Flexible integrated micro sensor to internal real-time microscopic diagnosis of vanadium redox flow battery

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ABSTRACT

The important physical parameters inside the vanadium redox flow battery (VRFB) are difficult to be measured accurately. They have critical influence on the vanadium redox battery performance and life cycle. Due to the uniformity and expendable nature of solution distribution, it will cause the phenomenon of uneven temperature distribution during the power generation process. As the vanadium pentoxide molecules are solid at normal temperature, once they are formed, the flow of vanadium electrolyte is affected severely. Particularly, the runner is even blocked, so that the heat carried away by the electrolyte flow is reduced, and inside the vanadium redox flow battery temperature rises continuously. However, the present bottleneck is outside, theory and simulation. The real information inside the vanadium redox flow battery cannot be obtained accurately and instantly. Therefore, according to the demand for internal *in-situ* microscopic diagnosis of vanadium redox flow battery, this work applied the micro-electro-mechanical systems (MEMS) technology to develop a flexible integrated (temperature and flow rate) micro sensor, which is embedded in the vanadium redox flow battery for in-situ microscopic sensing and diagnosis.

1. INTRODUCTION

In recent years, because of the rise of the renewable energy science and technology as well as the issue of inability to achieving balance between power generation and power utilization, the grid-level power storage device has become one of the important topics contributing to the sustainable development of electric power energy nowadays. In 2012, the United States has developed an energy storage technology development plan and has listed the vanadium redox flow battery in the first place. During the operation of the vanadium redox flow battery energy storage system under ambient temperature and pressure, the heat generated by the battery system can be discharged out efficiently through the electrolyte solution and then outside the system by way of heat exchange. The electrolyte solution is a kind of non-burning and non-explosive aqueous solution with high safety performance. The vanadium redox flow battery is characterized by high current density discharge, long life cycle, quick charging, wide application, low price relative to other energy storage devices and suitability for large static energy storage. Due to the many advantages possessed, the vanadium redox flow battery energy storage technologies and may change the overall energy arrangement in the future (Akinyele 2014 and Chen 2009).

The vanadium redox flow battery is one of the most representative types of flow batteries. The battery energy storage system mainly utilizes the oxidation-reduction reaction at the battery anode and cathode to conduct the battery charging and discharging. The vanadium ion has four valence states of +2, +3, +4 and +5 that all can exist stably and utilizes the electrolyte to realize the circular flow to convert the chemical energy into electric energy through the oxidation reduction of the active substances in the electrolyte. The vanadium redox flow battery is mainly composed of the proton exchange membrane, carbon fiber felt and bipolar plate where the electrolyte of the anode and cathode is pressurized by a pump and charged into the vanadium redox flow battery's flow channel to fulfill the electrochemical reaction to release the electric energy and the electrolyte flows back into the liquid storage tank again after the reaction, thus fulfilling the process of charging and discharging through the continuous circular flow of electrolyte (Lee 2014). The high-flow-velocity electrolyte reduces the vanadium redox flow battery's concentration overvoltage under normal circumstances. Although this may improve the efficiency effectively, the high flowrate would result in more power consumption (Zhang 2015). When the internal temperature of vanadium redox flow battery is increased, the voltage change drops along with it as well (Xiong 2014).

The vanadium redox flow battery's internal important physical parameters are hard to be accurately measured and have critical impacts on the vanadium redox flow battery's performance and life cycle. However, the information concerning the real environmental circumstances inside the vanadium redox flow battery are still unable to be obtained in a complete, real-time and accurate manner due to the current monitoring technology bottleneck, which can only be estimated indirectly by way of external measurement, theoretical evaluation or simulation analysis and other methods (Zhang 2015). Therefore, specific to the demand of the real-time microscopic diagnosis technology application inside the vanadium redox flow battery, the development of the real-time microscopic sensing and diagnosis technology by way of flexible micro temperature and flow sensor embedment inside the vanadium redox flow battery by utilizing the micro-electro-mechanical systems (MEMS) is proposed in this study innovatively. The advantages of this technology include: (1) the volume is extremely small; (2) the measurement locations are flexible and the embedment can be made accurately; (3) the measurement accuracy and sensitivity is high and reaction time is fast; (4) the customized design, development and production is available.

2. SENSING PRINCIPLE AND PROCESS OF FLEXIBLE MICRO SENSOR

2.1 Sensing principle of micro temperature sensor

The structural schematic diagram of the micro temperature sensor is as shown in Fig. 1. The resistance temperature sensor is applied within the linear range of the conductor's resistance, as shown in Eq. (1).

$$R_t = R_0 \left(1 + \alpha_1 \Delta T \right) \tag{1}$$

Eq. (1) can also be adapted to Eq. (2).

$$\alpha_1 = \frac{R_t - R_0}{R_0(\Delta T)} \tag{2}$$

where, the physical meaning of the temperature coefficient (α_1) is the sensitivity of sensor.



Fig. 1 Structural schematic diagram of micro temperature sensor

2.2 Sensing principle of micro flow sensor

The main measurement structure of the micro hot-wire flow sensor is the thermal-resistant heater where the heat source is generated by the constant voltage input to form the stable temperature field. In the flow field, the temperature field generated by the heater would change along with the forced thermal convection of fluid. If the heat supplied externally to the heater is fixed, the resistance of heater would decrease along with the increase of the fluid flow and the heat taken away. The micro hot-wire flow sensor is a kind of sensor designed by utilizing the positive correlation between the hot wire's thermal energy dissipation rate and the fluid flow. The sensing principle of the micro hot-wire flow sensor is as shown in Fig. 2.

