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Abstract

This paper describes the electrochemical characterisation of gold and platinum microdevices mass fabricated using silicon technology. Specific attention was paid to allow *in situ* electrochemical detection of silicate in seawater. Thus, using a silicon nitride (Si_3N_4) inorganic passivation layer patterned using Inductively Coupled Plasma Chemical Vapor Deposition (ICP-CVD), coupled with a non-aggressive lift-off based process, different electrodes were isolated electrically: one gold or platinum working electrode named "macroelectrode" (2 mm of diameter), four gold or platinum working ultramicroelectrodes (UME) (15 μm of diameter), one platinum counter electrode and one silver electrode which can be used as a reference electrode after its chlorination. Their small size and mass fabrication make them very promising for oceanographic applications. As some components of microdevices release silicate and contaminate the solution, after being immersed in seawater, these microdevices were inserted in a specific cell that only puts the electrodes in contact with the seawater solution. Gold has been tested as a possible material for working electrodes but its lack of adherence to the passivation layer in seawater solutions led to non-accurate measurements. On the contrary, passivation layer on platinum electrodes resists to the seawater corrosive medium. The analytical performances of the platinum microdevices has been tested through different silicate calibrations and shows an outstanding accuracy and reproducibility when measurements are performed, especially with the macroelectrodes which showed only 2.8 % signal variation after four months of use and a limit of quantification of 0.50 μmol.L^{-1} suitable for oceanographic applications.

1. Introduction

Continuous monitoring and real time transmission of key parameters from marine environments, such as macro-nutrients (silicate, phosphate, nitrate) help to better understand biogeochemical cycles and the role of the ocean in climate evolution. As of September 2014, 3579 ARGO floats equipped with physical CTD (conductivity, temperature, depth) sensors were profiling in the global ocean. Some of these floats were equipped with biogeochemical sensors (Oxygen (249), Bio-optics (77), Nitrate (47) and pH (14)) but none of them with a silicate one. An important challenge is to cover the ocean with as many biogeochemical profiling floats as physical floats. To reach this goal, *in situ* and autonomous nutrient sensors are needed to sample the largest range of spatio-temporal scales. In order to implement nutrients sensors on buoys, moorings, autonomous under vehicles, floats…, these sensors have to be robust and resistive to corrosive conditions, miniaturized, portable, may consume low energy, and be low cost. Electrochemistry has been chosen here to detect silicate because electrochemical methods may fulfill some of these requirements.

As a matter of fact electrochemistry is routinely used in analytical chemistry and provides a large scope of applications, in increasingly complex samples [1-4]. In marine environments, Reimers [5], Moore et al. [6] and Denuault [7] reviewed the electrochemical techniques and microelectrodes used into sensors for oceanic research. Mainly, there are four electrochemical methods used in oceanography using *in situ* commercial sensors: (i) impedimetry to measure conductivity and determine salinity [8], (ii) potentiometry to measure pH [9-13] and pCO_2 [14, 15], (iii) amperometry to measure dissolved oxygen using Clark sensors [16, 17] or STOX sensors [18, 19] and (iv) voltammetry for trace metals and speciation monitoring [20, 21]. In the last recent years, combination of modern electrochemistry with progress in microelectronics and microfabrication has allowed to develop new microarrays, flow-cells and microsensors for real-time monitoring of trace metals (Pb^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}…) in seawater using screen-printed electrodes [22, 23] or silicon-based

microelectrodes [24-27]. Cathodic [28] and anodic [29] stripping voltammetry methods are widely used for metals speciation, more often combined with square wave voltammetry (Square Wave Anodic Stripping Voltammetry SWASV) [30-32]. These methods are using either gel integrated Ir-based microelectrodes [21, 33, 34] or gold amalgam electrodes [20, 35-37] and allow to detect simultaneously several redox species in seawater within a single potential scan (O_2, Mn^{2+}, Fe^{2+}, I^-, FeS, S^{2-}, H_2S…).

It is now possible to detect silicate with electrochemical methods without any addition of liquid reagents even if silicate is a non-electroactive species and so cannot be detected directly. Indeed, Lacombe et al. developed a method to produce *in situ* the reagents and the pH conditions needed to form the Keggin anion $Si(Mo_{12}O_{40})^{4-}$ detectable by cyclic voltammetry on gold or platinum electrodes [38]. This method requires a simple oxidation of a molybdenum electrode in order to form molybdate and protons. To achieve the needed acidic pH and form the silicomolybdic complex, a non-proton exchange membrane is added in order to isolate the counter electrode and avoid the reduction of the H^+ formed at the anode [39]. We are currently working on the development of miniaturized and autonomous silicate sensors using this method and in order to reduce the associated cost, the use of silicon-based technologies for the mass fabrication of electrodes and the realization of integrated microdevices is proposed.

Development of microfabricated electrochemical devices (microelectrodes, microelectrode arrays and ultramicroelectrodes) has considerably increased in the last two decades [40]. The advantage of this technique is to create individual microdevices with identical physical and chemical performances, well defined and reproducible geometries of several electrodes with a mass fabrication approach. Several metals such as gold, platinum, silver…, can be deposited on silicon-based microdevices. The final capping insulation layer (passivation layer), which isolates the

circuit and defines the electrode surface area, is the critical step in the microfabrication process. Passivation layers can be either organic or inorganic.

Organic passivation layers such as polymers are generally deposited by spin coating processing and were used for medical applications [41, 42]. However, organic passivation layers suffer from water adsorption and are not suitable for liquid media such as seawater. The time of failure in such environment is in the range of a few hours [43].

