Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 15 (2011) 5232 – 5238

Procedia Engineering

www.elsevier.com/locate/procedia

Advanced in Control Engineering and Information Science

Development of Digital Microscale Dissolved Oxygen Analytical System

Xin Qi[a] Di Shu[a] Wang Hao[a] YunLong Chen[a] Juan Chen[b]*

[a]*Department of Physics and Electronics, Beijing University of Chemical Technology, Beijing 100029,China*
[b]*Department of Information Science and Technology, Beijing University of Chemical Technology, Beijing 100029,China*

Abstract

This paper introduces the working principles of the digital microscale dissolved oxygen analyzer and sensor. And it also introduces the design of the work system's hardware circuit, signal acquisition circuit and temperature compensation circuit. The instrument features stability and anti-interference with the singlechip as a core to control and process signal. After compared with the dissolved oxygen analyzer made in Switzerland Orbrisphere Company, the self-made dissolved oxygen analyzer was proven to reach the precision level of μg/L. The uncertainty is ±3%μg/L from the experiments, it shows the new-style electrochemical sensor can be widely used to detect dissolved oxygen in boiler feed water in power plant.

Keywords: dissolved oxygen, single chip microcomputer, control system, polarographic membrane.

1. Introduction

Micro-PPB (concentration unit: μg/L) dissolved oxygen detector is mostly used in thermal power and self-own power plant of large petrochemical enterprises, where the oxygen content in boiler feed water and condensate water is very active and tends to have a chemical reaction with the iron-made oven wall, producing rust [1]. Rust makes the thickness and pressure of oven wall unsymmetrical and at sometimes

* Corresponding author. Tel.: +86-13041057506; fax: +86-010-64434898
E-mail address: Jchen@mail.buct.edu.cn.

doi:10.1016/j.proeng.2011.08.970

eventually leads to explosion [2, 3]. Therefore, it is quite significant to precisely and quickly measure the oxygen content in the boiler feed water not only economically but also socially [4]. In the traditional methods of chemical measurement, samples are taken by hands, which are low in efficiency, slow in measurement speed, high in errors which can reach ± 20 %, harmful to environment [5, 6] and easily leading to hidden danger [7].

The oxygen detector introduced in this paper applies polarographic membrane oxygen sensor to measure dissolved oxygen concentration in water [8, 9]. The system is controlled by singlechip and features functions of automatic temperature compensation, sensor automatic cleaning, and high precision and high speed in response, fine stability and durability. Compared with the dissolved oxygen analyzer made in Switzerland Orbrisphere Company, the self-made dissolved oxygen analyzer can be calibrated and proved to have well stability and anti-interference.

2. Working Principles of Dissolved Oxygen Sensor

The sensor consists of a cylindrical cabinet that contains two metal electrodes (one gold cathode and one silver anode). The electrodes are soaked in the electrolyte of the cabinet and separated from measured medium by membrane (such as PTFE, PFA, and FEP) and straticulate electrolyte. Meantime it ensures oxygen can pass through the membrane and electrolyte. When a polarization direct voltage is applied to the electrodes, the reduction reaction occurs in anode and diffusion current is produced [10, 11]. The diffusion current is directly proportional to dissolved oxygen concentration, so the concentration of dissolved oxygen can be reflected by output current [12]. Unsaturated KCI solution and surfactant electrolyte are used in electrode to make the system durable and stable. The chemical reactions are as follows:

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(1)

Anode: $4Ag + 4CI^- \rightarrow 4AgCI + 4e^-$

(2)

When stable polarization voltage is applied to the two metal electrodes of sensor, the dissolved oxygen in water passes through membranes and produces stable diffusion current. The model is described as the equation of $I = KC$, where

$$K = \frac{nFDA}{l} \quad (3)$$

The new-design oxygen electrodes could be calibrated rapidly in air. After calibration, it can be kept for quite a long time with no drift. The zero point current of electrode (residual current) usually less than 1μg/L.

