Development of microsensors for chloride concentration in concrete

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Abstract— **Chloride infiltration into concrete structures causes corrosion of steel reinforcing rods and eventual failure. Here we report on a three-electrode electrochemical sensor suitable for monitoring chloride concentrations in concrete. We use voltammetry to characterize the sensor for stability and sensitivity in KCl and NaClO solutions. We also outline a process for fabrication of an integrated microsensor and demonstrate crucial process steps for the formation of electrodes on a CMOS chip.**

I. INTRODUCTION

Chloride ions from road salt are a major cause of failure of reinforced concrete structures such as highway bridges. Chloride infiltration causes depassivation of the iron oxide layer found on reinforcing rods, resulting in enhanced corrosion. The chloride ion concentration is normally below 150 ppm in concrete as fabricated but can be considerably increased by the application of deicing salt. The threshold chloride ion concentration for initiation of corrosion is 1500 ppm to 4000 ppm. There is therefore interest in embedded sensors that can monitor the chloride concentration inside the concrete, making it possible to effectively plan remediation or replacement of the damaged structures. An embedded sensor must be sensitive to chloride concentrations in the relevant range, must be stable and accurate over long periods of time, and must have low power requirements.

Previous chloride sensors for concrete have typically used the half-cell potential technique [1]. Researchers have proposed sensors based on embedded electrochemical cells with silver/silver chloride electrodes [2] that are sensitive to the chloride concentration. In this work we consider adapting amperometric sensors previously reported for monitoring chlorine concentrations in water [3]. Important issues include the fabrication technology for sensors integrated with silicon CMOS circuitry, including selective formation of the various electrodes, and the stability of the sensor response. In this paper, we use voltammetry to evaluate sensors that will eventually applied in the amperometric mode.

II. SENSOR SENSITIVITY AND STABILITY

Here we will use cyclic voltammetry to find the peak current response which is proportional to the ion concentration and to assess the stability of the sensor. Cyclic voltammetry is performed by a three-electrode electrochemical cell, which is driven by a potentiostat. Figure 1 shows the sensor which has three electrodes: the working electrode (WE), the reference electrode (RE) and the counter electrode (CE). A voltage sweep is applied to the working electrode and reference electrode, and the current response is measured using the working electrode and the counter electrode. This current response is influenced by the electrolyte of the cell. For our purposes, the current response measured indicates the chlorine ion concentration in the electrolyte.
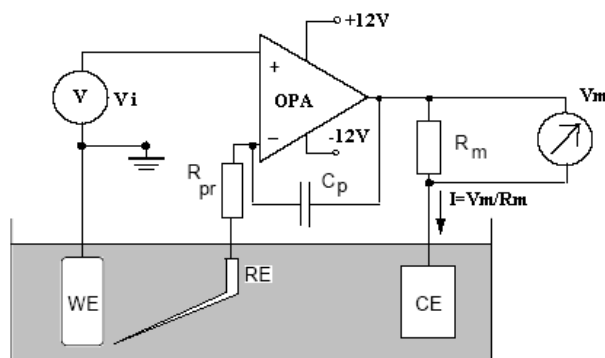

Figure 1. Three-electrode chloride sensor (showing control circuit for measurement of voltammogram. WE indicates the gold working electrode, RE the AgCl/Ag reference electrode, and CE the gold counter-electrode)

During cyclic voltammetry, a voltage sweep is applied between the WE and RE, changing the electrical potential near the working electrode and disturbing the equilibrium of the cell electrochemical reaction. The equilibrium at the working electrode can be expressed by the Nernst equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{C_O}{C_R},$$

where C_O and C_R are the concentrations of oxidized and reduced species in the electrolyte, F is the Faraday constant, n is the number of electrons transferred during the oxidation and reduction, R is the universal gas constant, and T is the Kelvin temperature.

During the voltage sweep the concentration of electro-active species in the electrolyte tends to change to reach a new equilibrium. This causes oxidation or reduction reactions and thus a current response (Faradic current). The plot of the resulting current versus potential between the working electrode and reference electrodes is referred to as a *cyclic voltammogram*, which provides considerable information on the redox reaction and can be used to analyze the properties of the electrolyte. In particular, the peak current in the voltammogram is proportional to the concentration of the reacting species. This is the basis of our sensor for monitoring chloride in concrete.
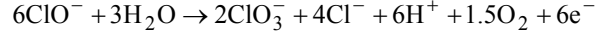
The working and counter electrodes are normally made of gold or platinum for stability. We chose gold so that we can use a previous developed process for forming gold electrodes on a CMOS chip [4]. The choice of a reference electrode is significant because it provides the precise control of applied potential. A good reference electrode needs to have a potential that is stable with time and temperature, and that is not altered by passing a small current. We chose a silver-silver chloride (Ag/AgCl) electrode for this purpose, because it has a stable potential and can be integrated into small devices.

