

# Superconductivity Web21

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## Feature Article: SQUID Application

### - System Designed to Visualize Electrochemical Reactions Using HTS-SQUID Gradiometer

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Measurements of the electrochemical reactions between electrodes and electrolyte have long since been essential for the diverse fields of science and engineering. The important roles played by such measurements in recent years have contributed to analytical chemistry, surface nano-science, and energy systems including highly efficient batteries and fuel cell developments. Amongst the number of methods available, voltammetry is most frequently used as an electro-analytical technique. The method employs three electrodes (a working electrode, a counter electrode and a reference electrode) placed in an electrolyte, and the current between the working and counter electrodes is measured as a function of the electrical potential. The measured current is typically not proportional to the difference between the electrical potential, but instead exhibits non-linear features that are attributed to redox reactions at the electrode/electrolyte interface. By analyzing such features therefore allows the identification of materials contained within the electrolyte as well as an understanding of the nano-region surface morphology of the electrode. However, electrochemical reaction measurements are influenced by a variety of factors such as the ion movement in the electrolyte and the electrode shape etc. Measuring ion currents in an electrolytic cell are essential to address these issues, and therefore there have been an array of R&D activities involved. For example, a technique employing a minute magnetic loop array mounted in the electrolytic cell to detect magnetic fields generated by the ion currents has been applied <sup>1)</sup>. However, the inserted coil disrupts the ion currents. To study this further, the author and his research group have constructed a noncontact measurement system employing an HTS-SQUID gradiometer that visualizes the magnetic fields generated by the ion currents in an electrolytic cell.

Figure 1 shows a schematic image of the electrolytic cell used in the experiment. A solution of 0.5 mM-K<sub>3</sub>[Fe(CN)<sub>6</sub>] dissolved in 0.5 M-Na<sub>2</sub>SO<sub>4</sub> was prepared. The depth profile of the cell is around 5mm, sufficiently small compared to the spatial resolution of magnetic measurement system and thus the depth profile of the ion current is negligible. The HTS-SQUID gradiometer employed here was a ramp-edge Josephson junction, comprising ISTECS' La<sub>0.1</sub>Er<sub>0.95</sub>Ba<sub>1.95</sub>Cu<sub>3</sub>O<sub>y</sub> and SmBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> electrode layers. The HTS-SQUID is mounted onto a planar gradiometer with a long baseline of 7.5mm, both of which are prepared on the same surface plane. For device details, please refer to [2\) ~ 4\)](#). Figure 2 (a)~(d), shows the distribution of the ion currents in the electrolytic cell when the electric potentials of working electrode vs. the reference electrode were +0.15 V, +0.80 V, +348 V, and -0.295 V, respectively. The vector component shown in the figure indicates the magnitude of the currents calculated from the magnetic signals. The magnetic signals from two independent directions in the cell were measured and the magnitudes of the ion current vectors were mapped corresponding to the ion current distribution. The figure shows that the direction of current vector shifts according to the electrical potential caused by a redox reaction between the electrodes. Also, the current distribution can be observed around the working electrode <sup>6)</sup>.

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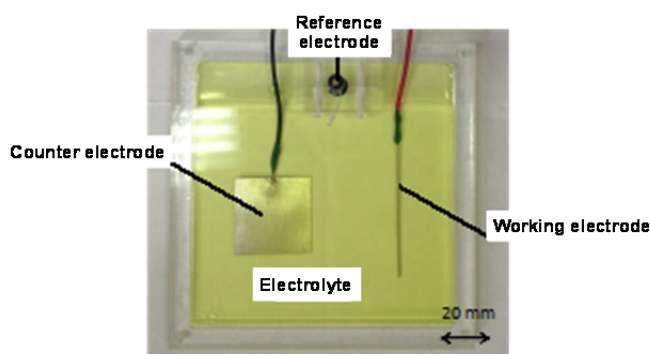


Fig. 1 Electrolytic cell used in the experiment

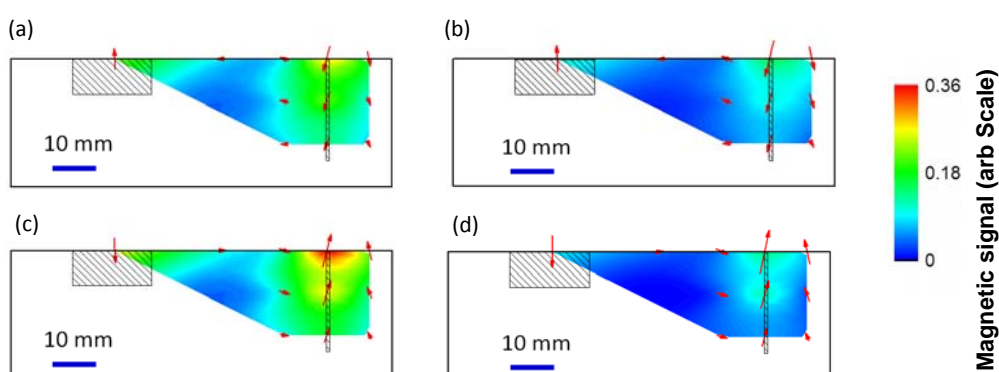


Fig. 2 Distribution of the ion currents in the electrolytic cell when the electric potentials vs. the reference electrode, respectively, (a) +0.15V, (b) +0.8V, (c) +348V, and (d) -0.295 V

Additionally, the magnetic signal response was successfully observed when a pulsed electrical potential was applied <sup>7)</sup>. The author considers that transient responses of electrochemical reactions can be visualized in the future, and measurements incorporating an HTS-SQUID gradiometer will become a valuable tool in analyzing electrochemical reaction mechanisms.

## Reference:

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