The system adopts integrative design of circulation detection cell and host. (Fig.1)The lateral wall of the detection system has an exit and entrance. The entrance is contacted to a duct and the duct platform is placed in the exit of the circulation detection cell. The oxygen electrode is inserted in and tightly fixed to the circulation detection cell. The electrode signal line fixed on the electrode cap is also connected to the input terminal of the host. The medium to be measured enters the circulation detection cell from the entrance passing ducts and duct platforms and outflows from the exit of circulation detection cell. The measuring signals produced by oxygen electrode are transmitted to the host to be processed and displayed. Circulation detection cell is equipped on the side of the host in order to make it conveniently measured and avoid the outside oxygen from permeating into the testing medium, which would influence the result.

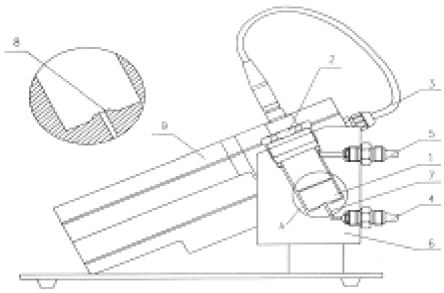

Fig.1. 1 oxygen electrode, 2 electrode cap, 3 electrode signal line, 4 entrance of circulation detection pool, 5 exit of circulation detection pool, 6 circulation detection pool, 7 catheter, 8 catheter platform, 9 host

3. Design of the Host

3.1. Design of Polarization Voltage Circuit

According to the measurement principle of DO electrode, the electrode should be polarized between a voltage of 0.6V and 0.8V. So a 5V voltage generates a 2.5V reference voltage, the output voltage is applied to one side of potentiometer which is tandem with a fixed resistor. With adjustment of a potentiometer the output voltage is generated and it can be applied to DO electrode by a voltage follower.

3.2. Design of Instrument Signal Acquisition Circuit

Two-stage magnifying and filter circuit is used by system. In the first stage high resistance amplifier is applied to couple high internal resistance electrodes. Then a bipolar amplifier circuit was used to select different magnification according to the change of dissolved oxygen concentration, so as to achieve linear amplification in wide bound.

The signal outputted by dissolved oxygen sensor is current signal. It will be converted to voltage signal and magnified. Firstly, the signal outputted by dissolved oxygen sensor (μA level) will be amplified by the first stage reverse amplifier of TLC272 Dual operational amplifier, and the magnification is 106.

Then, the signal will be amplified by the second stage reverse amplifier of low power consumption TLC272 operational amplifier, and the magnification is 20. Negative voltage is applied before the second stage amplifier to overcome the zero drift of amplifier and ensure that the final output voltage is larger than zero.

The output current signal of electrode is 0 nA-100 nA, and after passing the magnifying and filter system, the signal received by signal acquisition circuit will be 0.625 V-2.625 V.

Corresponding to the concentration of dissolved oxygen, the μA level current exported by dissolved oxygen consistence sensor converts to μV level output voltage. After being magnified by low noise bandpass filter, the full-scale output voltage into the system is 0.83 V-3.12 V and then it will be dealt by single chip microcomputer.

3.3. Design of Hardware Temperature-Compensation Circuit

An inner thermistor is connected to the input and output of operational amplifier as feedback resistance ，forming deep negative feedback circuit. When the output current of electrode input from input end, the voltage in output end accord with the formula as follow:

Including to Arrhenius' law:

$$V_{out} = ABP_{O_2}e^{b-a/T} + I_oBe^{b/T} \quad (4)$$

In the equation, α and T are two constants relative to electrode material and structure; B is the coefficient relative to physical properties and dimension of thermistor materials.

I_0 is the response current of electrode when oxygen partial pressure is zero. The value of I_0 is generally small and close to 0 nA.

P_{O_2} is the oxygen partial pressure of measured medium;

T is the work temperature of oxygen permeable membrane;

B is the coefficient of relevant to the physical characteristics and geometry of materials.

b is the material constant of thermistor, which is also called thermosensitive index.

