

# Design of a Dual-Mode Electrochemical Measurement and Analysis System

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**Abstract**—A dual-mode electrochemical measurement and analysis system is proposed. This system includes a dual-mode chip, which was designed and fabricated by using TSMC 0.35  $\mu\text{m}$  3.3V/5 V 2P4M mixed-signal CMOS process. Two electrochemical measurement and analysis methods, chronopotentiometry and voltammetry, can be performed by using the proposed chip and system. The proposed chip and system are verified successfully by performing voltammetry and chronopotentiometry on solutions.

## I. INTRODUCTION

Due to significant progress in technologies, human living quality is much better than ever before. When people do not have to worry about their livelihood, health-related issues have drawn more and more attentions, especially the care of chronic diseases. Most chronic diseases can be monitored by measuring the concentration of some specific bio-molecules and/or bio-substance in our blood or urine. Electrochemical sensing method is one of the commonly used methods to measure the solution concentration. Compared to other detection methods, its main advantage is that both its input and output signals are electrical, which makes it easier to implement the whole detection system into a chip.

Voltammetry and chronopotentiometry are two commonly used electrochemical measurement and analysis methods. Table I compares the advantages and disadvantages of these two methods. Voltammetry is to provide a voltage across electrodes and then measure the corresponding current. For example, a very popular electrochemical analysis method, cyclic voltammetry (CV), belongs to this category [1]. Chronopotentiometry is to provide a current between electrodes and measure the

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changes in voltage, and cyclic chronopotentiometry (CC) is an example [1].

A dual-mode electrochemical detection chip, which can operate both voltammetry and chronopotentiometry, is proposed in this work. Section II presents the fundamental theories of these two electrochemical analysis methods, voltammetry and chronopotentiometry, and Section III shows the block diagrams of the proposed dual-mode electrochemical measurement chip and system. The measured results are shown in Section IV, and a brief conclusion is drawn in Section V.

Table I Comparison between Two Electrochemical Measurement Methods

	Advantages	Disadvantages
Voltammetry	High selectivity Easy to operate	Sensitive to noise
Chronopotentiometry	Reaction rate can be well-controlled	Bad selectivity

## II. FUNDAMENTAL THEORY OF ELECTROCHEMICAL ANALYSIS METHODS

Three-electrode measurement is the most commonly used method in electrochemical analysis. It consists of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). WE is where the half-cell reaction occurs, and CE is the other end of half-cell reaction. RE is used as a voltage reference, and theoretically there is no current flowing through it. Typically, RE is made of Ag/AgCl or some other non-polarizable electrode, which has almost no overpotential in its electrode-electrolyte interface.

For the voltammetry methods, a voltage is built between RE and WE, and the current flowing through either RE or WE is measured. On the contrary, a current is provided between CE and WE, and the voltage between RE and WE is measured for the chronopotentiometry methods. Fig. 1

shows the setup of these two methods. The details of the voltammetry and chronopotentionmetry are described as follows.

### A. Voltammetry

Take CV as an example to explain the working principle of voltammetry method. The voltage between RE and WE is linearly and periodically scanned within a certain time, as illustrated in Fig. 2(a). By measuring the current between CE and WE, a cyclic voltammogram, which plots the applied voltage versus the measured current, can be obtained as Fig. 2(b). During the time between points A and B, the applied voltage cannot make the reduction reaction occur, so there is only a very small background current. At the time between points B and C, the voltage is high enough to activate the reduction reaction, and the amount of current at a fixed voltage is directly relative to the reaction rate. At point C, the measured current reaches its maximum. In fact, the reactant around the electrode is almost depleted at this time, and it is supplied by diffusion. During the time between C and D, the reaction slows down due to the insufficient reactant, and, hence, the current decreases. Similarly, the oxidation reaction occurs in the same sequence as the reduction reaction from point D, E, F, back to A. Moreover, the maximal (or minimal) current at point C (or F),  $I_p$ , is proportional to solution concentration [1]:

$$I_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} \nu^{1/2} \Rightarrow C^* \propto I_p \quad (1)$$

where  $n$  is the number of electrons transferred during the reactions,  $A$  is the surface area of the working electrode,  $C^*$  is the reactant concentration,  $D$  is the diffusion coefficient of the reactant, and  $\nu$  is the scan rate of the applied voltage. Therefore, CV can be used as a method to detect the reactant concentration in solution.

