Metallic Contaminant Detection in Liquids using a High-Tc RF-SQUID

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Abstract. We have developed a system using high-temperature radio frequency superconducting quantum interference device (RF-SQUID) for detecting metallic contaminants in the liquid component of a lithium-ion battery. Although we have executed detection experiments using a simulated system without liquid in the past[1], we have developed a new system to inspect real liquid components. Small cylindrical metallic contaminant samples were fabricated using a gallium-focused ion beam to evaluate the detection performance. Tap water containing the metallic contaminant sample was poured into the tube using a pump, and the magnetic signal of the contaminant matter was detected using the RF-SQUID. Among the tested small metallic contaminant samples, the volume of a minimum detectable metallic contaminant was evaluated to be $2 \times 10^4 \, \mu m^3$, which corresponded to that of a spherical sample with a diameter of $33 \, \mu m$ and a sensitivity of a signal-to-noise ratio of more than three. Moreover, the dependence of the detected signal strength on the volume of the metallic contaminant samples is discussed here.

1. Introduction
Higher performance due to the higher density of lithium-ion batteries increases the risk of overheating and causes fire. Therefore, technologies for ensuring product safety and quality control have become important for battery component manufacturers[2-6]. In this study, we have developed a radio frequency superconducting quantum interference device (RF-SQUID) system for detecting the amounts of metallic contaminants present in the liquid component of lithium-ion batteries[1]. The existing system that has been reported thus far does not use a liquid; however, a fishing line with a metallic contaminant is passed through a polyethylene tube, and the metallic contaminant is moved by winding the line with an electric motor. In this study, we have developed and evaluated a novel system that detects the metallic contaminants present in the flowing water in a tube.

Figure 1. Principle of detection of micro metal contaminants in liquids.
2. Principle of detection
The principle of the system that uses the RF-SQUID is depicted in Figure 1. It is assumed that the liquid that is to be tested for a metal contaminant flows in the tube. A permanent magnet was placed outside the tube. The metallic contaminant was magnetized using the permanent magnet, and as a result, it underwent remnant magnetization. The RF-SQUID detects the remnant magnetization of the metallic contaminant when it passes through.

3. Experimental Setup

3.1. Magnetic shield
A schematic diagram of the system is depicted in Figure 2. The LN$_2$ cryostat was used to cool the RF-SQUID sensor to below the superconducting transition temperature. A rectangular trench, which served as a flow path for the sample, was installed inside a micro metal magnetically shielded cylinder. It consisted of two layers of shield metal: (D $\times$ H) $\phi$550 mm $\times$ 750 mm for the outer layer and (D $\times$ H) $\phi$400 mm $\times$ 600 mm for the inner layer. Two apertures with dimensions of (W $\times$ H) 100 mm $\times$ 50 mm were provided on both sides of the magnetically shielded cylinder.

![Figure 2. Schematic diagram of the system. The RF-SQUID microscope-type cryostat was installed in the two-layered magnetically shielded cylinder. The trench (5 mm high and 8 mm wide) was placed below the sensing region of the cryostat, so that the RF-SQUID could detect a metallic contaminant at a distance as close as 1.0 mm.](image)

3.2. LN$_2$ Cryostat
The RF-SQUID microscope-type cryostat was designed and used to cool the RF-SQUID to 77 K. The outer dimensions of the cryostat were (D $\times$ H) 250 mm $\times$ 288 mm. A copper LN$_2$ tank (0.8 L) was installed inside the vacuum of the cryostat [7-9]. A sapphire rod with a diameter of 15 mm was anchored to the bottom of the LN$_2$ tank. The RF-SQUID magnetometer and a read-out loop connected to a semi-rigid coaxial cable were installed at the top of the sapphire rod. A sapphire vacuum window with a diameter of 50 mm and a thickness of 0.5 mm was sealed at the bottom of the cryostat. The structure
was designed to thermally isolate the RF-SQUID from the room temperature outside; this design allowed the RF-SQUID to get closer (approximately 1.0 mm) to the test object.