As V_{out} is close to 0 μA, the second part in the right side of the formula can be ignored.

$$V_{out} = ABP_{O_2}e^{b-a/T}\mu g/L \quad (5)$$

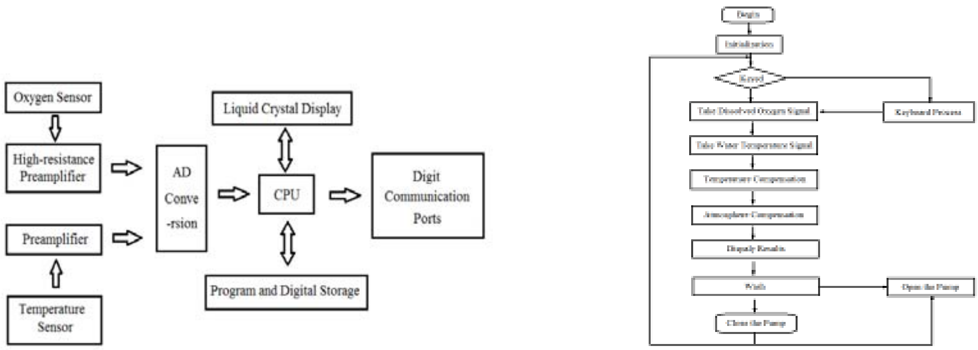

Fig. 2. (a) Work Block Diagram of Host; (b) Program Flow

The amplifier's output voltage is proportional to oxygen partial pressure in water and with no connection with temperature. Once the value of constant α is measured, the aim of temperature compensation can be achieved by selecting a thermistor with an appropriate value of b.

3.4. Signal Processing of Single Chip Microcomputer and Display Circuit

The host includes CPU, data acquisition section, display and communication section. The diagram is showed in Fig. 2 (a).

The system uses the embedded 8 bit digit single chip microcomputer of AT-mega128 CPU made in

ATMEL Company. A/D conversion takes a popular monolithic integration 4 bits half double integral converter that is called ICL7135. It has the characteristic of automatic zero adjustment, automatic polarity output and single reference voltage, which offers the instrument high precision and stability while measuring in low Oxygen（PPB level） condition.

3.5. Communication Interface of the System

To achieve the communication between dissolved oxygen measure system and PC machines, a rational communication circuit should be designed: transfer serial interface RS232 of PC machines to RS485 interface, and use RS485 for long-distance, high-speed serial asynchronous communication; connect the dedicated RS232/RS485 standard conversion chip S2-485 to the standard 9-pin interface and connect RS485 with other side.

RS485 bus interface with host computer forms a balanced differential transmission industry control network, which causes the strong anti-interference function of the instrument, the long transmitted distance, and the quick communicating velocity. Meantime, WATCHDOG power filter is used to increase the reliability of the system and the application of it effective inhibits power network noise.

3.6. . Design of Software of the System

The design of the software is standardized and modularized. (Fig. 2(b))

4. Measurement Results

4.1. Measurement of the Residual Current (Zero Oxygen)

Zero oxygen water being used: The zero oxygen water could be obtained by dissolving 5 g anhydrous sodium sulfite into 100 ml high purity water.

Place the electrode that has been polarized for two hours in air and measure the content of saturated oxygen. Then put the electrode in zero oxygen water. After it becomes stable, observe its measurement result that is the zero oxygen value. Repeat the measurement about 16 times，and the standard error is 0.16 $\mu g/L$. The results are shown in Table 1.

Table 1. Measure of zero oxygen ($\mu g \cdot L^{-1}$)

times	measured value （$\mu g \cdot L^{-1}$）	times	measured value （$\mu g \cdot L^{-1}$）	times	measured value （$\mu g \cdot L^{-1}$）	times	measured value （$\mu g \cdot L^{-1}$）
1	0.7	5	0.4	9	0.3	13	0.2
2	0.6	6	0.4	10	0.3	14	0.2
3	0.5	7	0.4	11	0.2	15	0.2
4	0.5	8	0.4	12	0.2	16	0.2

4.2. Contrasting Measurement

The system will have an actual test in the field and the measurement results should be contrasted with those of Swiss Orbisphere Company instrument.

