Supporting Information

Ultra-Sensitive Seawater pH Measurement by Capacitive Readout of Potentiometric Sensors

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Experimental section

Potassium chloride (KCl), sodium chloride (NaCl), Hydrogen ionophore I, high molecular weight poly(vinyl chloride) (PVC), 2-Nitrophenyl octyl ether (o-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), tetrakis(4-chlorophenyl)borate tetradeclammonium salt (ETH 500), and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Ultrapure Tris-(hydroxymethyl)aminomethane (Tris) and 0.1 M sodium hydroxide (NaOH) volumetric solution were purchased from PanReac AppliChem. 1 M hydrochloric acid (HCl) volumetric solution was purchased from Fisher Scientific. An Ag/AgCl electrode and a hydrogen ion-selective electrode (see membrane preparation and composition in the Supporting Information) served as indicator electrodes. A double junction Ag/AgCl/3 M KCl/1 M LiOAc electrode (Metrohm, Switzerland) and a platinum rod (Metrohm, Switzerland) were used as reference electrode and counter electrode, respectively. The working electrode was placed in series with a commercially available capacitor ranging from 4.7 to 470 μF. Solutions for chloride ion measurements were prepared in a 10 mM KNO₃ background electrolyte. Tris-HCl buffer solution was prepared in a 10 mM NaCl background electrolyte and used for all pH measurements. To avoid deteriorating signals from trapped air bubbles, the air gap was removed before measurement by a debubbler placed just before the wall-jet cell. Small, well defined changes of pH were achieved by automatic titration, delivering precise amounts of NaOH into a 0.1 M Tris-HCl buffer. The required volume of NaOH was determined from potentiometric titration of the buffer and used to achieve the desired change of pH as a function of added NaOH volume from the Henderson-Hasselbalch equation. A large buffer volume of 500 mL was used to minimize uncertainties. Each new sample composition was aspirated to the detection cell for measurement illustrated in Scheme S1. After each measurement the residual volume of the Tris-HCl buffer was corrected for calculating the precise amount of NaOH needed for the following pH change. Each new sample composition was passed through the cell for sufficient time to eliminate error from carry-over of the previous sample composition. The OCP was measured in the reference solution stream of Tris-HCl buffer and subsequently imposed for the sample as well. The OCP was re-measured before changing to a new pH value to minimize drift. The seawater sample from Arcachon bay with a salinity of 28.4 was filtered and prepared in 0.1 M Tris-HCl buffer to give a pH of 8.07 by adding NaOH solution. The automated system consisted of i) sample preparation: Tris-HCl buffer bulk solution was titrated by 0.1 M NaOH by a 765 Dosimat liquid delivery system (Metrohm, Switzerland). ii) Fluidics: the solutions were delivered by a peristaltic pump (ISMATEC, Switzerland) with tygon tubing (ISMATEC, I.D. 1.42 mm) at a flow rate of 333 μL/min to the detection cell. A switching valve (VICI, USA) was used to switch between solutions and air. iii) Detection: chronoamperometry was performed by NOVA software (Autolab, Metrohm, Switzerland) to record current-time signals and their integration to charge-time information. The open circuit potential (OCP) of the working electrode vs reference electrode was determined and subsequently enforced unto the cell by the potentiostat during the chronoamperometric measurements.
**Instrumentation and Measurements**

An Ag/AgCl electrode with electrode diameter of 3.00 ± 0.01 and a hydrogen ion-selective electrode (H⁺-ISE) were used as working electrodes in a conventional three-electrode system. A double junction Ag/AgCl/3 M KCl/1 M LiOAc electrode (Metrohm, Switzerland) and a platinum rod (Metrohm, Switzerland) were used as reference electrode and counter electrode, respectively. The working electrode was directly connected in series with a commercially available capacitor. Electrode bodies (Oesch Sensor Technology, Sargans, Switzerland) were used to mount the polymeric membranes for the H⁺-ISEs. For potentiometry, the H⁺-ISEs were measured and calibrated with a high impedance input 16-channel EMF monitor potentiometer (Lawson Laboratories, Inc., Malvern, PA) at zero current. Chronoamperometric measurements were performed with a PGSTAT302N Autolab (Metrohm Autolab B.V., Switzerland) controlled by Nova 2.1.4 software. The open circuit potential (OCP) of the working vs reference electrode was determined and enforced as a constant value by the potentiostat during the chronoamperometric measurements. The measured current signal was integrated over time to obtain the charge-time relationship. Cumulated charge was then plotted vs the logarithm of ion concentration (activity). Potentiometric experiments were performed with a high impedance input 16-channel potentiometer as mentioned before. The EMF vs the logarithm of ion activity was recorded. All experiments were carried out at ambient laboratory temperature.