Inorganic passivation layers such as silicon oxide (SiO_2) or silicon nitride (Si_3N_4), deposited by Plasma-Enhanced Chemical Vapor Deposition (PECVD), give excellent electrical barrier properties and resist much longer in fluids than polymers. Microdevices with these inorganic passivation layers were used to evaluate the quantity of herbicides in natural waters measuring the variations in consumption-production rates of species involved in metabolic activities of algae such as O_2, H_2O_2, and H_3O^+/OH^- ions [44]. Tercier-Waeber et al. developed a multi physical-chemical profiler for *in situ* monitoring of Cu(II), Pb(II) and Cd(II) in estuaries and coastal seawaters [21].

However, environments such as seawater where the chloride concentration is really high cause important damages on passivation layers. Indeed Nolan and Kounaves revealed that both chloride (Cl^-) concentration and acidity of the solution contribute to microdevice failure because of Cl^- infiltrations underneath the insulating layer [45].

Schmitt et al. compared different passivation layers in NaCl (1 $mol.L^{-1}$) solution at three different pH (i.e. pH = 2, 7 and 10) and concluded that the best results in term of life time resistance were obtained with SiO_2/Si_3N_4 duplex layers and $SiO_2/Si_3N_4/SiO_2$ triplex layers [43].

Vanhove et al. used this type of inorganic passivation layers and developed a new deposition process at low temperature which reduced surface damages and controlled residual stress using Inductively Coupled Plasma Chemical Vapor Deposition (ICP-CVD) coupled with a non-aggressive lift-off based process with T

shaped photoresist profiles [46]. They immersed three microdevices with twelve gold ultra-microelectrodes (UME) during approximatively two months in seawater and did electrochemical cleaning in sulfuric acid (H_2SO_4: 0.5 mol.L^{-1}) by cyclic voltammetry, then chronoamperometry measurements at 0.6 V in 5 mmol.L^{-1} solutions of potassium hexacyanoferrate (II) trihydrate in order to measure the electroactive surface areas of UME. They showed stable and reproducible results during 50 days.

In this work, we will present the results obtained with these new silicon-based microdevices developed by LAAS laboratory with Si_3N_4 passivation layer for the electrochemical detection of silicates in seawater in the concentration range observed in the open ocean. We will describe the structure of the new microdevices that integrate a macroelectrode (ME), four ultramicroelectrodes (UME) and a counter electrode. The materials used for the electrodes will be discussed as well as how these devices have been adapted for the first time for the silicate detection in seawater.

2. Material and methods

2.1. Microdevices fabrication

The electrochemical microdevices were fabricated according to the ElecCell (Electrochemical microcell) silicon-based technological platform previously developed in LAAS [42]. Starting from an oxidized silicon wafer (oxide thickness: ~ 1 μm) in order to ensure electrical insulation between the different metallic layers, the different thin metallic layers were deposited by evaporation in conventional Physical Vapour Deposition (PVD) equipment, and patterned using a bilayer lift-off process in order to improve fabrication reproducibility. Different PVD processes were performed in a row: firstly, a 200 nm platinum layer was deposited on a 20 nm titanium underlayer in order to ensure platinum adhesion on silicon oxide. Then other metallic layers could be deposited such as 400 nm gold (for working electrodes) and 400 nm silver that

can be used as a reference electrode after its chlorination. Finally, an inorganic Si_3N_4 passivation layer (thickness: 105 ± 5 nm) was deposited patterned using photolithography techniques [46]. This wafer-level passivation process was developed and optimized in order to fit with the long-term seawater analysis [46]. Through this final step, the different metallic layers were insulated electrically and their active surfaces were precisely defined. Finally, the different silicon chips were placed and glued by an epoxy insulating glue on a specifically coated printed circuit, wire bonded and packaged at the system level in order to be fully compatible with liquid phase analysis.

The dimensions of such a microdevice are 80 mm × 15 mm × 2 mm (Figure 1-A) and the photo shows one platinum counter electrode (3 mm × 1 mm), one silver electrode (3 mm × 1 mm) to be used further as reference electrode, one working macroelectrode (2 mm of diameter) and four working ultramicroelectrodes (15 μm of diameter) (Figure 1-B and C). The macroelectrode and ultramicroelectrodes are made of gold or platinum according to the fabrication process.

2.2. Apparatus and electrodes

Cyclic voltammetry measurements were carried out at room temperature with a potentiostat PGSTAT 128N (Metrohm) controlled by NOVA software. A multiplexer module (MUX) (Metrohm) allowed to connect several electrodes in the same time and to perform electrochemical measurements with the different macro- and ultramicroelectrodes from a microdevice, sequentially. All potentials are given versus an Ag/AgCl/KCl (3 mol.L^{-1}) (Metrohm) reference electrode.

The molybdenum slab was supplied by GoodFellow (purity, 99.9%). To realize some contamination tests of the different components and material used into microdevices, homemade gold ultramicroelectrodes (25 μm of diameter) were needed. They were prepared in the laboratory from gold wires purchased from GoodFellow and sealed

with epoxy resin made with a mix of DGEBA[1] (10 g) + IPDA[2] (2.44 g) and polymerized at 80°C during 3 days [47].

2.3. Reagents and solutions

All solutions were prepared in Milli-Q water (Millipore Milli-Q water system) and put into polypropylene containers because glass must not be used in order to avoid silicate contamination in solutions. Silicate solutions were prepared with sodium hexafluorosilicate (Na_2SiF_6, from Merck) between 0.50 and 134 $\mu mol.L^{-1}$. Standard calibration and silicate samples were prepared in sodium chloride (NaCl) solutions supplied by Merck at 34.5 $g.L^{-1}$ (0.6 $mol.L^{-1}$).

The electroactive surfaces of gold (especially for homemade electrodes) are activated using a 0.50 $mol.L^{-1}$ sulphuric acid solution (prepared from a 98% H_2SO_4 solution supplied by Merck).

