# Study of the microscopic structure of the electric double layer formed at the ionic liquid/electrode interface using Neutron reflectivity

Japan Atomic Energy Agency    Kazuhisa Tamura

## 1. Introduction

A salt, which exists as a liquid at room temperature, is called "ionic liquid". In the last two decades, ionic liquids (ILs) have been recognized as new type solvents. One of the characteristics of ILs is that ILs have high electric conductivity without adding any electrolyte. Further, ILs have a very low vapor pressure and a wide electrochemical window (high electrochemical stability). Therefore, many studies for the usage of IL as electrolyte solutions have been conducted. On the other hand, fundamental studies have not been carried out enough. Especially, the interface between IL and the electrode surface, where electrochemical reactions indeed occur, has not been well understood. Therefore, we have studied the electrochemical reactions in ILs in terms of IL/electrode interface structure. We have focused on the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([BMIM]TFSA)/Si(100) interface structure and studied it using electrochemical and quantum beam scattering techniques. Previously, it was found that there are three phases of the interface structure including one transition state. Further, there observed a hysteresis and irreversibility. In this study, we carried out neutron reflectivity measurements to elucidate the detail of the potential dependence of interface structure.

## 2. Experiment

The working electrode was a Si(100) (40 × 40 mm, t =3 mm). Prior to measurements, Si(100) electrode was pretreated with acetone, ethanol, and Milli-Q water. The reference and counter electrodes were Pt wires. The $d$-[BMIM]TFSA was synthesized in ANSTO and dehydrated under vacuum for 24 h before measurements. The electrochemical cell was assembled in a glove box filled with Ar gas. The electrochemical cell was placed at the center of a goniometer under the potential controlled condition. Reflectivity were measured between Q = 0.005 and 0.23 Å$^{-1}$ at BL17.

## 3. Results

Reflectivity profiles were measured every 0.26 V between E = -1.1 and 0.46 V. Figure 1 shows the potential dependence of reflected neutron intensity measured at Q = 0.1 Å$^{-1}$. In the potential scan, there observed a hysteresis and irreversibility as observed in our previous electrochemical and X-ray reflectivity measurements. According to the electrochemical measurements, both the peak potentials observed in Fig. 1 almost correspond to the transition potential between a steady state phase and a transition state phase. Therefore, this result indicates that in the
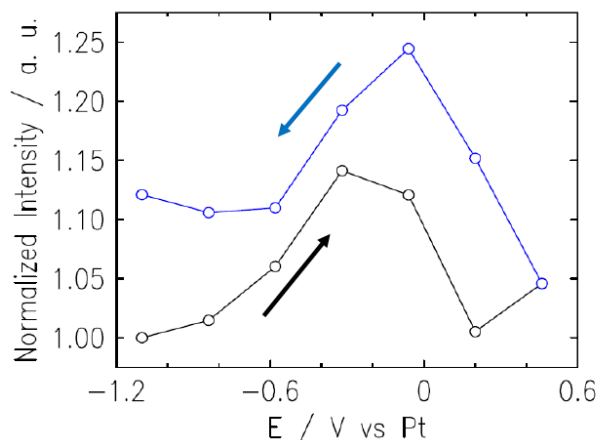


Fig. 1 The potential dependence of reflected neutron intensity measured at Q = 0.1 Å$^{-1}$.

phase transition state, the interface structure drastically changes and there is a hysteresis.

To elucidate the detail of the interface structure fitting analysis was carried out. In the fitting procedure, layered and monolayer structure models were used. Fig. 2 shows the result of the fitting analysis. It was found that in the steady state phase described as "Phase 1" in Fig. 2, IL molecules form a layered structure and the first and second layers are cation and anion layer, respectively. In the Phase1 state, both the cation and anion molecules adsorb perpendicular to the surface. Further, the
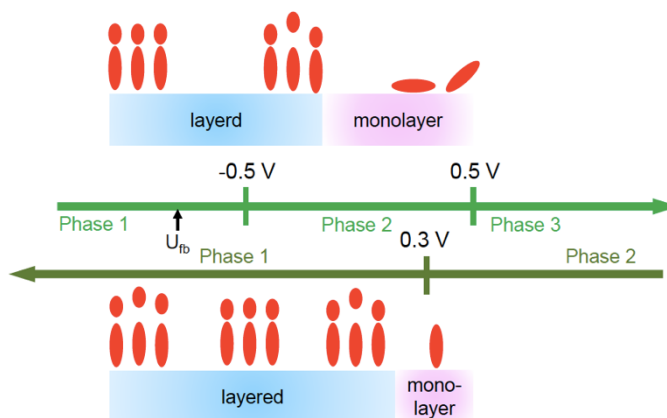


Fig. 2 Result of fitting analysis

anion layer becomes rough near the transition potential. In the transition phase described as "Phase 2" in Fig. 2, IL molecules form monolayer structure and the orientation of the cation molecules depends on the electrode potential.

We also carried out another neutron reflectivity measurement using partially deuterated [BMIM]TFSA to elucidate the inner structure of the adsorbed cation layer. At this point, the analysis is underway.

## 4. Conclusion

In this study, the potential dependence of the [BMIM]TFSA/Si(100) electrode interface structure was elucidated using *in-situ* neutron reflectivity technique. It was found that the IL molecules form a stable layered structure in the "Phase 1"; on the other hand, IL molecules form a dynamic structure in the "Phase 2". It was also found that there are hysteresis and irreversibility in potential dependence.