Supporting Information for:

Polymeric Membrane Ion-Selective Electrode Based on Potential-Modulated Ion Transfer: Ultrasensitive Measurement of Oceanic pH

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Contents

Reagents and chemicals

Tridodecylamine (hydrogen ionophore I), high molecular weight poly(vinyl chloride) (PVC), sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB), 2-nitrophenyl octyl ether (*o*-NPOE), Nafion (5 wt % solution in a mixture of lower aliphatic alcohols and water), tris-(hydroxymethyl)aminomethane (Tris) were purchased from Sigma-Aldrich. All other chemicals with analytical grade were obtained from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water (18.2 MΩ cm specific resistance) used for preparation the aqueous solutions was obtained with a Pall Cascada laboratory water system. Microporous polypropylene (PP) membranes (Celgard 2400, thickness: 25 μm, porosity: 41%, pore size: 43 nm) were supplied by Celgard Inc.

Membranes and electrodes

The hydrogen ion-selective membrane (H^+-ISM) contained 1.1 wt % hydrogen ionophore I, 0.6 wt % NaTFPB, 32.7 wt % PVC, and 65.6 wt % *o*-NPOE. The membrane was prepared by dissolving 360 mg of the membrane components into 3.6 mL of tetrahydrofuran (THF) with vigorous stirring and then pouring into a glass ring (3.6 cm in diameter) fixed onto a glass plate. After overnight evaporation, a transparent membrane was obtained. For each H^+-ISE, a disk of 7-mm diameter was cut from the membrane and glued to a plasticized PVC tube that was connected with a pipette tip. The inner filling solution was 0.01 M Tris-HCl buffer solution (pH 7.0) containing 10 mM NaCl. The internal reference electrode was Ag/AgCl (3 M KCl) electrode. All electrodes were conditioned in the inner filling solution overnight before measurements.

For preparation of the Nafion membrane based ion-transfer electrode, a microporous PP membrane of 8-mm diameter was used as the support substrate. After being thoroughly washed by THF for several times, the cleaned PP membrane was glued to the plasticized PVC tube with a THF/PVC slurry. 5 μL of the Nafion solution (5 wt % in lower aliphatic alcohols and water) was pipetted onto the PP membrane. After evaporation of the solvent, the Nafion membrane supported by a PP substrate was obtained and conditioned in 0.1 M KCl solution for 1 h. A 0.1 M $K_4Fe(CN)_6/K_3Fe(CN)_6$ solution was used as inner filling solution for the proposed ion-transfer membrane electrode with a glassy carbon electrode (GCE, 3.0 mm in diameter) as internal electrode.

Ultrasensitive detection of pH by the proposed method

For ultrasensitive detection of pH, the electrochemical cell with two compartments (for pH sensing in the sample solution and signal amplification in the detection solution, respectively) separated by a salt bridge was used (as shown in Scheme 1a). The inner filling gel solution of a salt bridge was prepared by dissolving 1 g of agar in 33 mL of 4 M KCl with stirring at 90°C for 20 min. The gel solution was added to a PVC-tube of 2-mm diameter, and then the salt bridge based on ager gel could be obtained at room temperature. The conventional three-electrode system was employed with a H^+-ISE as reference electrode (RE) placed in the sample solution, as well as a thin Nafion membrane-based electrode as working electrode (WE) and a platinum wire electrode as counter electrode (CE) both placed in the detection solution (50 mL of 0.1 M KCl). There were two steps involved in the pH measurements including the open circuit potential (OCP) measurements and amperometric measurements. OCP of the WE *vs* RE was first measured and subsequently applied onto the cell via a CHI 660E electrochemical station (Shanghai Chenhua Apparatus Corporation, China) at room temperature with a 0.1 M Tris-HCl buffer solution (pH 8.000) containing 10 mM NaCl (i.e., reference solution) as the sample solution. The transient currents were recorded, while the pH of the reference solution was alternated by changing the molarity ratio of the conjugate acid-base pair of Tris via Henderson-Hasselbalch equation.[1] It should be noted that the rapid diffusion of the K^+ ion away from the Nafion membrane surface could reduce the potential response of the working electrode. Therefore, the pH measurements were carried out without stirring the detection solution of 0.1 M KCl.