2.4. General analytical procedure

The methodology for the electrochemical determination of silicates with the microdevices is adapted from the one described in Lacombe et al. and consists of two steps [39]:

i) The molybdenum metal electrode oxidation is performed in a 3 mL sample by applying a constant potential of 1.0 V until a 14 C electric charge was reached in order to form molybdates (MoO_4^{2-} up to a concentration of 6.5 $mmol.L^{-1}$) and protons (H^+, pH $\approx$ 1.5). The cut off of the electric charge (14 C) was determined experimentally as it is not possible to calculate it with the Faraday's law since the oxidation of molybdenum involves the formation of different Mo oxides as MoO_2, MoO_3... [48]. After 6 minutes with stirring, the corresponding β-silicomolybdic complex (β-$Si(Mo_{12}O_{40})^{4-}$) is formed. This step is carried out in a homemade cell (see Figure 2) which is divided into 2 compartments separated by a Nafion® membrane

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[1] DGEBA : DiGlycidyl Ether of Bisphenol A
[2] IPDA : Isophorone Diamine

(N117 DuPont^{TM} PFSA). In the first compartment, 3 mL of sample is placed together with a molybdenum electrode and the reference electrode (Ag/AgCl/KCl 3 mol.L^{-1}). A platinum counter electrode is placed in the second compartment, on the other side of the non-proton exchange membrane, to limit the diffusion of H^{+} produced, avoid their reduction and obtain the required acidic pH for the complexation of silicates with molybdates [49, 50].

ii) The silicomolybdic complex is then detected by cyclic voltammetry (CV) using a gold or platinum working electrode immersed in the compartment of the cell (Figure 2) which contains the Mo electrode. The cyclic voltammograms are performed between 0.20 and 0.60 V, using a scan rate 0.1 V.s^{-1} for the macroelectrode and 0.01 V.s^{-1} for the ultramicroelectrodes. The CV plots show two reduction peaks at 0.26 V and 0.38 V and two oxidation peaks at 0.31 V and 0.41 V. In this work, the analytical signals have been either the intensity current in the reduction peak at 0.38 V (the most precise) or the oxidation intensity current at 0.41 V.

Finally, a cleaning procedure for the working electrode must be applied. This step has been previously performed with classical cleaning protocols using a H$_2$SO$_4$ solution; however, for *in situ* seawater measurements, this process is not suitable. A new procedure has been developed which consists in applying a potential of -0.2 V during 200 s in an seawater sample. This method has been successfully tested using classical gold or platinum macroelectrodes (2 mm of diameter) by applying it between different measurements of a sample containing a silicate concentration of 140 μmol.L^{-1}. The measured current in the detection cyclic voltammograms showed a variation of only 4.6% after 18 different measurements over 87 days.

3. Results and discussion

3.1. Contamination tests

The microdevices presented in this work were tested by measuring a 140 μmol.L^{-1} silicate solution made in sodium chloride solution. After the Mo oxidation, the silicomolydic complex detection was carried out with a microdevice directly immersed inside the 3 mL sample contained in the cell shown in Figure 2 (it was only needed to insert the side where are the electrodes of the microdevices). The silicate measurement was repeated several times in the same sample and an unexpected increase of the analytical signal with time was observed. Since all components from the microdevice were in contact with the sample during the detection process, a possible release of silicates was suspected from one or more of the microdevice components. Thus, a contamination study in sodium chloride solution was performed and the following materials were analysed one by one: i) an oxidized silicon wafer (SiO$_2$: thickness: 1 μm) where the metallic electrodes are deposited; ii) a silicon oxide wafer with a Si$_3$N$_4$ passivation layer (Figure 1A-a); iii) a silicone resin covering the electric micro-connections between the electrodes and the electric paths on the printed circuit board (Figure 1A-b); iv) a PolyChloroBiphenyl (PCB) plate where are the electric paths (Figure 1A-c).

Each material/component was immersed separately in different NaCl solutions during at least 10 minutes and, then, a silicate detection procedure (section 2.4) was applied. Cyclic voltammograms were recorded using a homemade gold ultramicroelectrode (see section 2.2) coupled with an Ag/AgCl/KCl (3 mol.L^{-1}) reference electrode and a platinum counter electrode. Figure 3 shows a comparison between results obtained in a blank solution (only NaCl solution) and the different samples in contact with every component of the microdevices.

The signal obtained on Figure 3-A with the oxidized silicon wafer without the Si$_3$N$_4$ layer (i: red line) shows a small peak at 0.30 V that might correspond to the silicomolybdic complex, indicating a release of silicates in the solution. However when the silicon wafer is covered with the passivation layer (ii: blue line) it did not

provide any contamination to the solution (see Figure 3-A). The silicon resin (iii) and the PCB printed circuit board (iv) clearly released silicates to the solution. The measurements of these solutions showed an oxidation peak corresponding to the silicomolybdic complex (Figure 3-B). For the resin, it has been also observed that the signal increases even more for longer immersion times up to 12 hours (see Figure 3-B). Therefore, components (iii) and (iv) must be isolated from the sample during its measurement.

An electrochemical cell has been developed where one microdevice can be integrated into it (see scheme in Figure 4) and allows to put only the electrode surfaces in contact with the sample during a measurement while the rest of the device, susceptible of releasing silicates, is properly isolated from the solution. This cell is made of Poly(methyl methacrylate) (PMMA) and has two distinct parts: at the bottom, there is a base where the microdevice is attached and, at the top, there is a reservoir where the sample is added (once the oxidation and complexation has been performed, for instance, using the procedure and cell described in section 2.4). Between the reservoir and the microdevice, a waterproof seal is placed to prevent the contact of the solution with other microdevice components apart from the electrodes and avoid any release of silicate. As a validation of the good device insulation, a synthetic seawater solution was kept in the cell reservoir with a microdevice attached into it for several days. The measurements performed afterwards did not detect any release of silicates to the sample.

