A current-mode ΣΔ AD based integrated potentiostat

Yuntao Liu\textsuperscript{1a), Xin Sui\textsuperscript{1}, and Mingyuan Ren\textsuperscript{2}}

\textsuperscript{1} College of Information and Communication Engineering, Harbin Engineering University, Harbin, China
\textsuperscript{2} Department of Microelectronics, Harbin University of Science and Technology, Harbin, China
\textsuperscript{a)} summer924@sina.com

Abstract: An integrated potentiostat designed for amperometric electrochemical sensors is presented in this paper. The analog input current is digitized using an A/D converter which employs a current-mode, first-order single-bit sigma-delta (ΣΔ) A/D architecture. Compared with traditional potentiostat, the new potentiostat topology consumes very low power, occupies a very small die area, and has potentially very low noise. These characteristics make the new topology very suitable for portable applications. The potentiostat circuit is implemented in a 0.18 um CMOS process. The circuit converts the sensor current to digital code and the results indicated that the potentiostat can measure the current as low as several nA, and the digital output has a good linearity.

Keywords: current-mode, ΣΔ AD, potentiostat, electrochemical sensor

Classification: Integrated circuits

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1 Introduction

Sensors which utilize electrochemical sensing principles are capable of detecting many important analytes and are utilized in applications such as biomedical devices, environmental monitoring, and laboratory research [1, 2]. Amperometric electrochemical sensors are three-electrode instruments which consists of a working electrode (WE), on which an electrochemical reaction takes place; a reference electrode (RE), which is used to measure the solution potential; and a counter electrode (CE), which is an inert conductor supplying the current required for the reaction at WE [3, 4]. The instrument used to measure current at the redox potential is a potentiostat. The potentiostat serves two main functions: inducing a specified potential drop between WE and RE; detecting the resulting current from the reaction at WE. VLSI technology offers several advantages for implementation of a highly integrated potentiostat: high sensitivity, small feature size, low noise, low power and modularity [5, 6]. Usually, the current generated at sensor is transferred to a voltage by trans-impedance amplifier (TIA), and then converted to digital by SAR or $\Sigma \Delta$ ADC [7, 8]. However, in this case, the trans-impedance should have a large value, which is difficult to be implemented in CMOS process. In this paper, we describe the design of a novel CMOS potentiostat, by directly integrating the current input within a current feedback modulator loop, the imprecision introduced by the amplification stage is avoided.

2 Implementation of the ASIC

Fig. 1 shows the schematic diagram of the proposed potentiostat, which consists of two major blocks, the control part and the amplifying part. The control part maintains the voltage between WE and RE to be a fixed potential and forcing the generated current into the counter electrode. The amplifying part reads out the current from CE and converts such current signal into a digital signal.

Fig. 1. Schematic diagram of the proposed potentiostat
2.1 Control part

In Fig. 1 the three-electrode electrochemical sensor, operational amplifier (OPA) A1, transistor M1 and M2 compose the control part. In this configuration, WE is directly connected to ground potential, RE is connected to the negative input port of an amplifier, and the positive input port is kept to a fix potential Vcell. As the working electrode has a direct connection to the true ground, the environmental noise and interference which may produce significant noise levels are shielded. The output of A1 is not directly connected to CE, but to the gate of transistor M1, and the source of M1 is connected to CE. As the counter electrode produces a large capacitive value, if CE is treated as the load of A1, it may contribute instability factor on the control amplifier. In this configuration, the output of A1 is connected to the gate of M1 instead of CE, preventing the control amplifier from being loaded with large capacitance. As RE is connected to the negative input port with very high impedance, the current generated at WE is forced to flow to CE, M1 and M2.

In the simulation of control part, the stability is the main consideration. OPA A1 is a two stage high gain operational amplifier. The electrochemical sensor, transistor M1 and M2 can be considered as the third stage of the closed-loop system. What more serious is that the current at the third stage varies from several nA to hundreds µA, making the pole of the third stage fluctuate over a wide frequency range. In order to ensure the closed system to be stable over a wide load current range, iterative simulation has been done. Fig. 2 shows the Bode diagram of the loop at different current and PVT (process-voltage-temperature). The results indicate that the system is stable over a very large range.

![Bode diagram of the loop at different current and PVT](image)

The electrical equivalent model of a three-electrode electrochemical sensor is shown in Fig. 3. Rc and Rw represent faradaic resistances, and Cc and Cw are the double-layer capacitances associated with AE and WE. Since, the AE is usually designed to be much larger than WE, Rc and Cc are much smaller than Rw and Cw. Generally speaking, for low frequencies, the electrical equivalent sensor model can be simplified in to series resistors. The two-resistor model, with Rw = 1 MΩ and Rc = 10 Ω is used for the simulation in this work.

![Equivalent model of a three-electrode electrochemical sensor](image)
2.2 Amplifying part

The amplifying part reads out cell current and converts such current into a digital signal. In a traditional configuration, the generated current is converted to a voltage by TIA, and then digitized by a ΣΔ or SAR ADC. In this method, when the reacted current is very tiny, a very large value resistor is needed, occupying a large die area. Besides that, the two-step conversion leads to a complicated circuit design and large chip area [10]. In this work, a first-order current ΣΔ ADC composed of a current integrator, comparators, switched-current D/A converter (DAC) and counter is designed. By directly integrating the generating current within a current feedback ΣΔ modulator loop, it avoids the imprecision introduced by the amplification stage. The integration of the input current is embedded within a ΣΔ modulator loop implementing a first-order incremental analog-to-digital converter for increased sensitivity and integrated digital output.

The amplifying part is composed of current mirror and a current ΣΔ ADC. In Fig. 1, switch S1, S2, S3, capacitor C1 and OPA A2 compose a current integrator, switch S4, S5, S6, S7, capacitor C1, C2 and OPA A3 compose a voltage integrator. The output of voltage integrator is connected to the positive input of comparator COMP1 and the negative input of comparator COMP2. The output of COMP1 and COMP2 are connected to set and reset ports of a D flip-flop respectively. The operation of this current ΣΔ ADC is as follow.

If the initial value of the voltage integrator is zero, then the output of DFF is low level, making M6 opened and M7 closed. Under this circumstance, the input signal of current integrator is the sum of $I_{in}$ and $I_{ref}$, where $I_{in}$ is the current generator at CE, and $I_{ref}$ is the reference current. In Fig. 1, the switch S1, S2 and S3 are working under the control of clk1 and clk2, which are the two phase non-overlap clock. When clk2 is high level, the current integrator is at the state of reset. When clk1 is high level, the current integrator is at the state of integration, allowing the input current charges the capacitor C1. At the time when clk1 changes from high to low, the output of current integrator can be expressed as:

$$V_O = (I_{in} + I_{ref}) \times \frac{1}{C_1 f_s}$$  

(1)

Where $f_s$ is the frequency of clk1. The above equation indicates that the output is proportional to the sum of $I_{in}$ and $I_{ref}$, and inversely proportional to $C_1$ and $f_s$. At the stage of current integration, the switch S4 and S6 are also closed, so the output of current integrator is sampled by C1. When clk1 changes to low level and clk2 changes to high level, the output of current integrator is reset to common mode voltage. During this period, switch S4, S6 open and S5, S7 close, the output of voltage integrator is setup. After N1 periods, the output can be expressed as:

$$V_{INT}(N_1) = \frac{(I_{ref} + I_{in}) N_1}{C_1} \frac{C_1}{C_2}$$  

(2)

Where $t$ means the half period. After N1 periods, when the integration voltage is higher than the threshold of COMP1, the output of COMP1 turns to 1, making the output of DFF changes to high level, opens M6 and closes M7. The input of current integrator turns to $I_{in} - I_{ref}$. After N2 periods, the output of voltage integrator is:
\[ V_{\text{INT}}(N_1 + N_2) = V_{\text{INT}}(N_1) + \frac{(-I_{\text{ref}} + I_{\text{in}})N_2}{C_1} C_2 \]  

As \( I_{\text{in}} \) is smaller than \( I_{\text{ref}} \), so during this process, the output becomes smaller gradually. When the output is smaller than the threshold of COMP2, DFF is reset by the output of COMP2. Repeating this process and counting the output of DFF, the output current reacted at CE can be obtained.

### 3 Experimental results

The proposed potentiostat is fabricated using 0.18 µm 1P4M CMOS process, as shown in the chip microphotograph in Fig. 4(a). The tested PCB is shown in Fig. 4(b). It dissipates a total current of 210 µA from a 3.3 V supply.

![a) Chip microphotograph b) Tested PCB](image)

**Fig. 4.** The chip microphotograph and tested PCB

In order to characterize the performance of the potentiostat, a circuit emulating a three-electrode electrochemical sensor was designed and connected to the potentiostat. The circuit is shown in Fig. 5, in which the emulated sensor current could be expressed as \( I_F = V_F/R_{\text{WE}} \), where \( V_F \) was swept from 0 V to 1 V. For the emulated current from 1 nA to 100 nA, the value of \( R_{\text{WE}} \) was chosen to be 10 MΩ, for the current range of 100 nA to 1 µA, the value of \( R_{\text{WE}} \) was chosen to be 1 MΩ, and for the current range of 1 µA to 10 µA, \( R_{\text{WE}} \) was chosen to be 100 KΩ.

![Fig. 5. The circuit that emulating a three-electrode electrochemical sensor](image)

Fig. 6 shows the experimental results that the current is at the order of nA and µA respectively. In this test, \( I_{\text{ref}} \) is set to be 5 µA and 100 µA respectively. The results indicated that the potentiostat can measure the current as low as several nA, and the digital output has a good linearity. The potentiostat is also used to detect unknown output of electrochemical sensor. An electrochemical dissolved oxygen (DO) sensor is connected to the potentiostat. This sensor can measure value of temperature and the concentration of solution. The measured data of temperature and DO is shown in Table I and Table II, as a comparison, the data measured by EUTECH DO100 which is an equipment for DO measurement is also shown in this table. The results indicate that the potentiostat has a similar measured accuracy with special DO equipment.
The performance comparison with previous works is shown in Table III.

### Table I. Temperature measured comparison

| Measured by potentiostat (°C) | Measured by DO100 (°C) | Error (°C) |
|------------------------------|------------------------|------------|
| 1                            | 4.6                    | 4.5        | 0.1        |
| 2                            | 9.6                    | 9.5        | 0.1        |
| 3                            | 20.7                   | 20.5       | 0.2        |
| 4                            | 31.9                   | 32         | −0.1       |
| 5                            | 42.2                   | 42         | 0.2        |
| 6                            | 50.6                   | 50.3       | 0.3        |

### Table II. DO measured comparison

| Measured by potentiostat (mg/L⁻¹) | Measured by DO100 (mg/L⁻¹) | Error (%FS) |
|-----------------------------------|-----------------------------|-------------|
| Air                               | 7.09                        | 7.24        | 0.75       |
| Water                             | 7.19                        | 7.56        | 1.85       |
| Salty water                       | 8.38                        | 8.61        | 1.15       |

### Table III. Performance comparison with previous works

| [2]    | [3]    | [4]    | [7]    | This work |
|--------|--------|--------|--------|-----------|
| Technology | 0.18 µm | 0.18 µm | 0.18 µm | 0.18 µm |
| Range   | 1 nA–1 mA | 1 nA–1 µA | 0.5 nA–10 µA | 10 nA–100 µA | 1 nA–100 µA |
| Dynamic range | 120 dB | 60 dB | 86 dB | 80 dB | 100 dB |
| Output type | Digital | Digital | Analog | Digital | Digital |
| Supply voltage | 3.3 V | 1.8 V | 1.8 V | 1.8 V | 3.3 V |
| Current  | 4.2 mA | 39 µA | 0.7 mA | 13 mA | 210 µA |

**4 Conclusions**

An integrated potentiostat designed for amperometric electrochemical sensors is presented in this paper. The analog input current is digitized using an A/D converter which employs a current-mode, first-order single-bit ΣΔ A/D architecture. The tested results have demonstrated the proposed potentiostat is capable of applying to electrochemical amperometric sensors, while achieving high resolution, having great potential for environmental monitoring application.

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