According to the King's law, the relationship between the thermal energy dissipation rate and the fluid flow velocity is as shown in Eq. (3)

$$Q = l^{2} \times R = l \times V = (A + B \times U^{n}) (T_{s} - T_{o})$$
(3)

where, Q is the electric power supplied by the external power supply; U is the flow velocity of fluid; n is the correlation coefficient of the heat (Q) and the flow velocity (U), which is about 0.5 as learned from the experiment; T_s is the hot-wire temperature; T_o is the inlet fluid temperature; A is an constant, the heat coefficient transferred by the heater when the flow is zero constantly; B is an constant, the heat coefficient affected by the fluid and heater when the flow is not zero; therefore, Eq. (3) can be adapted to Eq. (4).

$$Q = (A + B \times U^{0.5}) \Delta T$$
(4)



Fig. 2 Schematic diagram of principle of micro hot-wire flow sensor

2.3 Process development of flexible micro sensor

The flexible micro sensor is developed innovatively by using the MEMS technology on the flexible base material of polyimide with the thickness to be 50µm. The high PI polymer material has the main advantages like resistance to the internal environment of vanadium redox flow battery and the acidic electrolyte and other advantages of resistance to high temperature and compression, high flexibility and good durability.

The production process as shown in Fig. 3, which can be roughly divided into the following steps:

First clean the polyimide base material with acetone and organic methanol solution respectively and then remove the residual methanol, surface dirt and residual grease with deionized water to increase the adhesion of the film metal;

In the process, first conduct the chromium (Cr) evaporation to use it as the adhesive layer between the gold (Au) and the lower insulating layer to increase the adhesion between the gold and polyimide;

Conduct the exposure and development to define and fulfill the sensing graphics of the micro temperature and flow sensors;

Transfer the graphics once again onto the metal film of the chromium (Cr) and gold (Au) by way of wet etching;

Finally, spin coat PI 7505 onto and all around the flexible micro sensor to fulfill its protective layer and its production with the actual product and the optical micrograph as shown in Fig. 4.





Fig. 4 Diagram of actual product and optical micrograph of flexible micro sensor



Fig. 5 Calibration curve diagram of micro temperature sensor

2.4 Calibration of flexible micro sensor

The flexible micro sensor needs to be calibrated before it is embedded inside the vanadium redox flow battery to conduct the microscopic diagnosis to guarantee the reliability of signals. The method of flexible micro sensor calibration is to calibrate the micro sensors according to the respective physical quantity individually. The calibration methods are described briefly as follows:

2.4.1 Calibration of micro temperature sensor

After the micro temperature sensor is embedded in the vanadium redox flow battery, use the constant temperature and humidity machine as the temperature calibration reference and maintain the humidity at 100% to simulate the humidity status when the electrolyte flows by to conduct the temperature calibration of the micro temperature sensor. After the control temperature is stable, use the NI PXI 2575 data acquisition device to collect the resistance of the micro temperature sensor in a real-time manner, thus obtaining its calibration curve as shown in Fig. 5.

2.4.2 Calibration of micro flow sensor

The method of flow calibration is to embed the micro flow sensor in the graphite plate of a single flow channel and then provide a stable flow to it. Install an avometer by way of series connection between the power supply and the micro flow sensor to measure the current variation value. The calibration principle is to apply a constant voltage onto the micro flow sensor (heater) to heat up the heater so as to form a stable temperature field. According to the Ohm's Law, when the voltage is fixed, the resistance decreases and the current would increase relatively, thus the calibration curve of the flow and current variation able to be obtained. The calibration result curve is as shown in Fig. 6.



Fig. 6 Calibration curve diagram of micro flow sensor

3. EMBEDMENT OF FLEXIBLE MICRO SENSOR INTO VANADIUM REDOX FOLW BATTERY

Fig. 7 is the diagram of the flexible micro sensor embedment into the vanadium redox flow battery. The embedment locations are at the No.2 upstream flow channel and No.2 downstream flow channel of the graphite plate of the vanadium redox flow battery and used to measure its temperature and flow variation inside the battery on the same flow channel generated due to the internal electrochemical reaction downstream and to conduct the microscopic monitoring and diagnosis.



Fig. 7 Diagram of flexible micro sensor embedment into vanadium redox flow battery

4. CONCLUSIONS

This study successfully developed the flexible micro sensor applied on the PI base material using the MEMS technology. Its advantages include multiple functions, plug-and-play feature, high precision, high linearity, high sensitivity, strong flexibility, suitability for batch production and fast reaction time. The temperature calibration curve conforms to the calibration within the temperature range of the vanadium redox flow battery under the working status and under the relative humidity of 100% at the same time when the curve is still presented in the linear state. The flow also conforms to the

flow of the vanadium redox flow battery under the working status. The micro hot-wire flow sensors of this type are not so uniform for the heat of the temperature field, and may be taken away along with the flow velocity under the liquid environment. Currently, the flexible micro sensor is embedded into the vanadium redox flow battery successfully to conduct microscopic sensing and diagnosis inside the battery.

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