Title:

Visualization of ion transportation in an electrolyte using an HTS-SQUID gradiometer

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Abstract:

Direct detection of magnetic fields generated by the ion currents in electrolytic cells was performed and the ion currents were mapped during a cyclic voltammetry experiment. A high- T_C superconducting quantum interference device (SQUID) gradiometer with ramp-edge Josephson junctions was used as the detector and thus the first derivative of the magnetic field along the electrolytic cell surface was obtained. The electric potential vs. the reference electrode was measured between -0.3 V and 0.8 V and the hysteresis signals caused by the redox reactions of the electrolyte were observed. The vector component of the ion current during cyclic voltammetry was mapped along the electrolytic cell. As a demonstration of visualization of ion transportation, the magnetic signal was also measured at various positions above the electrolytic cell surface.

Keywords:

High- T_C SQUID, gradiometer, cyclic voltammetry, ion current, redox reaction

1. Introduction

Studies regarding the electrochemical reactions between the electrodes and the electrolyte in electrolytic cells are crucial for diverse fields of science and technology, such as in research on efficient batteries, analytical chemistry, and surface nano-science applications. Voltammetry is frequently used as an electro analytical technique. Voltammetry commonly uses a counter electrode, a working electrode, and a reference electrode in the electrolyte and the current between the counter and working electrodes is measured as a function of the electric potential of the working electrode vs. the reference electrode. Due to the redox reaction of the ions at the surface of the electrodes, specific features are observed in the current–voltage curves. Redox reactions largely depend on specific conditions of electrodes such as surface morphology, the electrolyte flow near the electrodes, and the shape of the electrodes, so this type of system measures limited information obtained via the electrodes. There are some studies that utilize a segmented electrode or a magnetic loop array mounted in the electrolytic cell to measure the ion current distribution [1-3]. One study has reported a noncontact measurement method for the current distribution in the electrolyte [4].

In our recent studies, we have measured ion currents in the electrolyte during cyclic voltammetry using a high-T_c (HTS-) SQUID gradiometer with a normal pick-up coil [5]. Although measurements using this type of system are limited to measurement of the rapid redox reactions at the electrodes because of the lower sensitivity to a low-frequency magnetic field, the system offers the advantage of stable operations independent of the external earth magnetic field. In this study, direct detection of magnetic fields generated by the ion currents in the electrolytic cells was performed and the ion current vectors were mapped during cyclic voltammetry.

2. Experimental

Figure 1 shows a photograph of the magnetic cyclic voltammetry system we developed. The electrolytic cell was mounted on an *x-y* movable stage in the magnetic shielding box made of high- μ metal. The three electrodes installed in the electrolyte were connected to a conventional potentiostat and the potential of the electrolyte vs. the reference electrode was controlled by this device. The HTS-SQUID gradiometer was mounted on a sapphire rod in the vacuum space of a liquid nitrogen Dewar container and cooled down via thermal conduction of the rod. The vacuum space was covered by a sapphire window with a diameter of 50 mm. The sensing axis was set to be along the *z*-axis, which is perpendicular to the cell's surface. Therefore, the system could detect the two independent components of the first derivative of the magnetic field along the *x*- and *y*-axes by rotating the Dewar. The lift off distance between the HTS-SQUID gradiometer and the cell's surface was approximately 2 mm. Ramp-edge Josephson junctions were applied to the HTS-SQUID gradiometer. The base and counter superconducting electrodes were composed of $\text{La}_{0.1}\text{Er}_{0.95}\text{Ba}_{1.95}\text{Cu}_3\text{O}_y$ and $\text{SmBa}_2\text{Cu}_3\text{O}_y$, respectively. The fabrication process and the structure of the HTS-SQUID are reported elsewhere

[6-8]. The baseline of the gradiometer was approximately 7.5 mm. The HTS-SQUID was driven by a conventional flux-locked loop (FLL) circuit. The electric potential vs. reference electrode, the current through the working electrode, and the output signal from the FLL circuit were simultaneously recorded by a personal computer using a conventional analog–digital converter.

Figure 2 shows a photograph of the electrolytic cell used in our experiment. The cell was made from a 1-mm-thick acrylic plastic sheet. The dimension of the cell was 104 mm (length) $\times$ 104 mm (width) $\times$ 5.5 mm (depth). The depth profile of the ion current was negligible because the depth of the cell was lower than the baseline of the gradiometer. A 56-mm-long platinum (Pt) wire was used as the working electrode with a diameter of approximately 1 mm. The counter electrode was made from a 30 mm $\times$ 30 mm Pt plate. Both electrodes were connected to the potentiostat via vinyl-coated electric wires, keeping approximately 50 mm distance between the two electrodes. To stabilize the electric potential of the electrolyte, a commercial Ag/AgCl reference electrode was installed in the cell. As the sample electrolyte, a solution of 0.5 mM potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$) dissolved in 0.5 M sodium sulfate (Na_2SO_4) was prepared. Between the electrolyte and the working electrode, the following reduction and oxidization process occurs:

This results in the generation of an ion current in the electrolytic cell [4, 5].