3.2. Passivation layers study

A big challenge is the development of capping passivation layers for electrochemical devices that provide the required accuracy and robustness for continuous analysis in seawater. Si_3N_4 has been the material tested for the passivation layer in the electrochemical devices described in this work, either when the working electrodes

are made of gold or platinum (ME and UME, see section 2.1). The effectiveness of the Si_3N_4 insulating layer has been checked by observing the state of the gold and platinum electrodes with Scanning Electron Microscopy (SEM Hitachi S4800) once 20 measurements of samples with different silicates concentrations had been performed. Gold electrodes did not present a proper adherence to the Si_3N_4 passivation layer in silicate solutions which led to strong damages on them and, thus, to an increase of their electroactive area surface. This resulted in a lack of accuracy and reproducibility on their silicate determinations increasing with the number of uses of the microdevices. Figure 5 shows both the damages observed by SEM on two representative ultramicroelectrodes from one microdevice (see Figure 5, inserts) and the evolution of cyclic voltammograms corresponding to three different detections of the same solution of 140 μmol.L^{-1} of silicates. Between the first and third detection, the analytical signal measured with the first UME increased more than three times (Figure 5-A) and, for the second UME, the signal nearly doubled (Figure 5-B).

Same results were obtained for the gold macroelectrode (see Figure 6), which led to the conclusion that gold is not appropriate for silicate determinations under the conditions used in this work. Moreover, the silver reference electrode also presented seawater infiltrations underneath the silicon nitride (results not shown). Studies and improvements are still underway for isolating properly this electrode but, meanwhile, an external reference can be used for any silicate determination with no problems even in the final version of the *in situ* sensor.

The platinum electrodes showed a good adherence with silicon nitride in seawater. The layer stayed intact on the corresponding electrodes even after several experiments or several days of immersion in seawater with silicates (see counter electrode on Figure 6). Thus, platinum has been chosen as the material for the microdevices working electrodes (the counter electrode is also made of platinum).

3.3. Analytical performances

Twelve different microdevices with platinum working electrodes (all the devices presented one ME of 2 mm of diameter and four UME of 15 μm of diameter) were tested by applying calibration measurements using the analytical procedures explained in sections 2.4 and the cell presented on Figure 4. Different concentrations of silicate were prepared between 0.50 and 12.12 μmol.L^{-1} and from 8.42 to 134.8 μmol.L^{-1} in sodium chloride solution, to cover the whole range of those found in the open ocean. An external Ag/AgCl/KCl (3 mol.L^{-1}) reference electrode was used for all the measurements. The analytical signal was the intensity current measured in the 0.38 V reduction peak of their corresponding cyclic voltammograms. Among the twelve analysed microsensors, only one presented mechanical problems and did not provide any measurable signal. This device will not be taken into account for the following description of the devices analytical behaviour.

On one hand, silicate calibrations carried out with the macroelectrodes showed excellent results: 91% of the analysed MEs showed linear regressions superior to R^2 = 0.995 which demonstrate their outstanding analytical performance. As an example, in Figure 7, two different calibrations (high concentration range) performed within a month of difference are presented (square and circle markers) using the ME of one microdevice for a concentration range from 8.42 to 134.8 μmol.L^{-1}. The agreement between both calibrations proves the good reproducibility that can be achieved with the macroelectrode. In fact, a low average deviation of 2.8 % was obtained for currents measured repeatedly during a month using the same ME in a solution containing 67.1 μmol.L^{-1} of silicates. After 3 months, the measurements could be replicated using the same microdevice. Similar results were obtained in a 134.8 μmol.L^{-1} silicate sample. The sensitivity of the microdevices ME is also excellent, given by the excellent signal-to-noise ratio shown in Figure 7-A. On Figure 7-B, the triangle markers correspond to the calibration obtained for the lowest concentration

range from 0.50 to 12.12 μmol.L^{-1} reported also in the insert of Figure 7-B with a larger scale. The limit of detection with ME is 0.50 μmol.L^{-1}. Altogether, the results obtained with the macroelectrodes demonstrate their remarkable precision, reproducibility, good stability and sensitivity that make them very useful for proper oceanographic applications.

On the other hand, 43 % of all analysed ultramicroelectrodes in the devices (the total number of UMEs tested was 44) showed a high analytical accuracy with calibrations where $R^2 \geq 0.99$ was obtained. More interesting is that seven of the eleven microdevices tested had at least one ultramicroelectrode with this excellent performance. Figure 8 shows both the different cyclic voltammograms of a silicate calibration performed with one ultramicroelecrode from a microdevice and the corresponding calibration curve (the analytical signal has been the current intensity measured in the reduction wave of the cyclic voltammograms). The limit of quantification obtained with UMEs is 8.44 μmol.L^{-1}.

It has been observed that, for the same silicate sample, the current intensity measured are not exactly reproducible between ultramicroelectrodes (even on the same microdevice). An inaccuracy on the UME surface during the microdevice fabrication seems to be the reason. Electrodes are fabricated with an imprecision of $\pm 1\mu$m on their diameter. For UMEs, this imprecision can lead to differences sufficiently large in their electroactive surface and, thus, to a difference on the measured currents for the same silicate concentration. This should not be a problem as the exact electroactive surface of UMEs can be electrochemically determined by analysing well known systems such as the ferri/ferrocyanide redox systems [46].

The presence of a ME and four UME altogether in a same microdevice offers a great advantage since it allows performing up to five automatic sequential silicate detections using a potentiostat and a MUX module (see Section 2.2). This provides to

the user a wider range of results and a better accuracy for the silicate concentration measurement. Moreover, the combination of detection experiments from both ME and UME paves the way for a future calibrationless procedure [51].

Platinum microdevices, especially using the integrated macroelectrodes, have provided excellent results and could be successfully integrated in silicate microsensors for oceanographic research. They will allow also to reduce the cost of the sensor and to facilitate its miniaturisation, as the design of the microdevices can be adapted as desired to fit into very small cells.