Figure 1 shows the circuit for the cyclic voltammetry experiment. The potentiostat uses an LF411ACN operational amplifier. The voltage control and the output current measurement are done using a Labview-controlled National Instrument AT-MIO-16XE-50 multifunction I/O board. For the three-electrode sensor, 0.25 mm diameter and 1 cm long gold wire was used for the working and counter electrodes and silver-silver chloride (Ag/AgCl) was used as the reference electrode. The reference electrode was 0.25 mm diameter and 1.5 cm long. The AgCl layer was formed by electroplating. The silver wire and a platinum wire are immersed in a 3 mol/L potassium chloride (KCl) solution. A platinum wire immersed in the solution was grounded and the silver wire was connected to a +2 V source for 5 minutes to form a silver chloride layer. The AgCl layer thickness can be estimated from the electroplating current using $I{\cdot}t{\cdot}M/\rho\pi dLF$ where I is the average electroplating current, t is the electroplating time, M the atomic mass, and ρ the density of AgCl. The average electroplating current was about 0.3 mA yielding an AgCl thickness of approximately 2 μm. The resulting AgCl layer is dark in color and easily distinguished from the starting silver wire.

Cyclic voltammetry was performed in sodium hypochlorite (NaClO) solutions and potassium chloride (KCl) solutions at various concentrations. The voltage scan between the working electrode and reference electrode was from -0.6 V to 0.6 V then back to -0.6 V at a scan rate is 0.24 V/sec.

The NaClO solution was diluted with DI water from a 5% stock solution. The chlorine in the solution is in the form of ClO$^-$ ions and HClO molecules. During voltammetry the reaction that takes place at the working electrode is

$$6ClO^- + 3H_2O \rightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 1.5O_2 + 6e^-$$

Measurements from 100 ppm to 1500 ppm ClO$^-$ resulted in the cyclic voltammograms shown in Fig. 2. We see that there is a positive peak for each voltammogram that depends on the NaClO concentration. Figure 3 shows that there is a nearly linear relation between the peak current value and concentration.
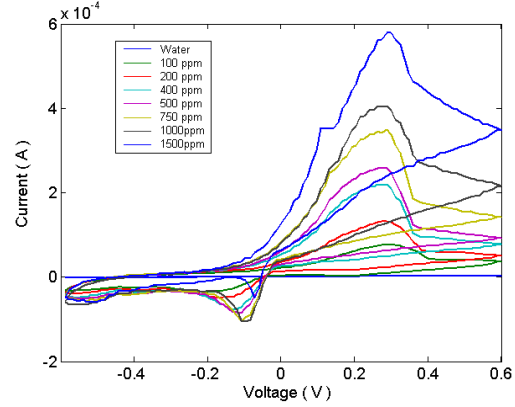

Figure 2. Voltammograms for large sensing electrodes in NaClO solutions.
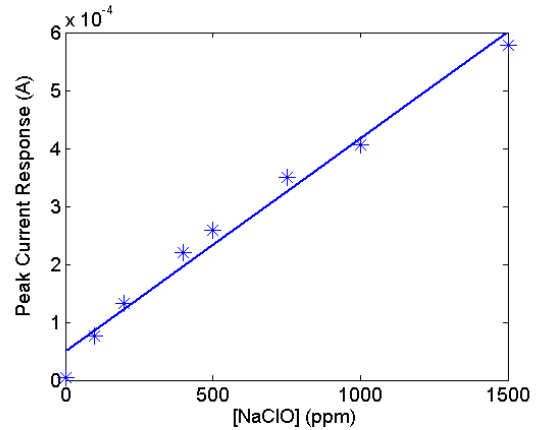

Figure 3. Peak Current Response in NaClO solutions

A lifetime test was conducted on the sensor. The peak current varied by less than 5% for voltammetry ramps conducted every 2 minutes for more than 15 days. The sensor lifetime is limited by the reference electrode. After 15 days, the peak current response began to decrease and the color of the reference electrode changed from black to gray, indicating that the silver chloride layer had almost disappeared. It was observed that there was a silver layer deposited on the working electrode. After cleaning all three electrodes and using a newly formed Ag/AgCl reference electrode for the same setup, we obtained a voltammogram which closely reproduces the initial response.