5. Conclusion

When it is calibrated in the air, the instrument could measure micro dissolved oxygen. The temperature compensation range is (0-40) ℃, the accuracy is $\pm 1.0\,\mu g/L$, and the response time is less than 60 s. The water dissolved oxygen analyzer is characterized in several aspects as follows:

(1). In the system, polarographic oxygen electrode method is taken, and two-stage operation amplifier and filter are designed to conversion weak current signal to voltage signal which can be processed by A/D. We use Arrhenius' law, ICL7135 and RS232 / RS485 to design temperature compensation circuit, A/D acquisition system and system communication respectively, which achieve stable and reliable oxygen content measurement of boiler feed water.

(2). Oxygen electrode responding fast, has a high sensitivity and low zero current (residual current). Special electrode structure and material are used to eliminate the inverse diffusion of internal oxygen in oxygen electrode and to ensure insulation strength of electrodes. Special equipment technology of preassemble membrane is adopted to ensure apt intervals and dynamics between membranes and the surface of gold electrodes.

(3). Inner temperature-measuring electrode, software system and hardware circuit are taken to compensate electrode temperature timely and precisely in the whole temperature range.

(4). Special designed integrative circulation cell. The system is mostly used to environmental monitoring and oxygen content measurement of power plant boiler feed water.

References

[1] Jin-Hwan Lee, Tae-Sun Lim, Youngwoo Seo, Needle-type dissolved oxygen microelectrode array sensors for in situ measurements, *Sensors and Actuators B* , 128(2007), 179-185.

[2] I. Nevares, M, del A' lamo, Measurement of dissolved oxygen during red wines tank aging with chips and micro-oxygenation, *analytica chimica acta*, 621(2008) , 68-78.

[3] Brian T. Glazer, Adam G. Marsh, The dynamic response of optical oxygen sensors and voltammetric electrodes to temporal changes in dissolved oxygen concentrations, *Analytica Chimica Acta* , 518(2004) , 93-100.

[4] C. McDonagh, C. Kolle, A.K. McEvoy, Phase -uorometric dissolved oxygen sensor, *Sensors and Actuators B* , 74(2001), 124-130.

[5] Pramatha Payra, Prabir K. Dutta, Development of a dissolved oxygen sensor using tris(bipyridyl) ruthenium (II) complexes entrapped in highly siliceous zeolites, *Microporous and Mesoporous Materials*, 64, (2003), 109-118.

[6] Paola Fisicaro, Annemie Adriaens, Enzo Ferrara, Assessment of the uncertainty budget for the amperometric measurement of dissolved oxygen, *Analytica Chimica Acta*, 597(2007), 75-81.

[7] Leah Tolosa, Yordan Kostov, Peter Harms, Noninvasive Measurement of Dissolved Oxygen in Shake Flasks, *Biotechnology and Bioengineering*, VOL. 80, NO. 5(2002) , 594-597.

[8] Frank G. Gao, 1 Antony S. Jeevarajan, 2 Melody M. Anderson, Long-Term Continuous Monitoring of Dissolved Oxygen in Detection cell Culture Medium for Perfused Bioreactors Using Optical Oxygen Sensors, Biotechnology and Bioengineering, VOL. 86, NO. 4(2004), 425-433.

[9] T.C. Chou, K.M. Ng, S.H. Wang, Gold-solid polymer electrolyte sensor for detecting dissolved oxygen in Water, *Sensors and Actuators B* , 66 (2000), 184-186.

[10] Glen W.McLaughlin, Katie Barden, Microfabricated solid-state dissolved oxygen sensor, *Sensor and Actuators B* , 83 (2002), 138-148.

[11] Mark A. Saarinen, Julie S. Reece, Monitoring and Controlling the Dissolved Oxygen (DO) Concentration within the High Aspect Ratio Vessel (HARV), *Biotechnol. Prog*, 19 (2003), 1335-1341.

[12] Carlos de la Rosa, Tong Yu, Development of an automation system to evaluate the three-dimensional oxygen distribution in

wastewater biofilms using microsensors, *Sensors and Actuators B*, 113 (2006), 47–54.