3.3. Liquid pumping mechanism
An acrylic trench with dimensions of (W × H) 8 mm × 5 mm was placed under the cryostat. The top of the pipe was covered with a plastic film that had a thickness of 0.5 mm to narrow the gap between the RF-SQUID and the path through which the liquid flowed. A tube (Masterflex Tigon E-Lab pump tube 06509-17) that was introduced to a liquid storage tank was connected to both ends of the rectangular trench. A tube (Masterflex 07555-00) was used to flow the liquid. The fluid was exposed to a parallel magnetic field (1.27 T), and thereafter, was inspected by the RF-SQUID when it passed below the RF-SQUID. A strainer was installed at the top of the tank, where the liquid was discharged to collect a sample of the metallic contaminant matter. Tap water was used as the liquid to be circulated. When the pumping speed was set to the maximum, the average flow rate at the trench was found to be 33 m/min.

3.4. Details of the RF-SQUID
The RF-SQUID magnetometer was fabricated by patterning a YBa$_2$Cu$_3$O$_y$ thin film with a thickness of 200 nm, which was deposited on a 10 mm × 10 mm SrTiO$_3$ bi-crystal substrate (36.8°). The outer dimensions of the RF-SQUID washer were 9 mm × 9 mm, and the inner dimensions were 100 µm × 100 µm. The flux noise spectrum of the RF-SQUID is depicted in Figure 3. The flux noise with the RF-SQUID in the system was 60 µΦ$_0$/Hz$^{1/2}$ in the white noise region [1]. The effective area of the RF-SQUID, $A_{eff}$, was 0.4 mm$^2$. The noise peak at a frequency of 34 Hz, inherent in the pump, increased from 84 µΦ$_0$/Hz$^{1/2}$ to 161 µΦ$_0$/Hz$^{1/2}$ when the pump operated.

![Figure 3. Noise spectrum of the RF-SQUID magnetometer. A noise peak at a frequency of 34 Hz, inherent in the pump, increased from 84 µΦ$_0$/Hz$^{1/2}$ to 161 µΦ$_0$/Hz$^{1/2}$ when the pump operated.](image)

The RF-SQUID was driven by driving electronics made by Jülicher SQUID GmbH, Germany. The signal from the electronics was passed through an analog filter (NF Corporation 3624) to attenuate the noise. A high-pass filter was set to a fourth-order Butterworth characteristic (24 dB/Oct), with a cutoff frequency of 10 Hz. A low-pass filter was set to a fourth-order Butterworth characteristic (24 dB/Oct), with a cutoff frequency of 100 Hz. The output signals from the electronics were recorded using a DAQ device (NI USB-6251) on a PC via a filter set.

4. Sample Pieces
Because it was difficult to obtain quantitative metallic contaminant samples with a geometry of less than 100 µm, a gallium-focused ion beam (Ga-FIB) was used to prepare the metallic samples. Stainless steel wires (Nilaco Corporation SUS-304 Wire, Cr18% - Ni8% - Fe) with diameters of 20 µm, 30 µm, and 50 µm were prepared. The wires were cut using a Ga-FIB system (Hitachi High-Tech NB5000).
parameters of the FIB process are listed in Table 1. The dimensions of the micro metal contaminant samples are listed in Table 2. A schematic diagram of the sample preparation is depicted in Figure 4. The diameter of the cylinder is denoted as \(D\), and the length is denoted as \(L\). The SEM image of the cut wire (after the FIB process) is depicted in Figure 5. Cut pieces that were molded with UV-curing resin (Bondic BD-SKEJ) to prevent losses were used as small metallic contaminant samples, as depicted in Figure 6. The dimensions of the cut samples are listed in Table 2.

| Table 1. Parameters of the Ga-FIB process |
|------------------------------------------|
| Accelerated voltage                      | 40 kV        |
| Condenser lens                           | Mode 1       |
| Aperture size                            | 550 \(\mu\)m |
| Beam current                             | 60 nA        |

| Table 2. Dimensions of the metallic contaminant samples |
|--------------------------------------------------------|
| Diameter \(D\) (\(\mu\)m) | Length \(L\) (\(\mu\)m) | Volume \(V\) (\(\mu\)m\(^3\)) | Time trace in Figure 7 |
|---------------------------|-----------------|-----------------|------------------|
| 20                        | 30              | 9425            | (c1) & (c2)      |
| 20                        | 50              | 15708           |                  |
| 20                        | 99              | 31102           |                  |
| 30                        | 30              | 21206           | (b)              |
| 30                        | 53              | 37463           |                  |
| 30                        | 101             | 71393           |                  |
| 50                        | 50              | 98175           | (a)              |
| 50                        | 101             | 198313          |                  |