The cyclic voltammetry experiment was also performed for potassium chloride solutions with Cl^- ranging from 125 ppm to 7500 ppm. In this case the reaction at the working electrode is $2Cl^- \leftrightarrow Cl_2 + 2e^-$. The cyclic voltammogram was not as stable as seen in the NaClO experiment. Figure 4 shows one set of voltammograms; peak current response is nearly linear with the concentration between 0 and 2500 ppm. The lifetime of the sensor is much shorter in KCl solution than in NaClO solution. The peak current response decreases much faster with time and the lifetime is less than one day.
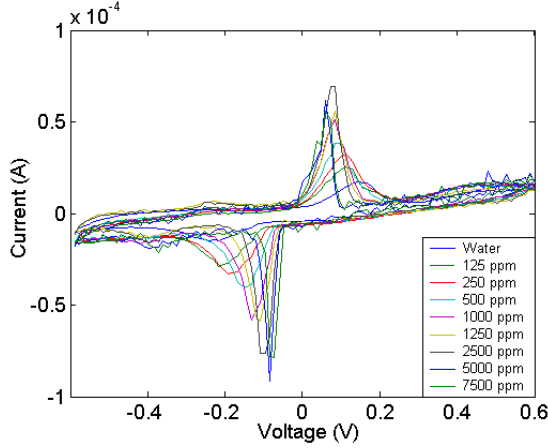

Figure 4.   Voltammograms for large sensing electrodes in KCl solutions
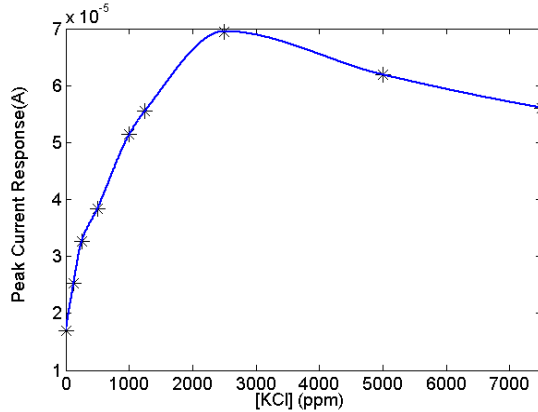

Figure 5.   Peak current response in KCl solutions

The reduced stability in KCl is due to more rapid degradation of the AgCl reference electrode in this solution. The reference electrode provides a stable potential through the reaction $AgCl_{(s)} + e^- \leftrightarrow Ag_{(s)} + Cl^-$. However for AgCl in aqueous solution there is also the solution/deposition equilibrium reaction $AgCl_{(s)} \leftrightarrow Ag^+ + Cl^-$. In the cyclic voltammetry with a KCl solution, Cl^- is consumed during the oxidation, which disturbs the equilibrium and causes the dissolution of AgCl. During the reduction half cycle, Ag^+ is deposited on the working electrode, which also causes the dissolution of AgCl. So during the entire cycle, AgCl is being dissolved. Eventually all of the AgCl is dissolved, and the reference electrode is no longer able to provide a stable potential. For the NaClO solution, the oxidation process pro-

tential. For the NaClO solution, the oxidation process produces excess Cl^-, causing the equilibrium to move to the left and reducing the concentration of Ag^+ in the solution. Consequently there was reduced Ag^+ deposition during the reduction half cycle and longer reference electrode life.

III.   FABRICATION OF INTEGRATED SENSOR

Microfabrication makes it possible to integrate microscale electrodes with a potentiostat or other I/O circuits on a small silicon chip. Our objective is a low-cost embeddable sensor for monitoring of the chloride concentration in concrete. Consequently we will use a foundry-processed CMOS wafer with a minimum number of non-critical post-processing steps. We outline the chip post-processing below followed by a demonstration of some of the crucial steps.

As fabricated the CMOS chip has aluminum pads. Figure 6 shows the post-process sequence required to form gold and Ag/AgCl electrodes. Post-processing requires (a) formation of gold on all pads; (b) selective formation of Ag/AgCl reference electrodes; (c) packaging including wirebonding; and (d) coarse photolithography to protect the wirebonds and expose the sensing area.
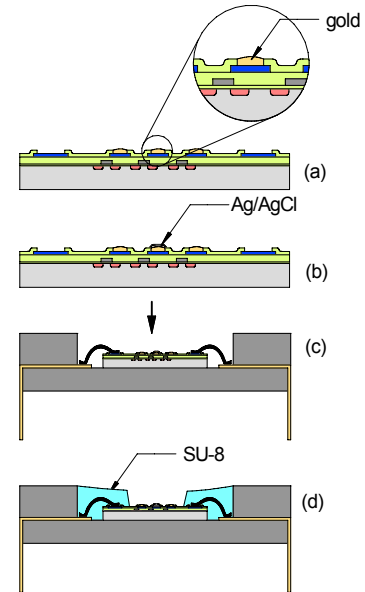

Figure 6.   Processing for fabrication of sensing electrodes on CMOS chip: (a) electroless plating of gold on the aluminum electrodes; (b) formation of the Ag/AgCl reference electrode; (c) mounting and wirebonding; and (d) coarse photolithography to expose the active electrodes.

