The most common means to analyze redox gradients in sediments is by push/pulling electrochemical probes through sediment strata while repeating measurements. Yet, as electrodes move up and down they disrupt the texture of the sediment layers thus biasing subsequent measurements. This makes it difficult to obtain reproducible measurements or to study the evolution of electrochemical gradients. One solution for solving this problem is to eliminate actuators and electrode movements altogether, while instead deploying probes with numerous electrodes positioned at various depths in the sediment. This mode of operation requires electrode switching. We discuss an electrode-switching solution for multi-electrode probes, based on Complementary Metal-Oxide-Semiconductor (CMOS) multiplexors. In this solution, electrodes can be individually activated in any order, sequence or time frame through digital software commands. We discuss constraints of CMOS-based multilayer electrochemical probes during cyclic voltammetry.

**Keyword:** sensor; SPEAR; multielectrode; redox interface; sediments; electrochemical gradients

1. Introduction

Biological activity frequently changes the electrochemical properties of sediments [1-3]. Yet, a means to monitor the dynamics of redox chemoclines is still lacking [4]. Throughout sediments various chemicals that are produced, transformed and transported generate complex chemoclines and interfaces [5-8], (Fig. 1).

Chemical patterns within sediments change continuously in response to physical, chemical and biological factors [9-12]. Monitoring how these patterns evolve is important for understanding natural processes [13-15]. But, measuring how such changes

![Simplified diagram of various chemical gradients, zones and biochemical processes that may be present in sediments (after [6-9])](image-url)

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occur within a reasonable timeframe is hard. Conventional means to study the electrochemical heterogeneity of sediments in a fixed location use probes that can either monitor chemical evolution at various depths, or measure chemoclines at a given time, but not both [16-17]. One the one hand, static electrodes are better at analyzing changes in specific locations, but cannot inform about gradients. On the other hand, mobile electrodes are better at analyzing chemoclines, but, they disrupt the texture of the sediment. In doing so, they create voids and zones of compaction. This in turn, leads to artifacts of subsequent measurements or other layers that are contrary to diffusion-based expectations. For these reasons, although the fields of theoretical electrochemistry and the level of electrochemical technology are quite advanced, explaining the evolution of redox chemoclines still lags behind.

The solution to this problem is deploying probes with numerous electrodes placed at various positions within sediments, and monitor these electrodes independently. Most companies that produce commercial electrochemical instruments (UniSense, Gantry, Pine, Keithley, and many others) focus on developing better electrodes, more sensitive meters, improved manipulators and user-friendlier software. in contrast, the production of multielectrode sensors is less explored, mostly because the technical solutions are generally complex, spatial resolution is still low and the cost of multielectrode or multi-potentiostat systems remains high.

The purpose of this work is to identify challenges to cyclic voltammetry with multilayer probes, that may be caused by adding electrode switching hardware via Complementary Metal-Oxide-Semiconductor (CMOS) multiplexers.

2. Materials and methods

Earlier, we have constructed a multi-probe instrument for monitoring the evolution of electrochemical gradients in sediments. Measurements that can be made with such probes include cyclic voltammetry (CV), redox potential, chronoanalyses, conductivity and impedance. Here, we used a probe with 64 working electrodes, reference and counter electrodes, a software-controlled electrode switchboard and potentiostat (Keithley 2450 and 2600). For the electrode selection and to trigger pre-programmed reading protocols a Python program was created (Python Software Inc.). The number of electrodes in a multilayer probe varies greatly depending on the specific field needs, the desired spatial resolution and the technology used to produce the probes.

Switching between the various working electrodes (WEs) was done by means of digital CMOS switches (i.e. Complementary Metal-Oxide-Semiconductor multiplexers) installed on a multichannel Printed Circuit Board (PCB). The PCB’s design was described earlier [18]. The specific CMOS for this work, namely MAX4781 (Maxim Integrated Products) was selected based on small resistance in the ON mode (R_{on}), quality of separation between channels (i.e. low signal interference), voltage range and best signal: noise performance at 1 nA electrical current flow-through. The architecture of the multilayer CV instrument is shown in Fig. 2. The probe used in this project had 64 working electrodes (WEs), each 3 mm in diameter and were distributed across 200 mm of sediment depth. It also contained a reference electrode (RE) and a platinum wire counter electrode (CE), (Sigma/Aldrich) The body of the probe was made of slow-curing epoxy resin (Epo-Tek 301). Inside the resin, each electrode’s back end was inserted in a brass shield connected to the graphite surface by means of conductive graphite paste. Multi thread electrical wires were soldered to the brass end of all electrodes and wires were embedded in the resin core of a cylinder-shaped probe.

After one week of curing, the epoxy rod/probe was polished into a blade shape for easier insertion into sediments. The front electrode’s edge of the blade was tapered in order to expose the WEs’ tip of the water. Then, the exposed surface of the WEs was polished with increasingly finer sandpaper up to 400 grit.

3. Results and discussion

The CMOS selected for this project was the MAX4781 high-speed, low-voltage, low on-resistance, analog switch configured as an 8-channel multiplexer (Maxim Integrated Products) [19]. Fig. 3 illustrates typical CV results and a package of seven voltammograms taken with seven electrodes of a multilayer
probe. Each CV program has 2-3 up-down cycles. Only one of these cycles is eventually selected as representative, based on the lowest noise and on the shape of the curve. At the end of each series of readings using one of the electrodes, a pre-programmed CMOS-based switch occurs, another WE is selected and the program is repeated.