3. Results and Discussion

Figure 3 shows a typical curve of the electric potential of the working electrode vs. the reference electrodes. The electric potential was swept between -0.3 V and 0.8 V with a sweep speed of 50 mV/s. The initial potential was set to be 70 mV and the sweeping direction is indicated by the arrows in Fig. 3. The hysteresis loop caused by the redox reactions was observed in our electrolytic cell. Fig. 4 (a) shows the positions above which the HTS-SQUID gradiometer was set and was used to measure the magnetic fields. Cyclic voltammetry was performed at each position and the magnetic signal due to the ion currents was observed. Figs. 4 (b), (c), and (d) show the observed first derivative of the magnetic fields B_z along the x - and y -axes (dB_z/dx and dB_z/dy , respectively) measured at positions A, B, and C during cyclic voltammetry, respectively. The dB_z/dx direction at position A was opposite to that at position C. This difference in direction was observed because of the difference in the direction of the ion currents. Although dB_z/dx was larger in magnitude than dB_z/dy at positions A and C, dB_z/dx was smaller in magnitude than dB_z/dy at position B. This result was obtained because the main vector components of the ion currents were along the y -axis at positions A and C, whereas the main vector component at position B was along the x -axis.

Figures 5 (a), (b), (c), and (d), respectively, show the distribution of the ion currents in the electrolytic cell when the electric potentials vs. the reference electrode were $+0.15$ V, where the oxidation process occurred at the working electrode, and $+0.80$, $+0.348$ V, and -0.295 V, where the

reduction process occurred. The direction and the length of the arrows in Fig. 5 indicate the direction and the magnitude of the currents at the indicated positions. The color scale also indicates the magnitude of the currents. The vector component of the current is simply calculated by assuming a 2-D model [9-11] that is given by following equation.

$$\mathbf{I}(t) \propto -\frac{dB_z}{dy} \mathbf{e}_x + \frac{dB_z}{dx} \mathbf{e}_y. \quad (1)$$

Here $B_x(t)$ and $B_y(t)$ represent the x and y components of the measured magnetic fields, and $\mathbf{e}_x$ and $\mathbf{e}_y$ are the unit vectors along the x- and y-axes, respectively. The direction of the current vector during the reduction process was different from that during the oxidation process; however, a nonuniform current distribution was observed at all electric potential conditions. These results suggest that the direct detection of the current using an HTS-SQUID gradiometer is effective for noncontact detection of the ion currents and their distribution during the electrochemical reactions.

Figure 6 shows dB_z/dy measured at position B indicated in Fig. 4(a). Pulse responses were observed at the times when the pulsed voltage was applied, and the baseline of the signals shifted depending on the electric potential of the working electrode. This shift is also caused by the redox reactions of the electrolyte. Further analyses of the signal decay after improving the signal-to-noise ratio are required; however, these results suggest that useful observation of the time-domain process of the redox reactions and the ion transportation is possible using the system we developed.

4. Summary

Direct detection of magnetic fields generated by the ion currents in electrolytic cells was performed and the vector components of the ion currents were visualized during cyclic voltammetry. As a demonstration of time-domain measurements of ion transportation, the magnetic signal during pulsed voltammetry was also measured at various positions above the electrolytic cell surface. These results suggest that the direct detection of the current using an HTS-SQUID gradiometer is effective for noncontact detection of ion currents and their distribution during electrochemical reactions.

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Figure captions

Fig. 1. Photograph of the magnetic cyclic voltammetry system.

Fig. 2. Schematic image of the electrolytic cell used in the experiment.

Fig. 3. Typical curves of the electric potential of the working electrode vs. the reference electrode.

Fig. 4. (a) Measurement positions, and (b), (c), and (d) the signal at positions A, B, and C.

Fig. 5. Distribution of the ion currents in the electrolytic cell when the electric potentials vs. the reference electrode, respectively, were (a) +0.15 V, (b) +0.80, (c) +0.348 V, and (d) -0.295 V.

Fig. 6. dB_z/dx measured at position B indicated in Fig. 4(a)

Fig. 1.

Fig. 2.

Fig. 3

Fig. 4.

Fig. 5.

Fig. 6.