5. Results and discussion

Figure 7 depicts the typical time traces of the signal when the RF-SQUID detects a metallic sample with different sizes in water. Time traces shown in (a) and (b) correspond to a size of \(\phi 50 \mu\)m \(\times\) \(L50 \mu\)m and \(\phi 30 \mu\)m \(\times\) \(L32 \mu\)m, respectively, and those in (c1) and (c2) correspond to \(\phi 20 \mu\)m \(\times\) \(L30 \mu\)m of the sample. The conversion coefficient of the voltage and flux is 5.5 \(\Phi_0/V\). The tail of the waveform was due to a long time constant of the high-pass filter. Among the time traces depicted in (a), (b), (c1), and (c2), the largest voltage fluctuation, unrelated to the signal, was found in the time trace in (c1); it was defined as noise voltage \(V_n = 1.5 \text{ mV}_{PP}\). The signal-to-noise ratio (SNR) was determined as follows. It was 12 for (a), 7.2 for (b), 3.0 for (c1), and 1.1 for (c2). Although time traces in (c1) and (c2) were obtained from the same sample, the peak-to-peak values and waveforms were different. In the case of (c2), the SNR was 1.1. Thus, the success rate of the detection of \(\phi 20 \mu\)m \(\times\) \(L30 \mu\)m was not 100%; the signal was identified seven out of ten times. Only three times did the results exceed SNR > 3. This may be due to the variation of the magnitude of the signal depending on the dipole orientation and the
direction of the sample passed below the RF-SQUID with each measurement. Therefore, we measured ten times and averaged them to increase the accuracy. Figure 8 depicts the dependence of the ten times averaged peak-to-peak signal on the sample volume. The signals that were not identified were plotted as noise voltage $V_n$. The magnitude of the remnant magnetization from a metallic sample that was magnetized using the permanent magnet was expected to be proportional to the volume of the sample. It was almost fitted in proportion to the sample volume, but the peak-to-peak values of the signal, except for the $\phi 50 \, \mu m \times L50 \, \mu m$, exhibited a linear relationship. Because the values of the $\phi 50 \, \mu m \times L50 \, \mu m$ sample were lower than the fitting line, the molded sample was observed under the microscope; it was found that the cut wire solidified with the cylinder collapsed against the bowl-shaped molded resin. The bowl-shaped object was expected to maintain a posture in which the curved surface of the bowl and the direction of flow are parallel to each other to minimize the resistance while flowing in the fluid. When the sample passed through the permanent magnet in a horizontal magnetic field direction, it was magnetized in the radial direction of the cylinder, which was expected to have a larger antimagnetic field coefficient. As a result, it had a smaller remnant magnetization than that of the axial magnetization. When defining $\text{SNR} = 3$ as the threshold for detection, the volume of a detectable metallic contaminant was evaluated as $2 \times 10^4 \, \mu m^3$, which corresponded to that of a spherical sample with a diameter of 33 $\mu m$.

![Figure 7. Typical time traces of the signal. (a) $\phi 50 \, \mu m \times L50 \, \mu m$. (b) $\phi 30 \, \mu m \times 32 \, \mu m$, (c1) & (c2) $\phi 20 \, \mu m \times 30 \, \mu m$. Offset is added on both vertical and horizontal axes.](image)

![Figure 8. Relationship between the signal and the volume of the sample. The signals that were not identified were plotted as noise voltage $V_n$.](image)

### 6. Conclusion

An inspection system using an RF-SQUID magnetometer for detecting metallic contaminants in the liquid component of a lithium-ion battery was developed, and its performance was verified. The detection limit of the system was evaluated using tap water as a substitute for the liquid. Because it was difficult to obtain quantitative metallic contaminant samples that had a geometry of less than 100 $\mu m$, a Ga-FIB was used to prepare the metallic samples. The results reveal that, when SNR = 3 was defined as the threshold of detection, the smallest contaminant sample with a dimension of $\phi 20 \, \mu m \times 30 \, \mu m$ could be detected. However, the success rate of the detection was not 100 %. Thus, the dependence of the signal strength on the volume of the contaminant sample was systematically investigated. The signals were almost proportional to the sample volume; the volume of a detectable metallic contaminant was $2 \times 10^4 \, \mu m^3$, which further corresponded to that of a spherical sample with a diameter of 33 $\mu m$. In the future, we plan to conduct detection experiments using actual liquid components.

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