For detection of pH changes in the marine environment, the seawater sample was collected from the Yellow Sea, China (37°5’ N, 121°46’ E) and prepared with a 0.1 M Tris-HCl buffer solution to maintain a pH of 8.000. The resulting solution was used as the reference solution for the OCP and amperometric measurements. The pH value of such a solution was adjusted by adding an HCl solution (2 M) based on the Henderson-Hasselbalch equation and the pK_a of this solution that was determined at room temperature by potentiometric titration. It should be noted that the temperature change could influence the mass transport of K^+ across Nafion membrane, thus leading to a source of error in the obtained data. Such a temperature effect occurring during the on-site measurement of oceanic pH could be effectively eliminated by a real-time correction process previously reported by our group,[2] which could be explored in the further.

Potentiometric detection of pH

Potentiometric measurements of pH were carried out via an electrochemical workstation (CHI 660E, Shanghai Chenhua Apparatus Corporation, China) with an Ag/AgCl electrode served as reference electrode in the galvanic cell: Ag / AgCl / 3 M KCl / sample solution / H^+-selective membrane / inner filling solution / 3 M KCl / AgCl / Ag. Prior to potentiometric measurements, all the H^+-selective electrodes (H^+-ISEs) were conditioned in inner filling solution (0.01 M Tris-HCl buffer solution (pH 7.0) containing 10 mM NaCl) overnight. The obtained electromotive force (EMF) values were corrected with the Henderson equation.

Amperometric detection of pH based on the potential-modulated oxidation of the redox couple

Amperometric measurements of small pH changes based on the potential-modulated oxidation of the redox couple were carried out with a setup previously reported.[3] Briefly, the electrochemical cell with two compartments (i.e., a detection cell and a sample cell) separated by a salt bridge was used. The conventional three-electrode system was employed with a H^+-ISE as the RE placed in the sample cell containing the sample solutions with different pH, as well as a GCE (3.0 mm in diameter) as the WE and a platinum wire electrode as the CE which were placed in the detection cell containing 5 mM $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ and 0.1 M KCl. A constant potential of 0.25 V was enforced onto the cell via a CHI 660E electrochemical station at room temperature with a 0.1 M Tris-HCl buffer solution (pH 8.0) containing 10 mM NaCl (universal reference solution) as the sample solution. The oxidation currents were recorded, while the pH of the universal reference solution was alternated by changing the molarity ratio of the conjugate acid-base pair of Tris via Henderson-Hasselbalch equation. All chronoamperometric measurements were performed in the above electrochemical cells with stirring the detection solution.

