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Current pulse based ion-selective electrodes for chronopotentiometric determination of calcium in seawater

Shuwen Liu^{a, c}, Jiawang Ding^{a, b, *}, Wei Qin^{a, b}

^a Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China

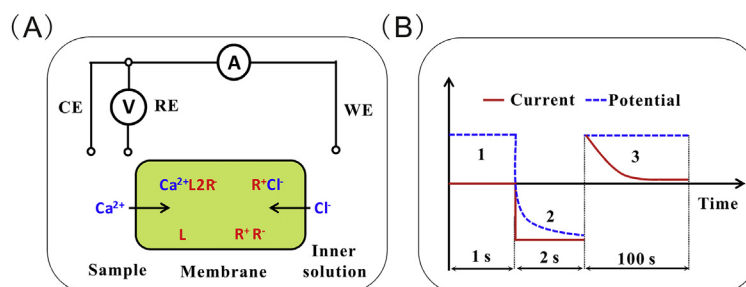
^b Laboratory for Marine Biology and Biotechnology, Qingdao National Laboratory for Marine Science and Technology, Qingdao, 266237, PR China

^c University of the Chinese Academy of Sciences, Beijing, 100049, PR China

HIGHLIGHTS

- A current pulse based ion-selective electrode with enhanced sensitivity is proposed.
- The super-Nernstian responses of the electrode could be modulated by current pulse.
- The current pulse based Ca-ISE was successfully used for seawater analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Calcium is closely related to the oceanic biosphere and carbonate system. Potentiometry based on a calcium-selective electrode (Ca-ISE) represents a promising tool for detection of calcium ion activities in seawater. This technique, however, generally is limited by the low sensitivity for the inherent Nernstian response (i.e. ca 30 mV/dec). A current pulse based ion-selective electrode with enhanced sensitivity for chronopotentiometric measurements of calcium in seawater is proposed. The Ca^{2+} -selective membrane containing lipophilic salt ETH 500 instead of traditional ion-exchanger is galvanostatically controlled. An applied constant cathodic current pulse can lead to the extraction of the calcium ions into the membrane to produce a chronopotential response, which shows a stable and reproducible super-Nernstian response in a narrow calcium activity range. The super-Nernstian region of the electrode depends on not only the magnitude and duration of the applied current pulse but also the interfering ions. Under optimal conditions, the proposed Ca-ISE exhibits a super-Nernstian response between the calcium concentrations of $10^{-2.5}$ – $10^{-1.5}$ M with a slope of ca 80 mV/dec. The current pulse based Ca-ISE has been applied to determination of calcium in seawater with satisfactory results.

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1. Introduction

Calcium, one of the major cations in seawater, is closely related to oceanic biosphere and carbonate system. It is the essential nutrient element in the growth of marine organism [1,2], especially in the formation of skeletons and shells [3]. In the context of the

* Corresponding author. Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China.

E-mail address: jwding@yic.ac.cn (J. Ding).

oceanic carbonate system, calcium carbonate plays an important role in global climate change and ocean acidification, as the precipitation and dissolution of calcium carbonate easily lead to variations in pH [4,5], total alkalinity [5–8], total carbon dioxide [5,9], and partial pressure of carbon dioxide [2,4,5,10]. In spite of the presence of continental and oceanic rock weathering and oceanic carbonate sedimentation, previous research has confirmed that the present-day ocean is in a steady state with regard to calcium [2], and the degree of Ca^{2+} variation is rather small. Therefore, methods for the determination of calcium in seawater with high sensitivity and accuracy are required.

Titration, as a high-precision Ca^{2+} determination technique, has been widely used over the past decades [11–13]. The potential interference of Mg^{2+} , however, is the main challenge to improve the accuracy of the technique. Advanced techniques such as capillary electrophoresis [14–16], inductively coupled plasma atomic emission spectrometry [17] and mass spectrometry [18,19], can detect Ca^{2+} with high accuracy and precision but suffer from some intrinsic drawbacks of complicated preparation procedures, high cost, extensive laboratory experience and incapability for onsite measurements [19,20]. In recent years, ion-selective electrodes (ISEs) have been applied to the *in situ* detection of ionized calcium in seawater [21,22]. ISEs ideally operate on the basis of the Nernst equation, which predicts ca 30 mV potential changes for a 10-fold activity change of calcium at room temperature. Thus, a small Ca^{2+} activity variation (for example 10%) can be translated into just a few millivolt (ca 1 mV) potential changes. Moreover, the concentrations of interfering ions such as Na^+ (0.047 M), Mg^{2+} (0.053 M), and K^+ (0.010 M) in seawater are rather high. Therefore, new ISEs for the determination Ca^{2+} in seawater with high sensitivity and good selectivity are highly required.