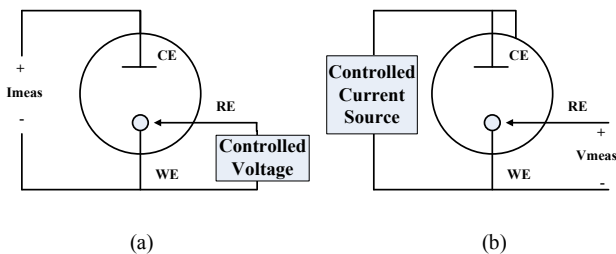


Fig. 1. Measurement setup of (a) voltammetry and (b) chronopotentionmetry

### B. Chronopotentionmetry

Similarly, CC is taken as an example to explain the working principle of chronopotentionmetry method. The applied current keeps changing directions, as shown in Fig. 3(a). For a given electrode surface current  $i(t)$ , the reactant concentration around the electrode can be expressed by the Fick's Law:

$$i(t) = nFAD \frac{\partial C(x,t)}{\partial x} \Big|_{x=0}, \quad (2)$$

where  $x$  is the distance from the electrode,  $t$  is time,  $F$  is Faraday constant,  $C(x,t)$  is the reactant concentration at distance  $x$  at time  $t$ . Therefore, the reactant concentration at the electrode surface at time  $t$ ,  $C(0,t)$ , can be got as [1]

$$C(0,t) = C^* - \frac{2i(t)t^{1/2}}{nFAD^{1/2}\pi^{1/2}} \quad (3)$$

where  $C^*$  is the initial reactant concentration, which is actually what we want to obtain. It can be found from Eq. (3) that the reactant concentration at the electrode surface decrease rapidly as time increases. The resulting voltage between RE and WE will be similar to Fig. 3(b). The voltage increases suddenly after a time  $\tau$ , because the reactant concentration around the electrode surface at this time (i.e.,  $C(0, \tau)$ ) has almost depleted, and the diffusion rate is slower than the reaction rate. Accordingly, charge starts to accumulate on the electrode, and the voltage at the electrode starts to rise rapidly. The time  $\tau$  is defined as transition time, which is the time when  $C(0,t)$  drops to zero, i.e.

$$C^* = \frac{2i(\tau)\tau^{1/2}}{nFAD^{1/2}\pi^{1/2}} \Rightarrow C^* \propto \tau \quad (4)$$

Therefore, if diffusion coefficient  $D$  and the applied current  $i(t)$  are known, the initial reactant concentration  $C^*$  can be got by measuring  $\tau$ .

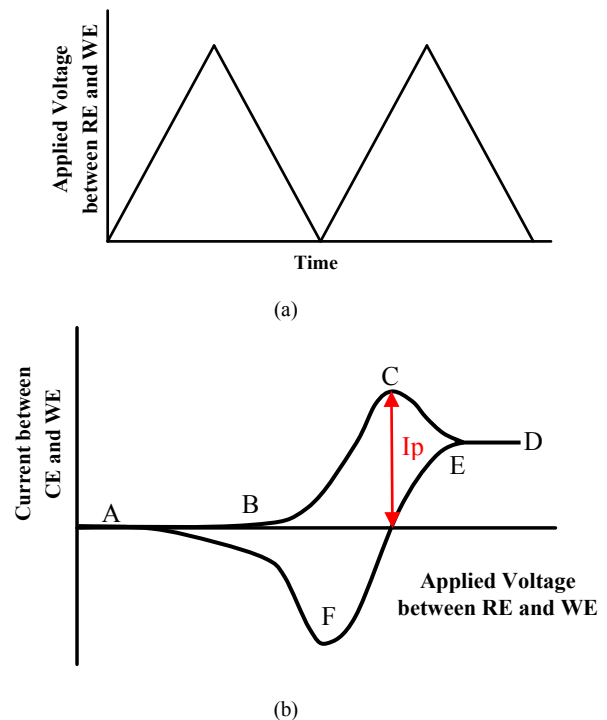


Fig. 2 Cyclic voltammetry (a) applied voltage between RE and WE (b) resulting cyclic voltammogram