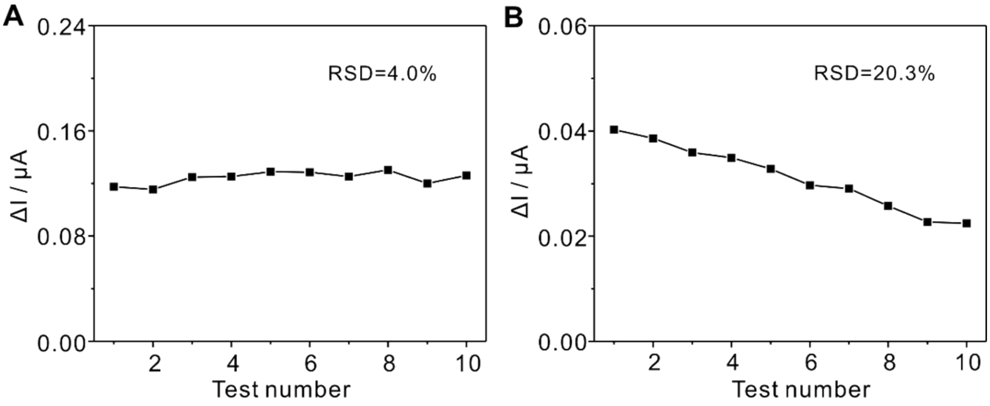

Fig. S1 Effect of the internal transducing element of the WE on the current response for the multiple measurements of a 0.003-pH unit change: (A) a GCE in 0.1 M $[Fe(CN)_6^{4-}]/[Fe(CN)_6^{3-}]$; (B) an Ag/AgCl electrode in 0.1 M KCl. The pH was decreased from 8.000 to 7.997 in a 0.1 M Tris-HCl buffer solution containing 10 mM NaCl. A PP substrate (8 mm in diameter) modified with 5 µL of the Nafion solution (5 wt %) was used as the ion-transfer membrane, and 0.1 M KCl was used as the detection solution. For using the $[Fe(CN)_6^{4-}]/[Fe(CN)_6^{3-}]$ redox couple (A), 0.1 M $K_4Fe(CN)_6/K_3Fe(CN)_6$ and a GCE with a diameter of 3.0 mm were used as the inner filling solution and inner reference electrode, respectively. For using the Ag/AgCl redox couple (B), 0.1 M KCl and an AgCl coated Ag wire with a diameter of 0.5 mm were used as the inner filling solution and internal electrode, respectively.

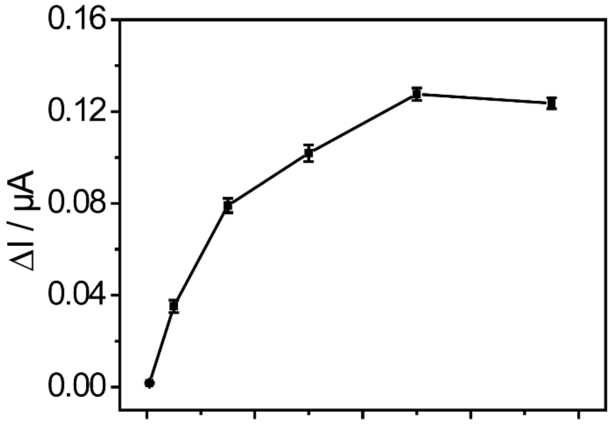

Fig. S2 Effect of the concentration of the WE's inner filling solution on the current response. The pH was decreased from 8.000 to 7.997 in a 0.1 M Tris-HCl buffer solution (pH 8.000) containing 10 mM NaCl. The other experimental conditions for preparation of the Nafion membrane based ion-transfer electrode are as given in Fig. S1. Error bars represent one standard deviation of three measurements.

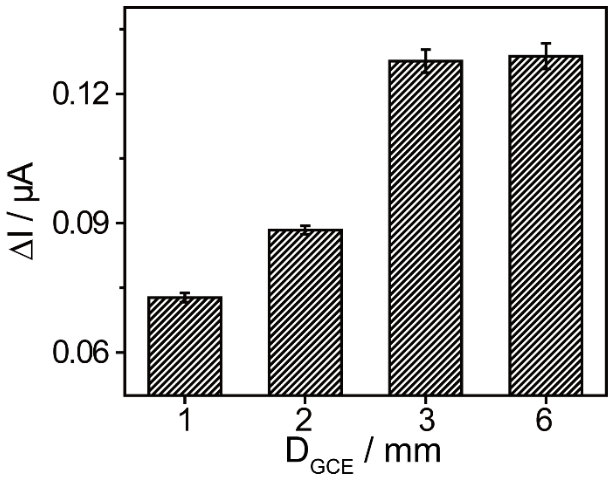

Fig. S3 Effect of the diameter of GCE on the current response. The pH was decreased from 8.000 to 7.997. The other experimental conditions for preparation of the Nafion membrane based ion-transfer electrode are as given in Fig. S1. Error bars represent one standard deviation of three measurements.