The formation of the gold electrodes uses a previous developed process. This process consists of several steps: (1) removal of the surface oxide; (2) activation of the surface by single or double zincation; (3) plating of a thick layer of nickel and (4) immersion electroless plating of gold. For the reference electrode, we need to *selectively* electroplate a silver layer on top of a gold electrode, and then perform a chlorination process to form the AgCl layer. This electroplating can be performed by immersing the chip in a saturated

solution of Ag_2SO_4 in 0.5 mol/L H_2SO_4 and forcing a current into the electrodes that will act as reference electrodes. Lithography to expose the active area will be performed using a thick SU-8 photoresist layer. This process has been previously demonstrated in a biosensor application (not shown, [5]).

A final crucial issue is the lifetime of the reference electrode for this sensor. Our experimental results have shown that the ion transfer from the Ag/AgCl electrode to the electrolyte is the main cause of the eventual failure of the electrode. Based on the experiments described above, a protective layer on the reference electrode will be necessary in order to increase the lifetime of the sensor. This layer needs to be conductive but not permeable for silver or chlorine ions. Research has shown that an Ag/AgCl electrode coated with Nafion or polyurethane has a stable potential for more than 90 days in water [6]. We plan to use this protective layer technique on our integrated sensor to improve the lifetime.

In the following section we discuss the fabrication and characterization of microelectrodes fabricated as discussed above. Fabrication of a CMOS chip for the integrated sensor is presently in progress.

IV. EXPERIMENTAL TESTING OF MICROELECTRODES

Microelectrodes exhibit several attractive and important properties in electro analysis like cyclic voltammetry. For microelectrodes, the total current is very small while the current density remains very large. This is a significant advantage when working in highly resistive solutions that can develop large ohmic drops with conventional electrodes. The performance of a microscale sensor may be greatly improved as the concrete structure is a highly resistive environment with little electrolyte.

We have fabricated a three-electrode cell at reduced scale for testing. The fabrication steps are: (1) Deposit a chromium/ gold layer on a fused silica wafer, followed by photolithography to form three planar electrodes; and (2) silver electroplating on one of the electrodes and followed by chlorination to form the reference electrode. The silver electroplating is performed in a saturated solution of Ag_2SO_4 in 0.5 mol/L H_2SO_4. The gold electrode that is used to form the reference electrode is connected to the negative terminal of a current source and a platinum wire is connected to the positive terminal. The other two gold electrodes were left floating. For 10 minutes at a current of 10 µA this yields a silver layer of thickness 30 µm. The chlorination setup is the same as used in the large scale reference electrodes process. The final result is two gold electrodes for the working and counter-electrodes and an Ag/AgCl reference electrode. The areas of the working, counter- and reference electrodes are about 0.5 mm^2, 0.8 mm^2, and 0.02 mm^2 respectively.

A cyclic voltammetry test has been performed using the miniaturized electrodes in NaClO and KCl solutions. The resulting voltammogram for a 3000 ppm KCl solution is shown in Fig. 7. The stability of the sensor in KCl is improved due to the smaller current. This electrode provides a stable output within 5% deviation for two days.
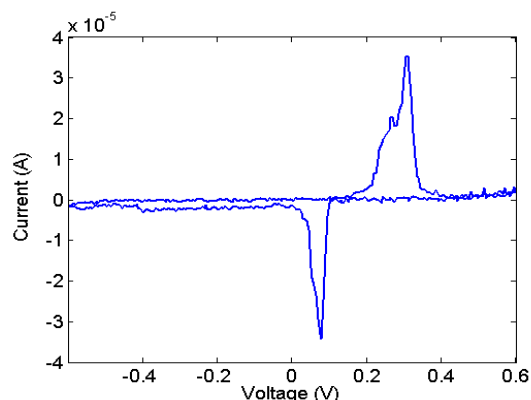

Figure 7. Voltammogram for small scale sensing electrode measured in a 3000 ppm KCl solution.

V. CONCLUSION

We have reported on progress toward developing an amperometric sensor based on cyclic voltammetry for chlorine monitoring in concrete infrastructure. The sensitivity and stability of the sensor have been tested in different solutions and shows a good stable relation between the concentration and peak current response, especially in NaClO solutions. The lifetime of the reference electrode still need to be improved for practical application. Future work is focused on developing an integrated microsensor with CMOS technology.

VI. ACKNOWLEDGEMENTS

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