### III. SYSTEM BLOCK DIAGRAM AND PROPOSED CHIP

Fig. 4(a) shows the block diagram of the proposed dual-mode electrochemical measurement and analysis system,

while Fig. 4(b) shows the block diagram of the proposed chip. LabView and its GUI interface are used in the laptop to control the process of electrochemical measurement, including data recording and the operational mode selection, i.e., voltammetry or chronopotentionmetry. A FPGA board is used to provide the 12-bit input digital signals to the chip. In the chip, the digital signal is first converted to analog signal by using a 12-bit current-steering DAC. Because only positive power supplies (no negative) are available in our chip, the signal ground is set at half of the power supply voltage,  $V_{DD}/2$ . Accordingly, a level shifter is required to adjust the voltage level of the signal. Then, according to the chosen operational mode, the corresponding voltage or current signal is generated by the driver circuits in the chip. The resulting current or voltage signals between the electrodes are measured by the sensing amplifiers of the chip, which are then sent back to the laptop through the DAQ box for further real-time processing, such as filtering. Matlab is also used for off-line post processing.

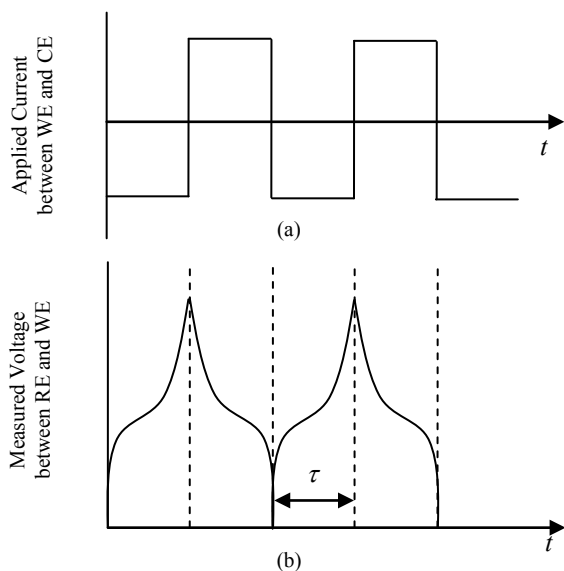


Fig. 3 Cyclic chronopotentionmetry (a) applied current between CE and WE (b) resulting voltage between RE and WE

The proposed chip was designed and fabricated by using TSMC 0.35  $\mu\text{m}$  3.3V/5 V 2P4M mixed-signal CMOS process. There are dual power supplies: 3.3V and 5V. For increasing the driving and sensing voltage range, both the driver circuits and sensing amplifiers are powered by 5V. However, since the level shifter is required anyway, the 12-bit current-steering DAC is powered by 3.3V for saving power. Then its output analog signal is shifted to the desired voltage by the following level shifter.

#### IV. MEASURED RESULTS

Fig. 5 shows the layout of this chip, whose area is  $1.65 \times 1.71 \text{ mm}^2$ . By changing the off-chip resistance, the output driving current may go up to  $\pm 600 \mu\text{A}$ , and its finest resolution is 6 nA. Similarly, the output driving voltage may

range from 2.1V to 3.1V. The power dissipation of the 5V-powered circuits is 5.66mW, while that of the 3.3V-powered circuits is 2.65mW.