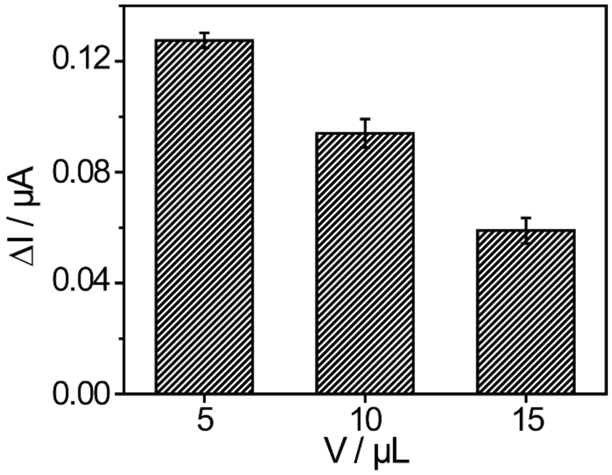

Fig. S4 Effect of the modified volume of the Nafion solution (5 wt %) on the current response. The pH was decreased from 8.000 to 7.997. The other experimental conditions for preparation of the Nafion membrane based ion-transfer electrode are as given in Fig. S1. Error bars represent one standard deviation of three measurements.

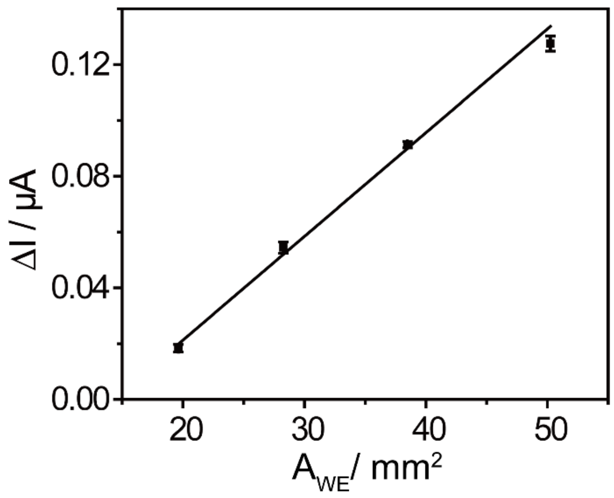

Fig. S5 Effect of the WE's area on the current response. The pH was decreased from 8.000 to 7.997. The other experimental conditions for preparation of the Nafion membrane based ion-transfer electrode are as given in Fig. S1. Error bars represent one standard deviation of five measurements.

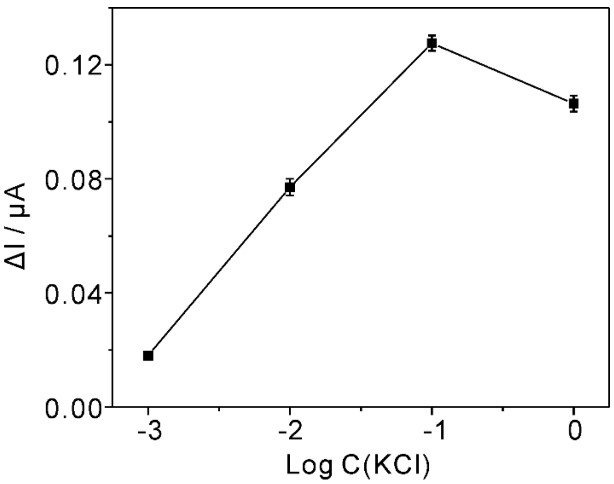

Fig. S6 Effect of the concentration of KCl in the detection solution on the current response. The pH was decreased from 8.000 to 7.997. The experimental conditions for preparation of the Nafion membrane based ion-transfer electrode are as given in Fig. S1. Error bars represent one standard deviation of three measurements.