In figure 3B the shape of selected voltammograms indicates voltage peaks for oxidation and reduction of the chemical species that are present in the environment at each designated level. It is not possible in this stage to predict which peak represents which process. This correspondence is only possible with any accuracy in experimental laboratory systems where the known chemical is added to the solution. The most important benefit of the multielectrode solution we propose that not come at the ability to precisely identify chemical but, from the fact that moving the probe is no longer necessary to analyses profiles and that evolution redox profiles can be monitored over time. In implementation changes in voltammogram shapes are expected to generate primary information about the fate and distribution of redox chemicals as well as about the oxidation/reduction state of marine sediments at various depths.

Assuming that CV is the main type of measurement done with multilayer probes with CMOS switches the questions we have asked are the following:

- What is the effect of the added hardware on the overall CV profile?
- Is switching between electrodes influencing the reads (and do theoretically closed channels influence currently-occurring reads)?
- How are changes in temperature influencing the CV reads? and
- How is the CMOS’ supply voltage influencing the CV voltammograms?

Our results show that the voltage variation \( \text{dV} \) value from Fig. 4B depends on the evolution of the ON resistance of the CMOS switch \( R_{\text{ON}} = f(V(V)) \). The \( R_{\text{ON}} \) value and its consequences on the electrical current reads were derived and calculated based on the MAX4781 CMOS technical characteristics [12]. Our measurements (Fig. 4) were done with a CMOS supply voltage \( \text{VCC} = 3 \text{ V} \). Because under these conditions \( R_{\text{ON}} \) changes are relatively flat (i.e. between 0.68-0.75 Ohms) over the range of CV measurements we have done, the amperage variations are less than 0.02% from the electrical current reads.

Under these conditions, and given the fact the shape and peak locations of CV voltammograms did not change we have concluded that it no necessary to introduce corrections in the CV profile software to account for changes in the CMOS MAX4781 \( R_{\text{ON}} \) values. However, from analyzing technical characteristics of other market options we have also concluded that this result cannot be extrapolated to other CMOS models or to other VCC conditions. This is because \( R_{\text{ON}} \) values show large variations in other CMOSs as a function of the applied voltage. Therefore,
if another CMOS type is selected software corrections may be necessary.

At environmentally common temperature ranges (0-40°C) the leakage current of the MAX4781 CMOS is between 0.1 and 0.2 nA at 3.6 V VCC. Our analysis also indicates that at the currents encountered during electrochemical measurements with Keithley 2450 potentiostats (in the $10^{-6}$ A domain) the CMOS leakage does not significantly influence measurements. The variation of $R_{ON}$ with temperature ($dR_{ON}/dT$) is larger at extreme temperatures, but less than 0.1 Ohm between 0 and 40°C. Hence, in moderate environmental conditions $R_{ON}$ variations will not be relevant in most CV measurements. However, measurements in extreme environments (such as less than 0°C hypersaline pools or thermophilic environments at >40°C) should add temperature corrections based on the $R_{ON}$ technical specifications of each CMOS model. One of the largest sources of electrical current variation when using CMOS electrode switching comes from the effect of a wrongfully selected CMOS supply voltage (VCC). The VCC influences most operating features of CMOS, including the $R_{ON}$, the leakage current, the charge injection, the logic threshold, the supply current, the turn-on-turn-off time as well as the frequency response and the frequency distortions. But, for CV measurements at -0.8 to 0.8 V with flow-through currents in the $10^{-6}$ A domains, the key feature remains $R_{ON}$. In the particular case of the MAX4781 CMOS, at VCC = 3V, the beneficial characteristics of $R_{ON}$ is relative flatness, with Resistance Flatness of approximately 0.2 Ohm (on the entire range of applied voltage, insufficient to significantly bias the CV readings). Yet, the choice of CMOS will dictate the need for temperature corrections.

4. Conclusions

An electrochemical instrument with a probe having 64 multilayered working electrodes was used for laboratory tests on >200 cm deep marine sediments. We have analyzed the effect of added hardware (namely MAX4781 CMOS multiplexors) on the quality of CV voltammograms. Our results showed that if CV voltammetry analyses are performed in the range -0.8 to 0.8 V applied voltage, at 0-40°C, with VCC ~3 V (from Li batteries) and if the flow-through electrical current is in the $10^{-6}$ A domain no plot corrections are necessary to account for changes in temperature and channel leakage. Although factory specifications do allow channel switching at other VCC values as well, we advise against this practice because the VCC will greatly influence changes in $R_{ON}$ (significant at very low VCC). These changes do not follow an easy to define formula. Extreme temperatures outside the recommended range (not pertinent here), larger applied and measured current voltage (not apply here), smaller VCC (possible to apply here), larger flow-through currents and other CMOS multiplexors chips would require software corrections. Until more technical information becomes available, we recommend using the MAX4781 CMOS multiplexors in current multilayered electrochemical probes. Due to $R_{ON}$ variation with temperature at extreme temperatures conditions we recommend selecting temperature robust CMOSs, rather than trying to correct readings from the predicted $dR_{ON}/dT$ of MAX4781 multiplexors.

Acknowledgements

This research was funded by NSF, grant number 1638216 and by NASA - Astrobiology Institute, grant number 1611900. This work was supported by a grant of the Romanian Ministry of Education and Research, CCDI - UFISCDI, project number PN-III-P2-2.1-PTE-2019-0198, within PNDI III.

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