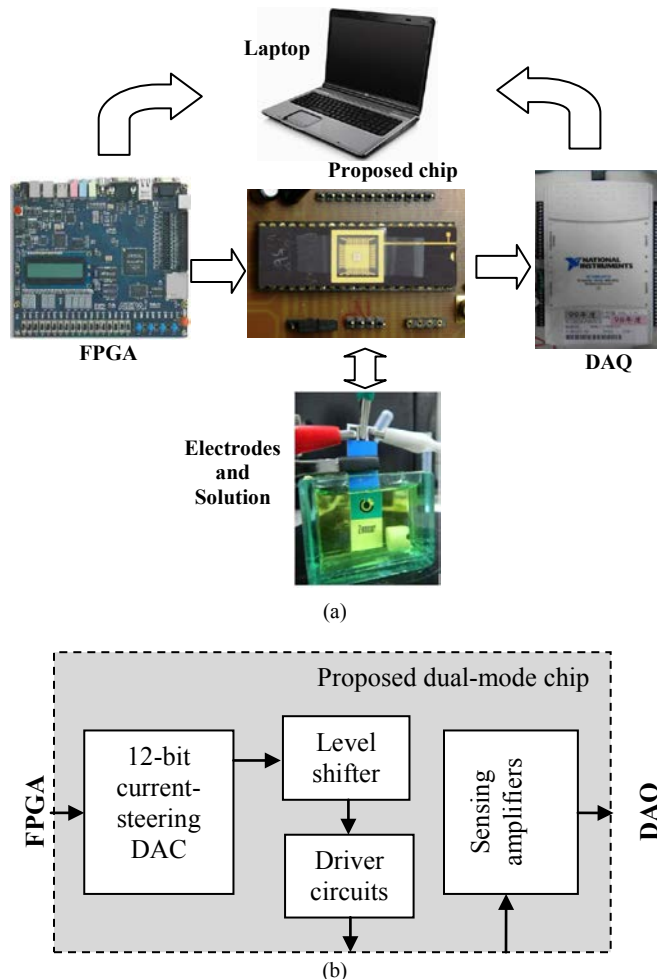


Fig. 4 (a) Block diagram of proposed dual-mode electrochemical measurement and analysis system (b) block diagram of the proposed dual-mode chip

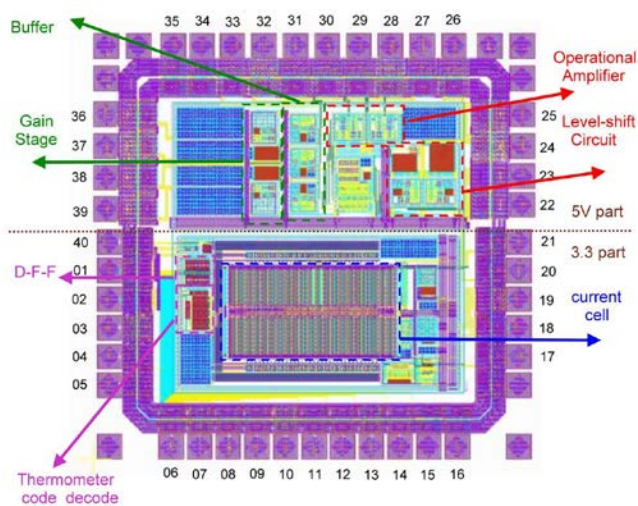


Fig. 5 Layout of the proposed dual-mode chip

Ferricyanide solution was used to test the function of the proposed dual-mode electrochemical sensing chip and system. By using the CV analysis with the scan rate setting to 15mV/s, the resulting cyclic voltammogram is shown in Fig. 6, where the concentration of the Ferricyanide solutions is 0.004, 0.012, 0.016 and 0.020M from bottom to top. It can be found that the peak current indeed is proportional to the concentration. Fig. 7 plots the concentration of Ferricyanide solution versus the peak current of the measured cyclic voltammogram, and the relationship is very linear.