4. Conclusions

New silicon-based electrochemical microdevices with Si_3N_4 passivation layer, deposited at low temperature by ICP-CVD coupled with a non-aggressive lift-off process, have been developed for the determination of nutrients in seawater. A microdevice combines one macroelectrode (2 mm of diameter), four ultramicroelectrodes (15 μm of diameter), one platinum counter electrode and one silver electrode that can be used a reference electrode in seawater after chlorination. All the components of microdevices have been immersed individually in seawater during 10 minutes and the resulting solutions have been analysed using the electrochemical procedure for silicate determination. It appears that some of the materials used for the fabrication of the microdevice release silicates to the sample and contaminate it. Therefore, a new cell has been developed where the devices are inserted during the detection process in order to isolate all their components from the solution except the electrodes. Two different metals (Au and Pt) have been evaluated as working electrodes for *in situ* detection of silicate in seawater. On one hand, gold is not suitable for seawater applications since infiltrations of water were observed underneath the passivation layer due to a weak adherence between gold and Si_3N_4 layer in such a corrosive medium.

On the other hand, platinum working electrodes gave good results. Silicate calibrations, between 0.50 and 134.8 μmol.L^{-1}, in synthetic seawater have been performed to test the analytical performance of the microdevices. Ten of the eleven studied platinum macroelectrodes showed excellent linear regressions (R^2>0.995), very good limit of detection (0.50 μmol.L^{-1}) and remarkable stability, lifetime and reproducibility as only 2.8 % of the signal for a 67.1 μmol.L^{-1} silicate sample decreased after 4 months of use. Moreover, seven of the eleven microdevices had at least one ultramicroelectrode that provided linear regressions superior to 0.99% in silicate calibrations. Work is underway to improve even more the performance of ultramicroelectrodes.

Altogether, the new Pt microdevices can be integrated in electrochemical sensors for the *in situ* determination of nutrients concentration in seawater. The sensors will be easily adaptable on different platforms due to the small size, low weight and low cost of fabrication of the microdevices. These properties will also allow the multiplication of the sensors to increase the spatio-temporal resolution of silicate data in the global ocean.

Acknowledgements

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Figure captions:

Figure 1: A) Photo of microdevice with a) oxidized silicon wafer covered with the electrodes and Si_3N_4 passivation layer, b) silicone resin covering the electric micro-connections, c) PolyChloroBiphenyl (PBC) plate, d) printed circuit board and e) connection pin. B) Zoom on the electrodes with the silver electrode (Ag), the platinum counter electrode (Pt), the macroelectrode (ME, ɸ=2 mm) and 4 ultramicroelectrodes (small dots around the ME) and C) Zoom on one ultramicroelectrode (UME, ɸ=15 μm).

Figure 2: Scheme of the homemade cell designed for the Mo oxidation and the formation of the silicomolybdic complex.

Figure 3: Cyclic voltammograms recorded with a gold ultramicroelectrode with 10 mV.s^{-1} (IPDA, 25 μm diameter) and an Ag/AgCl/KCl (3 mol.L^{-1}) reference electrode in: A) sodium chloride solution alone (black line), seawater where the silicon wafer was immersed (red line), seawater where a silicon wafer covered with Si_3N_4 was immersed (blue line); B) sodium chloride solution alone (black line), seawater where silicon resin was immersed for 10 minutes (blue line), seawater where silicon resin was immersed for 12 hours (red line), seawater where PCB was immersed (green line).

Figure 4: Scheme of the cell adapted for the microdevices and the silicate detection measurement.

Figure 5: Evolution with time of cyclic voltammograms obtained in sodium chloride solution containing 140 μmol.L^{-1} of silicates using two gold UMEs (A and B) and

Platinum counter electrode from the same microdevice and an external Ag/AgCl/KCl 3 mol.L^{-1} reference electrode; scan rate 5 mV.s^{-1}(blue line) 1st detection, (red line) 2nd detection and (green line) 3rd detection – Inserts A and B correspond to SEM observations of the gold UMEs in the center and the damaged Si$_3$N$_4$ layer.

Figure 6: Photo of a Scanning Electron Microscopy observation of a microdevice with gold ME and UME electrodes and a platinum counter electrode. In yellow/beige: Au; In grey: Pt; In blue: passivation layer (Si$_3$N$_4$) on the Pt; In light yellow: passivation layer (Si$_3$N$_4$) on Au; In green: passivation layer (Si$_3$N$_4$) on silicon oxide.

Figure 7: A) Cyclic voltammograms obtained in an sodium chloride solution containing [Si(OH)$_4$]=8.42 (blue line), 33.69 (red line) , 67.38 (green line), 101.08 (orange line), 134.77 (black line) μmol.L^{-1} using the platinum working macroelectrode and Pt counter electrode from a microdevice and an external Ag/AgCl/KCl (3 mol.L^{-1}) reference electrode; scan rate 100 mV.s^{-1}. B) Calibration curves obtained between 8.42 and 134.77 μmol.L^{-1} within a month of difference (□ and o markers) and between 0.50 and 12.12 μmol.L^{-1} (△ markers) – Insert: zoom of calibration curve obtained between 0.50 and 12.12 μmol.L^{-1}.