**Sample preparation**

Aqueous solutions were prepared by dissolving the respective salts in deionized water (>18 MΩ cm). All chemicals were of at least analytical grade. 0.1 mM KCl solution was prepared in 10 mM KNO₃ background electrolyte and was used as reference solution of measure the OCP for chloride ions analysis. The concentration of KCl in a range of 0.1 mM to 3.3 mM was used for this experiment with 0.2 mM increment. For pH measurement, 0.1 M Tris-HCl buffer solution pH 7.00 was prepared in 10 mM NaCl background electrolyte and was used as reference solution of OCP measurement. Seawater from Arcachon Bay (France) with salinity of 28.4 was used as sample solution. After filtration the seawater sample was prepared in 0.1 M Tris-HCl buffer to maintain the pH at 8.0 and used as reference solution. The measurement of seawater sample was carried out over a range of Tris buffer concentration. The pH values were assigned by the molarity ratio of the conjugate acid-base pair of Tris using Henderson–Hasselbalch equation. The ion matrices including sulfate ion were considered by potentiometric titration to identify the pKₐ of sample solution (Figure S5). The desired pH was adjusted by addition of NaOH solution.
Preparation of the Electrodes

Ag/AgCl electrode was prepared by electrochemical oxidation of an Ag electrode in 1 M HCl for 1 h at constant anodic current of 1 mA/cm². The coated electrode was washed with deionized water prior to use. A PVC based ion-selective membrane was used for pH measurements, which was composed of 15 mmol kg⁻¹ hydrogen ionophore I, 5 mmol kg⁻¹ NaTFPB ion-exchanger, 90 mmol kg⁻¹ ETH 500, 118 mg o-NPOE and 59 mg PVC (total mass of 200 mg). The cocktail was dissolved in 2.0 mL of THF and poured into glass ring (22 mm ID) affixed onto a glass slide. The solution was allowed to evaporate overnight. This initial membrane was cut with a hole-puncher into small pieces of 8 mm diameter and mounted into Ostec electrode bodies. The electrodes was conditioned overnight in the 0.1 mM Tris-HCl and 10 mM NaCl pH 7.0 inner filling solution. For seawater experiment, seawater sample in 0.1 M Tris-buffer (pH 8.0, salinity 28.4) was used as inner filling solution.

In-line measurement

The solution was delivered by peristaltic pumps (ISMATEC, model ISM935c, Clattbrug, Switzerland) equipped with tygon tubing (ISMATEC, inner diameter 1.42 mm). An air gap was used to separate each solution plug at a constant flow rate of 333 μL/min. The tygon tube installed on the pumps was connected to the electrochemical flow cell using PTFE tube (BOLA, inner diameter 0.8 mm). The tip of the working electrode was inserted into a wall-jet flow cell which allowed the solution stream to flow through. The open circuit potential (OCP) was determined for the reference solution flow prior the measurement. The chronoamperometric experiments were carried out with the same continuous flow system. The fully automated system was controlled by LabVIEW 10.0. Small pH change of 0.1 M Tris-HCl buffer solution in bulk solution (500 mL) was prepared by automatic titration by a 765-Dosimat (Metrohm, Switzerland). The bulk solution was stirred continuously. 1 mL of each sample solution and reference solution were switched and separated by 11 μL air. Signals were automatically recorded by Nova software (Autolab, Metrohm, Switzerland). The flow path was flushed with new sample solution before the next measurement. The same methodology as standard solution was applied to measure pH in seawater sample. Small pH change were imposed by adding NaOH to seawater sample in 0.1 M Tris-HCl buffer (500 mL). Seawater sample in Tris-HCl buffer is also used as reference solution.
Scheme S1. A) Schematic illustration and B) photos of fully automated system for determination of small pH change. The system consists of a dosimat for preparing the sample solution, a peristaltic pump equipped with a switch valve for delivering all solutions to the detection cell, a debubbler device for eliminating the air bubble just before measurement, and an electrochemical system for recording the signal controlled by Nova software. The lower chart shows the sequence of the flow of analytes and air-gap before and after passing though the debubbler; S1 and S2 are sample 1 and sample 2, Ref. is the reference solution.
Figure S1. Long-term stability test of used polymeric membraned electrode based tridodecylamine (TDDA). The membrane electrodes were used for several experiments in seawater sample and stored for 3 months before this test. A Calibration curve between EMF and pH with linear regression (solid line) shows Nernstian behaviour with

\[ EMF = 515.79 \text{ mV} + 59.61 \text{ mV} \times pH, \quad r^2 = 0.9998. \]
Figure S2. Repeatability of potentiometric measurement of small pH change utilizing the fully automated system for tris buffer solution. Inset: Correlation between EMF change and ΔpH (open circles) together with linear regression (solid line, $\Delta EMF = -0.04 mV - 37.0 mV \times \Delta pH$ and $r^2 = 0.98$). The sub-Nernstian slope contrasts to that found in a wide pH range, see Figure S3.
Figure S3. A) Potentiometric measurement of wide range pH change using hydrogen-selective membrane electrode in universal buffer and 10 mM NaCl, demonstrating Nernstian response slope (compare to Figure S2 above where a narrow pH range gives an undesired sub-Nernstian slope). B) Corresponding calibration curve of EMF versus pH. Nernstian response is observed with a linear regression of $EMF = 499 \text{ mV} - 59.7 \text{ mV} \times \text{pH}$ and $r^2 = 0.9999$. 
Figure S4. Chronoamperometric measurement of small pH change in the range of 0.001 to 0.005 units of unmodified seawater sample using polymeric membrane electrode assembled with 100-μF electronic capacitor. Increasing sample pH (positive current) was switched to reference solution (seawater, negative current) by continuous flow system. Each sample was repeated three times.
**Figure S5.** Potentiometric titration curve of Tris buffer in seawater sample (red) and first derivative plot (blue).

Concentration of Tris buffer of 0.084 M was obtained respected to the pKₐ value of 8.24.
Figure S6. Repeatability of potentiometric measurement of small pH change of seawater sample in Tris-HCl buffer utilizing the fully automated system. Inset: Correlation between EMF change and ΔpH (open circles) together with linear regression (solid line, \( \Delta EMF = -0.03mV - 67.7mV \times \Delta pH \) and \( r^2 = 0.99 \)).