A schematic diagram of the internal structure of the MPCS is shown in Figure 5.

On 7 March 2021, MPCS was attached on the cable of the television camera grab (TVG) for underwater operations. The TVG was launched at 11:18 p.m. on 6 March 2021 and recovered at 02:50 a.m. on 7 March 2021. It was hauled by the research vessel Dayang Hao at a depth of 1400–1450 m during the Dayang 65 cruise. During the sulfide investigation, the near-bottom data obtained by the MPCS are of practical significance, thus we only presented the data between 00:29 and 01:36 a.m. in Figure 6. The MPCS was at a height of around 50 m above the seabed during operation. The potential anomaly at MPCS

occurred at around 00:40 a.m. From 00:29 to 00:39 a.m., all three electrodes exhibited a smooth potential response. At 00:40 a.m., the three electrodes showed a synchronous sudden decrease in potential and returned to normal seawater background values within the next few minutes. The potential anomalies for the Eh, CO_3^{2-} and pH electrodes were 24 mV (from -44 mV to -68 mV), 30 mV (-67 mV to -37 mV) and 32 mV (from 136 mV to 104 mV), respectively. The possibility of the sensor bottoming was ruled out after reviewing the board on site, the potential anomaly was predicted to be influenced by environmental changes of the water.

Figure 5. Assembly structure diagram of the MPCS.

Figure 6. The pH, Eh, CO_3^{2-} data obtained from the MPCS during the Dayang 65 cruise.

The pH, Eh and CO_3^{2-} electrodes showing a simultaneous decrease in potential meant the MPCS was in a strongly reducing water body with low pH value and high CO_3^{2-} concentration. Figure 7 showed the screenshot from TVG video at 00:40 a.m. When potential anomalies occurred, the substrate type was an inactive sulphide accumulation,

this area is a hydrothermal field. Potential anomalies detected by the MPCS were influenced by the particular environment of hydrothermal fields. With the movement of the TVG, the MPCS passed through the hydrothermal field, and returned to normal potential values at 01:10 a.m.

Figure 7. Screenshot of underwater the TVG camera video at 00:40 on 7 March 2021.

Then we grabbed a sulphide with the TVG at the hydrothermal field. Figure 8 showed its interior characteristic. The sample had a yellowish-brown surface with a dark grey fresh surface, massive structure, metallic lustrous pyrite grains visible to the naked eye. Hand specimen size: 15 cm × 10 cm × 7 cm. The sulphide samples provided more information of the hydrothermal field. This carbonate electrode showed a corresponding potential anomaly in the defined hydrothermal field. The results demonstrated the carbonate electrode prepared in this paper is applicable to the search for hydrothermal activity in deep-sea environments, providing more abundant environmental information for sulphide exploration.

Figure 8. Interior photograph of the hydrothermal sulphide.

However, the deep-sea environment is characterised by low temperature, high salinity and high pressure, in situ CO_3^{2-} concentrations cannot be obtained directly from the

regular laboratory calibration curves. As a result, the detected potential signal cannot be converted into a quantitative concentration but the qualitative signals. Future work will focus on accurate measurement in the extreme environment to map the distribution of hydrothermal fields. Nonetheless, this carbonate electrode is already capable of preliminary hydrothermal activity detection and deep-sea resource exploration. An attempt will be made to integrate more functions into the sensor together with the carbonate electrode, in order to detect hydrothermal activity such as heat sensing, pressure sensing, acoustic sensing, photo sensing, etc. [56,57]

4. Conclusions

This work describes a novel all-solid-state carbonate ion-selective electrode with Ni wire as the base material and carbon film as the transducers and polymeric membrane as the carbonate-sensitive layer. The prepared ISE showed wide linear responses at an Na_2CO_3 concentration range of 10^{-5} – 10^{-1} mol/L with a response time of no more than 1 s and the detection limit of 2.821×10^{-6} mol/L. The electrode response slope for CO_3^{2-} was -30.4 mV/decade which was comparable to the theoretical Nernstian slope for divalent ions. It had good selectivity for CO_3^{2-} and good resistance to the main interfering ions present in seawater, such as Cl^- , SO_4^{2-} , Br^- and NO_3^- . Meanwhile, the response of the ISE to carbonate ions barely affected by the pH of the solution. The prepared electrode, with a diameter of 0.5 mm and a length of 6–12 mm, was easy to integrate with other electrodes. We integrated this carbonate electrode with pH electrode and Eh electrode in a multi-parameter chemical sensor. During the survey, the carbonic electrode showed the synchronous potential anomaly signal with the other electrodes in the hydrothermal field, providing enhanced information of the water column for hydrothermal field exploration. To our knowledge, this is the first report on the successful use of carbonate electrode for the detection of deep-sea hydrothermal activity. The application of this carbonate electrode in the field of marine environmental monitoring and its calibration curve in the extreme environment will be our future research direction.

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