Figure 8: A) Cyclic voltammograms obtained in an sodium chloride solution containing [Si(OH)$_4$]=8.44 (blue line), 33.52 (red line) , 67.14 (green line), 100.82 (orange line), 134.12(black line) μmol.L^{-1} using a platinum working ultramicroelectrode and Pt counter electrode from a microdevice and an external Ag/AgCl/KCl (3 mol.L^{-1}) reference electrode; scan rate 10 mV.s^{-1}. B) Calibration curve obtained measuring the intensity current of the reduction wave in the corresponding cyclic voltammograms.
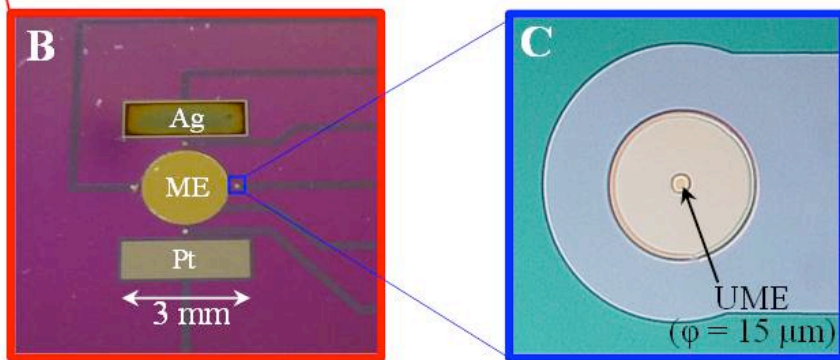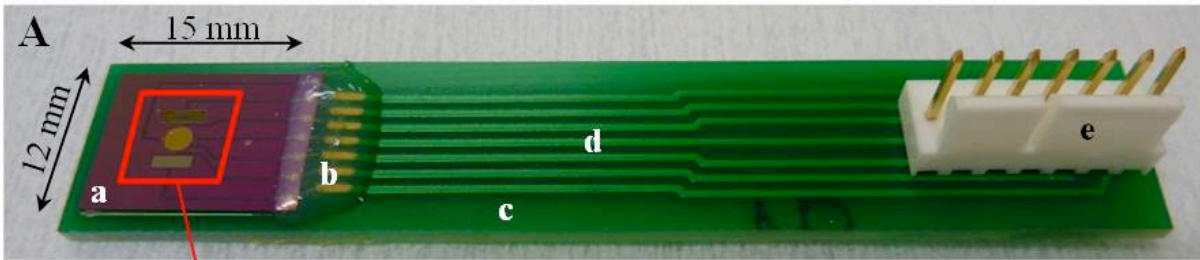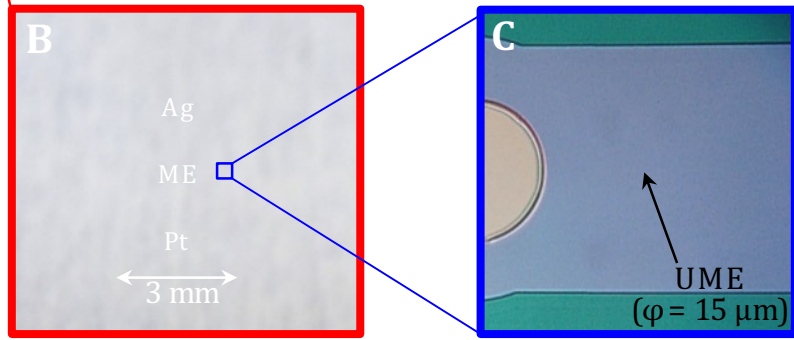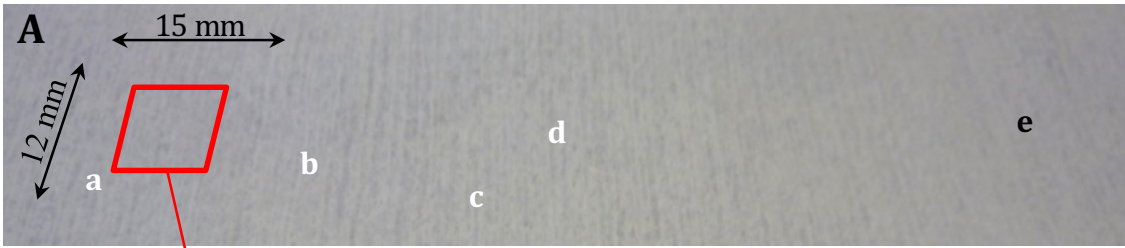
Figure 1:

A 15 mm 12 mm a b c d e

B Ag ME Pt 3 mm

C UME (φ = 15 μm)

A 15 mm 12 mm a b c d e

B Ag ME Pt 3 mm

C UME (φ = 15 μm)

Figure 2:

Counter electrode

Working electrode

Mo electrode

Non-proton exchange membrane (Nafion®)

Ag/AgCl reference electrode

Figure 4:

Reservoir

Seal

Microdevice

Base

Screw
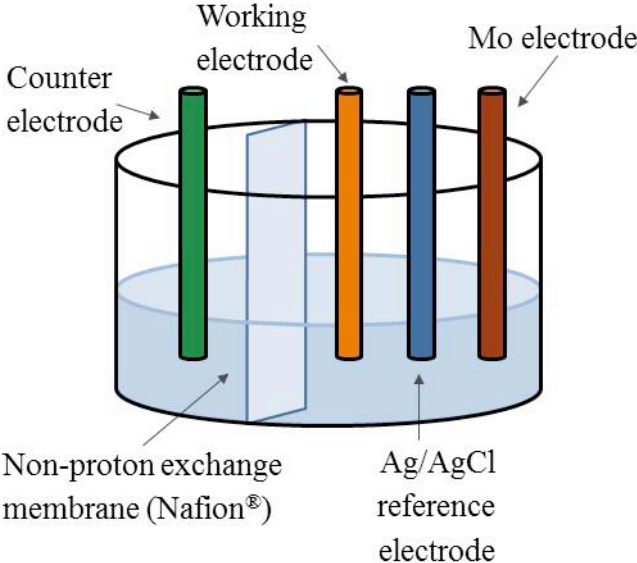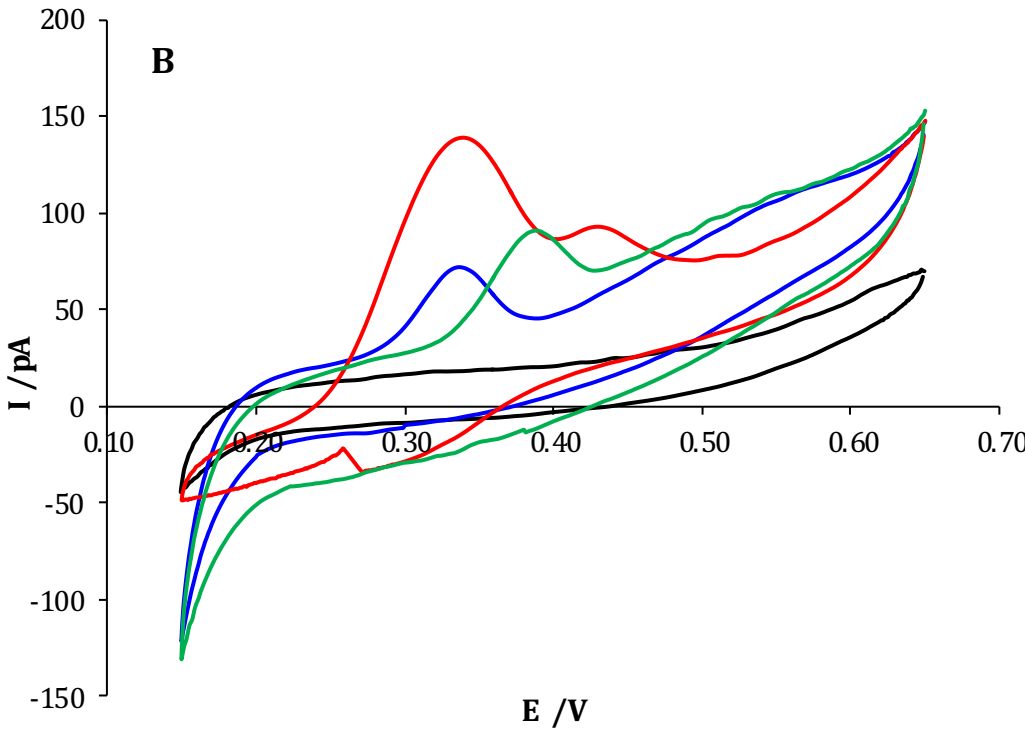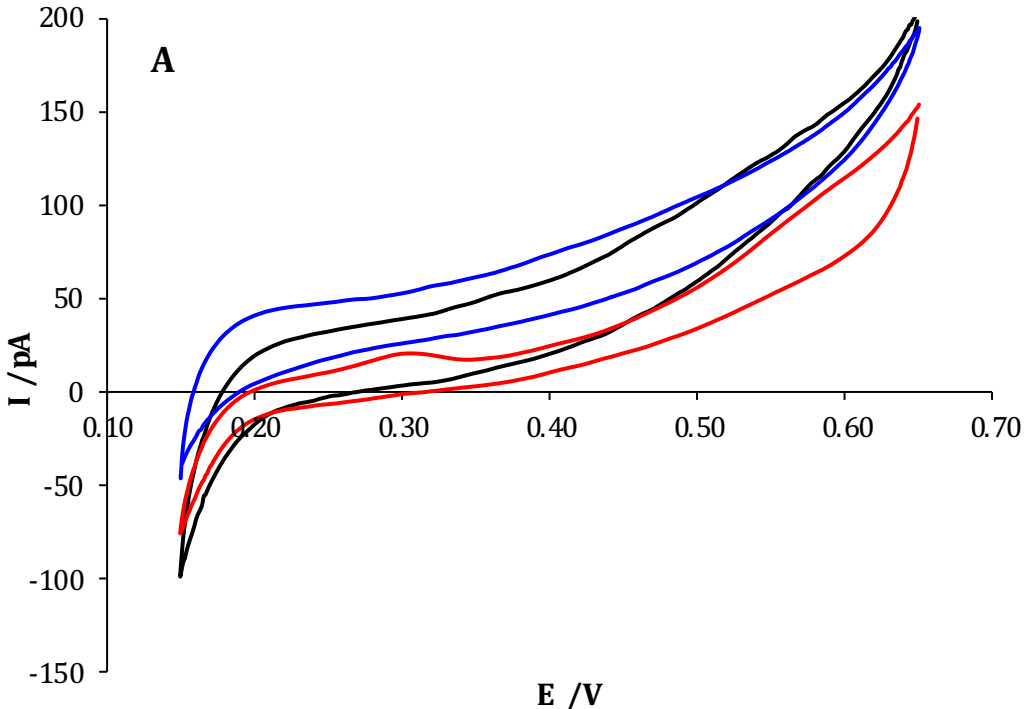