With the introduction of dynamic electrochemistry protocols, ISEs can be interrogated under galvanostatic control and used for the chronopotentiometric detection in analogy to zero-current potentiometry [23]. An applied constant current pulse fully controls the ion flux from the sample into the membrane and determines the concentration of extracted ions in the phase boundary region for membranes with no intrinsic ion-exchange properties [24–27]. Besides the zero-current potential and chronopotential, the transition time has been served as an alternative readout developed by Bakker's group [28–31]. In contrast to the chronopotentiometry based on the potentials, which could be influenced by changes in the background electrolyte, the latter approach using the transition times as the analytical signals may offer linearizable calibration curves that are less prone to matrix effects [32]. The pulsed galvanostatic-controlled ion-selective sensors offer several advantages, including the capability of multianalyte detection [25,33], reversible response to polyionic compounds [34,35], drastic improvement of sensitivity [24] and selectivity [36,37]. Moreover, it has the possibility to detect activity and the total concentration of each sample simultaneously [38,39]. Interestingly, Bakker and coworkers developed a pulsed galvanostatic-controlled ISE to obtain robust and reproducible potential readings in the super-Nernstian region, which was instrumentally adjusted and controlled [24,26]. This technique can be used for enhancing sensitivity and was developed for sensitive and selective determination of silver and calcium ions with low levels of electrolyte background [24,26]. However, to the best of our knowledge, pulsed galvanostatic-controlled ion-selective sensors based on super-Nernstian response mode have not been applied in real samples, especially those with a high-interfering background such as seawater.

Herein, a highly sensitive and selective pulsed galvanostatic-controlled Ca^{2+} -ISE was designed for the direct determination of calcium in seawater with enhanced sensitivity. The extraction of

calcium ions from the sample side to the membrane can be assisted by the ionophore and lead to a stable and reproducible super-Nernstian response. The super-Nernstian region can be modulated by the magnitude and duration of the applied current pulse and other parameters. Each applied constant current pulse is followed by a baseline potential pulse to regenerate the phase boundary region of the membrane [40]. It will be shown that the proposed pulsed galvanostatic technique can be used for sensitive and selective detection of calcium in marine environment.

2. Experimental

2.1. Reagents and materials

High-molecular-weight poly(vinyl chloride) (PVC), tetradodecylammonium tetrakis(4-chlorophenyl)-borate (ETH 500), sodium tetrakis[3,3-bis(trifluoromethyl) phenyl]borate (NaTFPB), 2-nitrophenyloxy ether (*o*-NPOE), the calcium ionophore-N,N-dicyclohexyl-N',N'-dioctadecyl-3-oxapentanamide (ETH 5234) and sodium chloride (NaCl, 99.99%) were purchased from Sigma-Aldrich (St. Louis, MO). Calcium chloride was obtained from Macklin Biochemical (Shanghai, China) and all other chemical reagents were purchased from Sinopharm Chemical Reagent (Shanghai, China). All chemicals were analytical grade and were used without further purification. All the aqueous solutions were prepared with freshly deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada Laboratory Water System.

2.2. Preparation of calcium ion-selective electrodes

The calcium-selective membrane contained 1.0 wt% calcium ionophore (ETH 5234), 7.0 wt% inert lipophilic salt (ETH 500), 30 wt% PVC, and 62 wt% *o*-NPOE. The conventional calcium-selective membrane contained 1.0 wt% calcium ionophore (ETH 5234), 0.5 wt% sodium tetrakis[3,3-bis(trifluoromethyl)phenyl]borate (NaTFPB), 33 wt% PVC, and 65.5 wt% *o*-NPOE. The membrane was prepared as described before [41]. The membrane thickness was measured using a CX31-32C02 Olympus microscope (Tokyo, Japan).

For each working electrode, a disk with a 5 mm diameter was punched from the membranes and glued to a plastic PVC tube (i.d. 4 mm, o. d. 6 mm) with THF. 0.1 M NaCl was used as inner filling solution. Before measurements, all the working electrodes were conditioned in the same solution for 24 h.

2.3. EMF measurements

All measurements were carried out at room temperature using a CHI 660 E electrochemical workstation (Shanghai Chenhua Apparatus Corporation, Shanghai, China). A conventional three-electrode cell with an ISE as the working electrode, a platinum wire as the auxiliary electrode, and Ag/AgCl (3.0 M KCl) as the reference electrode was used. The activity coefficients were calculated according to the Debye-Hückel approximation. All EMF values were corrected for liquid-junction potential with the Henderson equation.

All measurements were controlled by a macro-command, which executed a series of commands in a specified order. The procedures for switching between the galvanostatic and potentiostatic steps were designed according to the macro-command dialog box to execute consecutive measurements [40]. The open-circuit potential of the electrode in 0.5 M NaCl was first recorded for 1 s (step 1). Then, a cathodic pulsed current of 4 μA with a duration of 2 s was applied for step 2, which was followed by a recovery time of 100 s for step 3 (Scheme 1).

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