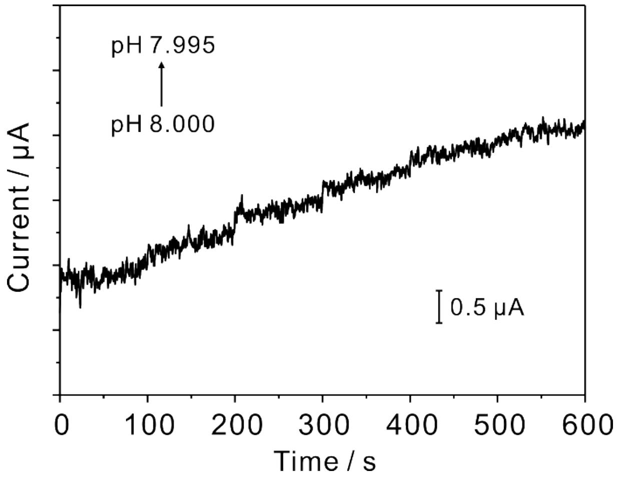

Fig. S7 Time-dependent amperometric responses of the polymeric membrane H^+-ISE to pH by using the $[Fe(CN)_6^{4-}]/[Fe(CN)_6^{3-}]$ redox couple-based amperometric readout strategy.

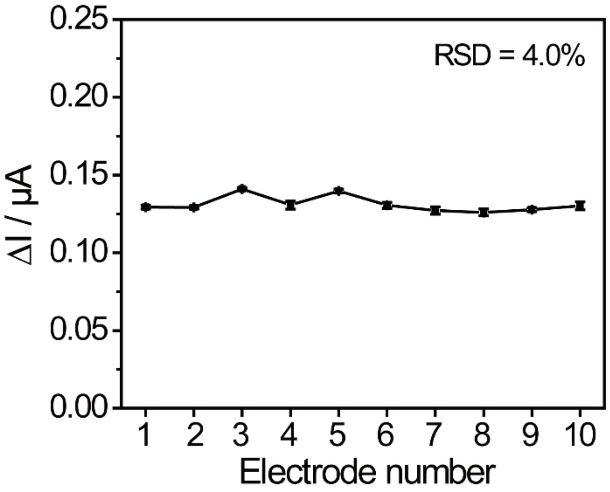

Fig. S8 Current responses of a pH change of 0.003 obtained at different WEs (NO. 1-10). Error bars represent one standard deviation of three measurements.

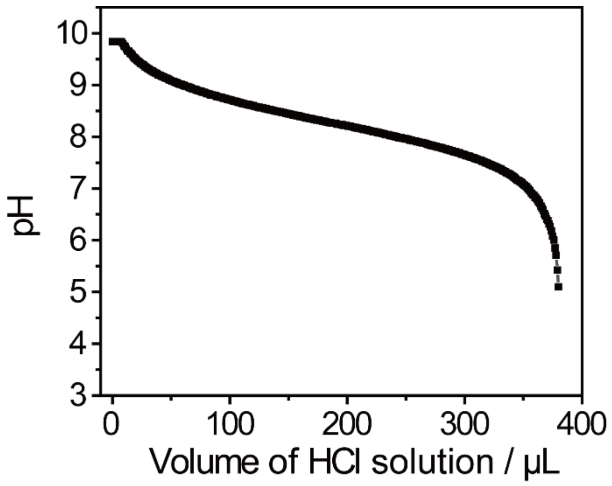

Fig. S9 Potentiometric titration curve of the seawater sample prepared in 0.1 M Tris-HCl buffer solution. The pKa value was calculated to be 8.26. The concentration of the used HCl solution was 2 M.

References

1. P. Kraikaew, S. Jeanneret, Y. Soda, T. Cherubini and E. Bakker, *ACS Sens.*, 2020, **5**, 650-654.
2. Z. Liao, T. Jiang and W. Qin, *ACS Earth Space Chem.*, 2023, **7**, 2182-2189.
3. X. Sun, T. Yin, Z. Zhang and W. Qin, *Talanta*, 2022, **239**, 123114.