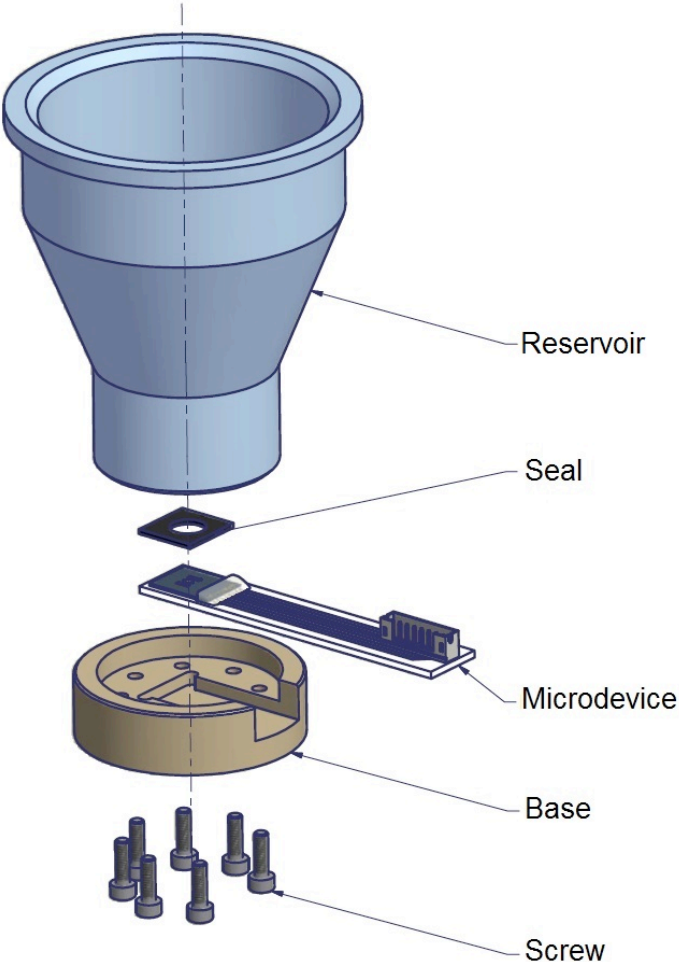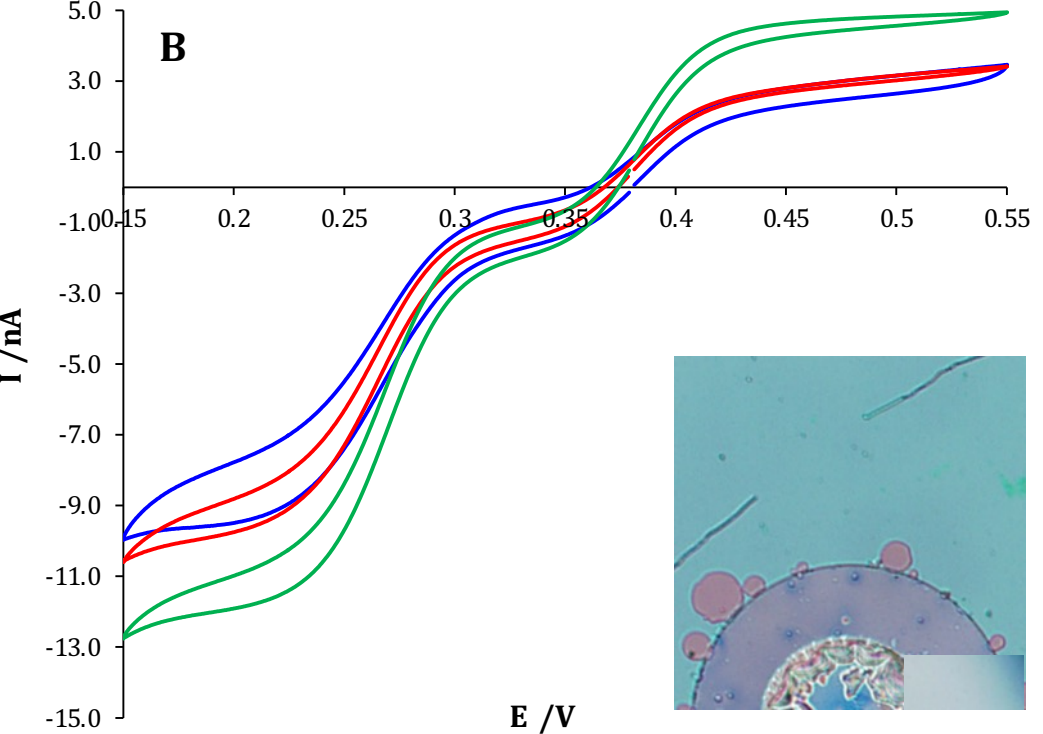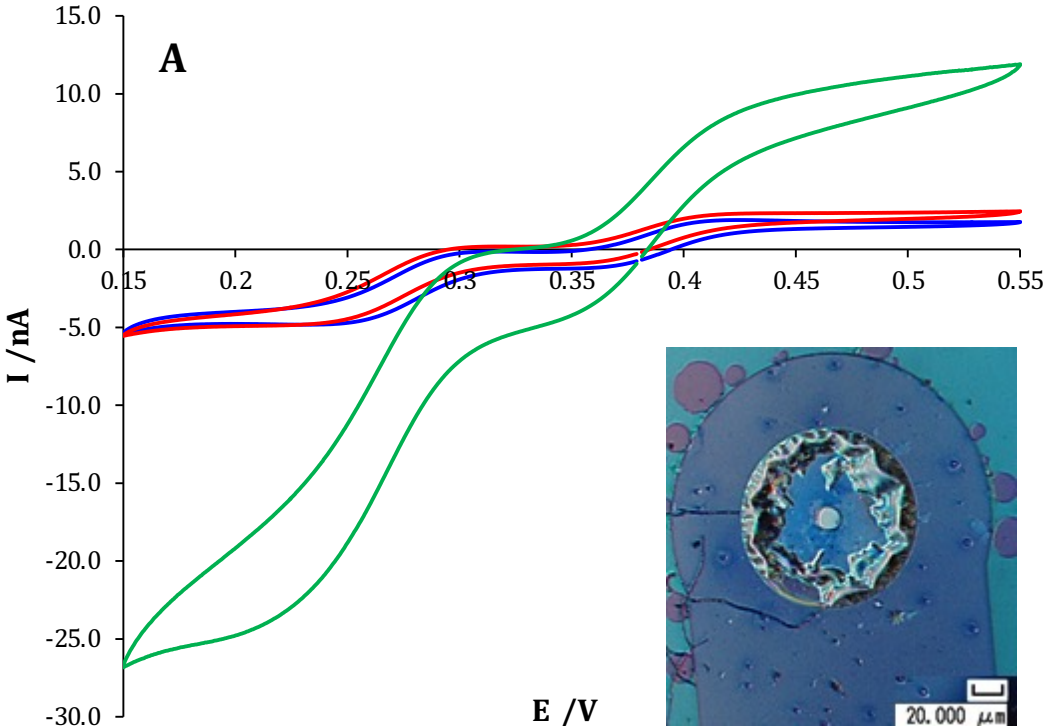
Figure 5:

Figure 6:

Figure 7:

Figure 8: