

Clarification of the Energy Conversion Mechanism at the Surface and Interface by Scanning Probe Microscopy

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Surface and interface are the places for energy conversion processes in physics, chemistry, and biology. The detailed mechanism of such energy conversion processes is yet to be clarified. The reaction at the interface between the electrode and electrolyte of rechargeable batteries are a typical system of the energy conversion. At the interface in lithium ion battery, which is most widely used rechargeable battery,¹⁾ the energy transfer is proceeded by the insertion and extraction of the carrier ions at the interface during the charge and discharge reactions. Also, at the interface, the carrier ions, counter ions, solvents, additives, and crystal structures of the electrode surface forms characteristic structures that induce different properties from the material bulk. Traditionally, the reaction mechanism at the interface has been discussed based on electrochemical measurements. However, the nature of the interface is still unclear due to the difficulty of the analysis of the buried interface.



Figure 1. The scanning probe microscope system for the analysis of electrochemical reactions installed in the instrument center of Institute for Molecular Science.

Scanning probe microscopy (SPM) is an excellent technique to analyze the geometric, mechanical, electric, and electronic properties at the surfaces and interfaces. Thus, it has been employed for the analysis of the energy conversion processes. SPM can directly access to the buried interfaces such as the interface between electrode and electrolyte and has abilities to provide important information to clarify the reaction mechanism. In 2020, two specially designed SPMs have been launched at the instrument center of the Institution for Molecular Science. One is designed for the analysis of the

geometric, mechanical, electric, and electronic properties at the surface and interface under photo excitation or magnetic field with high resolution. The another is solely designed for the analysis under electrochemical reactions (Figure 1). Using the two SPM systems, both the physical properties and the reaction mechanism of the energy conversion processes at the surface and interface could be clarified.

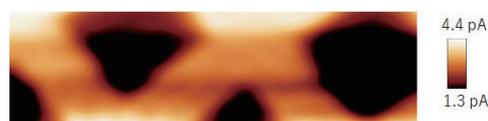


Figure 2. A Faraday current mapping on SiN/Pt obtained by scanning electrochemical microscopy in 5 mM hexamine RuCl₃ and 0.1 M KNO₃ aqueous solution. Cantilever: Pt; counter electrode: Pt, reference electrode: Ag, sample potential: -0.1 V (vs reference), image size: $25 \mu\text{m} \times 6 \mu\text{m}$.

In electrochemical devices, the local distribution of the reactions at the interface between the electrode and electrolyte strongly influences the device performances. The direct observation of the local distribution at the interface provides important information that aids the understanding of the reaction mechanism of the system. Using the SPM system with the specially designed cantilever having Pt tip, the local distribution of the electrochemical reactions was visualized. Figure 2 shows an example of the mapping of the electrochemical reaction on SiN/Pt in hexamine RuCl₃ electrolyte. The bright area shows the area with higher Faraday current than the dark area. The higher Faraday current is caused by the redox reactions of Ru ions in the electrolyte. From the simultaneous observation of the mechanical properties of the electrode surface using the SPM, the bright and dark areas are assigned to the regions of Pt and SiN, respectively. The results reveal the high reactivity of the Pt in the reaction. Employing this technique in the present and innovative battery systems,¹⁻³⁾ the local distribution of the reactions in the batteries can be visualized. This will avail more vital information for the design of new energy devices.

References

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