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Flexible micro sensor for in-situ monitoring temperature and voltage of coin cells

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ABSTRACT

In this study, a novel integrated two-in-one flexible micro sensors are fabricated using the micro-electro-mechanical systems (MEMS) process for in-situ monitoring of temperature and voltage in a coin cell. Temperatures fluctuate in a coin cell, as evidenced by the inner temperature changing more rapidly than the outer one. Additionally, monitoring the inner temperature is faster than the outer one. Charging and discharging causes non-uniform distributions of the inner voltage.

1. Introduction

The lithium battery is characterized by portability, wide range of service temperature, high energy density, high operating voltage, no memory effect, long life and numerous charges and discharges. It has been used as an energy storage device tightly related to human life. The smart phones, notebook computers, tablet PCs and electric vehicles are all equipped with lithium batteries as energy storage device.

In the charging and discharging processes of lithium battery, the electrochemical reaction between anode material and electrolyte generates a great deal of heat [1,2]. When the lithium battery is not cooled effectively, the temperature will rise rapidly and the oxygen in the anode material structure may escape [3,4]. The escaped oxygen will react with the organic solvent in the electrolyte, releasing dangerous inflammable gases [5]. The excessive charge and discharge of lithium battery will cause unstable voltage even thermal explosion [6], as well as safety problems [7]. In addition, the operation of lithium battery at extreme temperature may result in worse performance, shorter life or failure [8]. Therefore, the lithium battery failure analysis is absolutely important.

In order to obtain accurate central temperature of lithium battery, Forgez [9] drilled in the center position of a 18,650 cylindrical lithium battery and inserted two T-type thermocouples in diameter of 1 mm, which were attached to the outside of battery and inserted into the central cathode of battery respectively. The side holes were sealed with synthetic resin, the internal temperature was measured in a glove box full of argon.

Chacko [10] researched polymer lithium battery electro thermal model, the anode and cathode materials were $LiMn_2O_4$ and graphite respectively, and the capacity of this lithium battery was 20 Ah. The battery surface was attached 10 thermocouples to measure the temperature change on the battery surface, and a 3D model was built by software to forecast the temperature change on the battery surface. Finally, the battery surface temperature profile models were drawn one by one by different loop tests.

Yang [11] mentioned the probable safety problems in lithium battery. Low temperature may cause undervoltage, overvoltage and overcurrent, and high temperature may cause severe problems of electrolyte decomposition, anode material decomposition and battery material oxidation.

There were some previous works of the Lee's group using MEMS in flexible sensors for lithium-ion battery, fuel cell, reformer and light emitting diodes. Lee [12] measured the temperature in the lithium-ion battery. They found the important advantage that monitoring the inner temperature yields information on thermal changes 45–90 s before monitoring the outer temperature. Lee [13] monitored temperature and voltage of high-temperature fuel cell

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stack at the operating temperature of 170 °C and constant current (2, 10, 20A). Lee [14] confirms the feasibility and compatibility of thin-film sensor applications with a flexible substrate for the micro-reformer. Lee [15] measured the temperature obtained using the micro temperature sensor was 1.52 °C lower than that obtained by thermal resistance measurement at 120 mA, and 5.45 °C lower at 350 mA.

The existing commercial temperature and voltage sensors are too large, and they are unlikely to be embedded in lithium battery. Thus, there may be poor airtightness causing electrolyte leakage, or the internal temperature and voltage are measured destructively, influencing the lithium battery performance and safety.

Therefore, this study uses MEMS technology to develop a two-in-one flexible micro sensor which can be embedded in a coin cell for real-time internal temperature and voltage monitoring. The R&D objectives are as follows:

1. A compact micro sensor with two sensing capabilities is developed for the operation of coin cell. The micro sensor can be embedded in the designated position accurately for its compactness.
2. The airtightness should be concerned in lithium battery packaging to avoid electrolyte leakage, so the micro sensor is not too thick, and can withstand the pulling stress in the packaging process.
3. High accuracy, high sensitivity and quick response.
4. The micro sensor must be able to withstand the harsh environment inside the coin cell in operation.