Fig. 8 shows the measured voltage waveform and the applied current signal by using CC. The applied current alternates between 300  $\mu$ A and -300  $\mu$ A, and the concentration of Ferricyanide solution is 0.02M. Notably, the instantaneous voltage change when reversing the current direction might be due to the resistance components of the electrode-electrolyte interface. The transition time ( $\tau$ ) is approximately 4 sec.

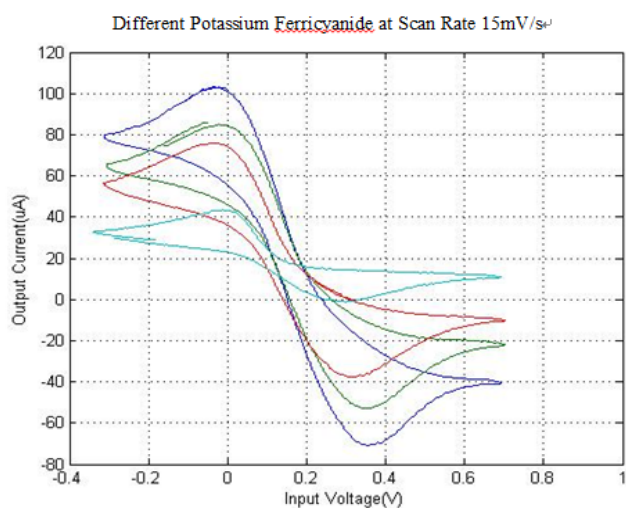


Fig. 6 Measured cyclic voltammogram of Ferricyanide solution with different concentrations. The scan rate is set to 15 mV/s scan rate, and the concentration is 0.004, 0.012, 0.016 and 0.020M from bottom to top.

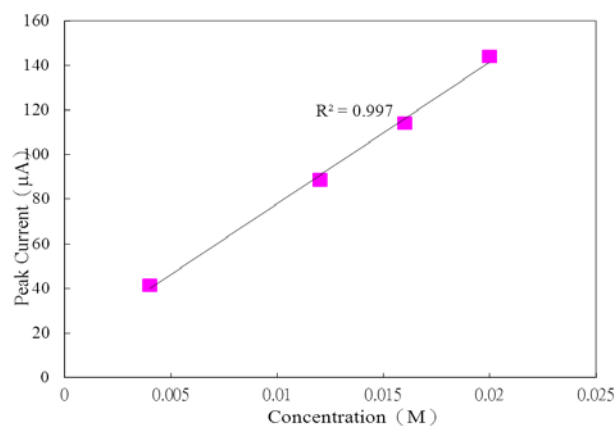
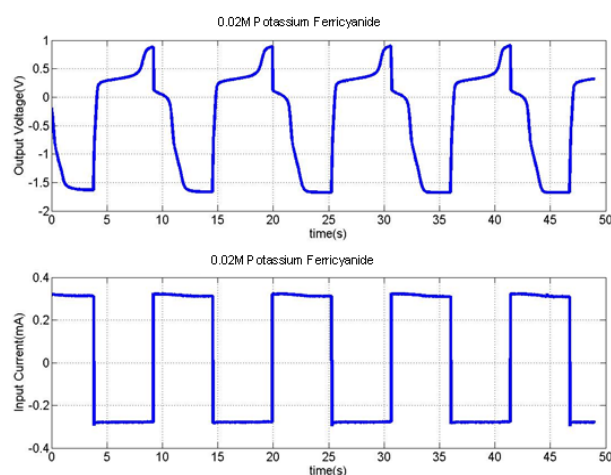


Fig. 7 Plot of the concentration of Ferricyanide solution versus the peak current of the measured cyclic voltammogram.



solution is 0.02 M.

## V. CONCLUSION

In this work, an electrochemical measurement system, which can perform voltammetry and chronopotentiometry, is proposed. Moreover, the main core of this proposed system is our designed dual-mode electrochemical sensing chip. The proposed chip and system are verified successfully by performing CV and CC analysis on Ferricyanide solutions.

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