The completed two-in-one flexible micro sensor is embedded in the half coin cell for real-time internal information monitoring. The reaction conditions inside the coin cell can be known accurately and instantly, analyzing the internal temperature uniformity and voltage variation microscopically. The database about interior of coin cell may be created in the future to provide information for assisting improvement and research, so as to complete the measuring tool for internal real-time microscopic monitoring and safety diagnosis of coin cells.

2. Methodology

2.1. Design and sensing principle of the temperature sensors

Based on the temperature coefficient of resistance (TCR), the resistances of metals increase with the environmental temperature increases. When the temperature of the resistance temperature detectors (RTD) is in the linear region, the relationship between the measured resistance and the change in environmental temperature can be expressed as,

$$R_t = R_r(1 + \alpha_T \Delta T) \quad (1)$$

where R_t is the resistance at t °C; R_r is the resistance at r °C, and α_T is the sensitivity of the micro temperature sensor (°C^{-1}) [16,17].

The micro temperature sensor used in this study is RTD (Resistance temperature detector). Its electrode type is of the serpentine structure and the sensing area is 310 μm × 620 μm, the minimum wire width is 10 μm, it is shown as Fig. 1. Its temperature sensing resistant material is gold (Au). As its chemical properties are stable, the process is simple and of high linear degree.

2.2. Design and sensing principle of the voltage sensors

The micro voltage sensor developed in this study is a miniaturized voltmeter probe in size of 135 μm × 100 μm. The design drawing is shown as Fig. 1. Only the forefront probe is exposed, the other parts are covered with insulating material, so as to make sure the sensing head contact area is fixed and in the designated zone. The probe is extended by conductor to the pad side, and the measuring instrument is connected to measure the voltage directly. The principle of sensing is that the analyte is supplied with a firm power to measure the voltage difference between two probes.

3. Fabrication

This section introduces how to develop the two-in-one flexible micro sensor which can withstand half coin cell packaging pressing and harsh electrochemical environment, including selecting appropriate process materials and introducing production process, so that the accurate internal information can be obtained in the half coin cell testing process.

This study uses the surface micromachining technology of MEMS manufacturing technology to develop the two-in-one flexible micro sensor. The concept is derived from the integrated circuit process. The semiconductor processing technologies of coating, photolithography and wet etching are used to define the structural layer. The wet etching technology is used to remove the sacrificial layer, so as to liberalize the structure to finish the surface micromachining structure. The fabrication process performed in the cleanroom is shown in Fig. 2.

The flexible substrate of this two-in-one micro sensor was 50 μm thick polyimide (PI) foil. The PI foil was cleaned in acetone and methanol. An E-beam evaporator (EBS-500) evaporated Cr (500 Å) as adhesion layer and Au (2500 Å) as sensing layer by evaporate rate 0.1 Å/s, as shown in Fig. 2 (A and B). The unnecessary Au/Cr film was removed by photolithography with a wet etch to complete the two-in-one micro sensor layout structure, as shown in Fig. 2 (C and D). Finally, the polyimide 7505 was spin coated on the sample as insulating layer. The voltage and sensor pad end were exposed by using photolithography process again to complete the flexible two-in-one micro sensor, as shown in Fig. 2 (E and F). The finished flexible two-in-one micro sensor and optical micrograph are shown in Fig. 3.

4. Results and discussions

When the two-in-one flexible micro sensor is completed, the micro sensor shall be calibrated to validate its reliability. After the calibration procedure, the coin cell testing machine and National Instrument (NI) data acquisition system are used for half coin cell test and internal information acquisition and microscopic diagnostic analysis, to determine the differences in the electric property of the half cells with and without two-in-one flexible micro sensor. The local temperature and voltage variations in the coin cell are monitored and analyzed instantly in different operating conditions.

4.1. Calibration of two-in-one flexible micro sensor

4.1.1. Calibration of micro temperature sensor

The flexible micro sensor is embedded in the coin cell for diagnostic analysis after repeated calibration. Each calibration curve shall have high linearity and reproducibility, so as to create the database of temperature corresponding to electrical resistance accurately, to provide temperature corresponding data for measurement.

The temperature correction range of flexible micro temperature sensor is 0–60 °C, measured once every 10 °C, there are three calibration cycles. The testing machine temperature stabilization time is 120 min. Three calibration curves of flexible micro temperature sensor are shown in Fig. 4. Three calibration curves of micro temperature sensor have high linearity and reproducibility. Table 1