

Electrochemical behavior of hydrophilic ionic liquid-water mixture

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The electrochemical properties of hydrophilic ionic liquid mixed with water and ethanol were investigated. In undiluted solution, a slight anodic current was observed around 0.9 V. An anodic peak appeared around 0.7 V when slight water was added to the ionic liquid. Such peaks were also observed when ethanol was added to the ionic liquid, indicating that the origin of this peak should be the bond formation between the anions of the ionic liquid and the gold atoms of the electrode. The peak shift with constant onset for varied water concentration can be interpreted as acceleration of anion adsorption due to dilution of the ionic liquid. The viscosity decreases at higher water concentration support this interpretation.

Key words: Ionic liquid, Electrochemistry, Surface science, Ionic liquid-water mixture

1. INTRODUCTION

Ionic liquids (IL) have been attracted wide attention as third-class of liquids which is different from water and oil. ILs are liquid salts at room temperature which consist of an organic cation and an organic/inorganic anion. ILs generally have the characteristics of chemical stability, non-volatility, flame retardancy and high ionic conductivity. Due to these fascinating properties, ILs are expected as novel electrolytes in electrochemical energy devices such as batteries, capacitors, and so on [1]. For improving their performance, it is important to understand the environment of IL/electrode interfaces.

From recent intensive studies using various techniques, alternatively stacked multiple anion and cation layers has been proposed as a model for the structure of pure IL/electrode interfaces [2]. On the other hand, dilute aqueous solutions of hydrophilic ILs are expected to form well known electric double layer consisting of the Helmholtz layer and the diffuse layer as in the case of conventional electrolyte solutions such as aqueous solutions. However, the interface of the mixture between ILs and slight water content, which can be regarded as the super high ion concentration aqueous solution [3], have not sufficiently been studied yet. The presence of water in IL can influence not only solvent properties such as polarity, viscosity, and conductivity, but also the interfacial structure and electrochemical response. Interfacial structures have been recently studied from theoretical [2] and experimental [3] points of view.

The effect of slight water on electrochemical response has also been studied but understanding is not sufficient yet. Origin of each peak in cyclic voltammograms (CVs) is difficult to identify, which is partly because ILs have generally hygroscopic nature and unavoidable impurities.

In the present study, we measure the cyclic voltammograms of an Au electrode in hydrophilic IL, 1-ethyl-3-methyl hydrogen sulfate (Fig. 1), mixed with small amount of water or ethanol. Similar electrochemical behavior observed for both water and ethanol mixtures enables us to conclude that the obtained oxidation peaks in CVs are originated from anion adsorption accelerated by dilution of the IL.

2. EXPERIMENTAL

Ionic liquid, 1-Ethyl-3-methylimidazolium hydrogen sulfate (io-li-tec) was used (Fig. 1) as an undiluted solution (water amount approximately 0.3 wt %).

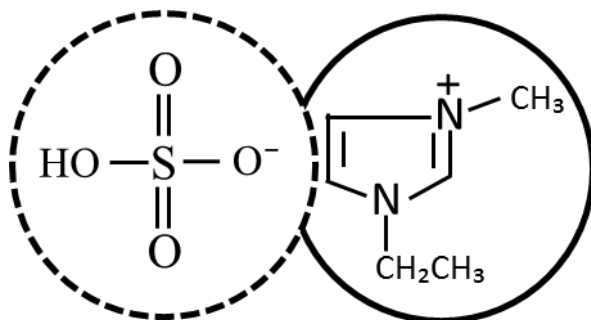


Fig. 1 Structure of 1-Ethyl-3-methylimidazolium hydrogen sulfate

Water amount 2-10 wt % solution was prepared as ionic liquid/water mixing solution. 10 weight percent ethanol mixing solution was prepared as well. Solutions were investigated by Cyclic Voltammetry (CV). A gold plate (0.79 cm²) and a platinum plate were used as working and counter electrodes, respectively. Silver / silver chloride electrodes immersed in ionic liquid in which KCl was dissolved at saturated concentration was used for a reference electrode. CVs were measured with a multi potentiostat (PS-04, TOHO) to investigate the electrochemical behavior of the IL depending on water or ethanol content. The potential scan range was -0.2 ~ +1.7 V and the electrode potentials were calibrated by the redox potential of ferrocene/ferrocenium (Fc/Fc⁺) and expressed in values relative to this potential. The potential scan rate was 20 mV/s. The viscosities of the solutions were measured at 22 °C by Sine-wave Vibro Viscomter (A&D).

3. RESULTS & DISCUSSION

3-1. CV

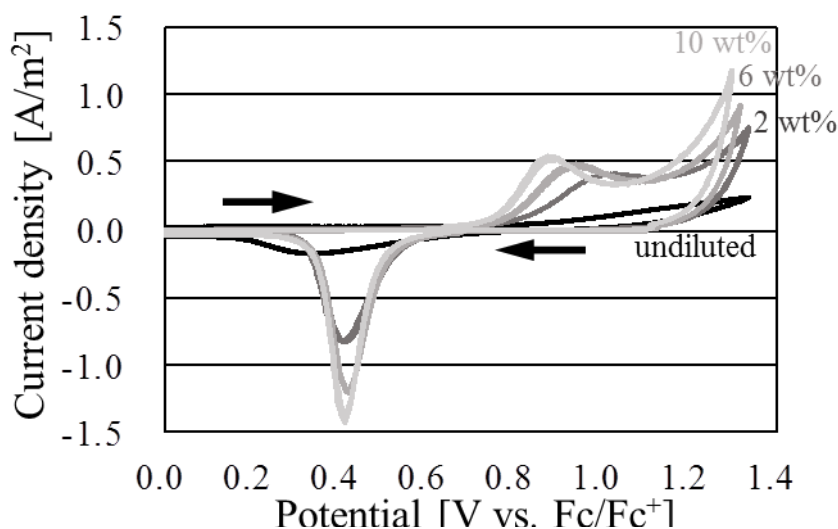


Fig. 2 Cyclic voltammograms in the ionic liquid-water mixtures with different water concentrations at a scan rate of 20 mV/s

Figure 2 shows the cyclic voltammograms of an Au electrode in ionic liquid/water mixtures with different amount of water. Here the electrode potential was changed from open circuit potential to -0.2 V, followed with positive-going scan to 1.7 V and backward scan to open circuit potential. In undiluted solution (0.3 wt%), the slight oxidation current was generated from 0.9 V. During the negative scan, the broad reduction peak appeared around 0.4 V. In water mixed solutions, 2-10 wt%, the oxidation peaks appeared around 0.9 V, and successive increases in current, probably due to the decomposition of ionic liquid molecules, was observed from 1.1 V. The peaks around 0.9 V increased their intensities and shifted to lower potentials as the water amount increased, although the onset potentials were almost constant. During the negative scans, the sharp reduction peaks appeared around 0.4 V without significant shift due to different water concentration.

In order to identify the reactive species, the voltammogram of the IL mixed with ethanol was measured (Fig. 3).

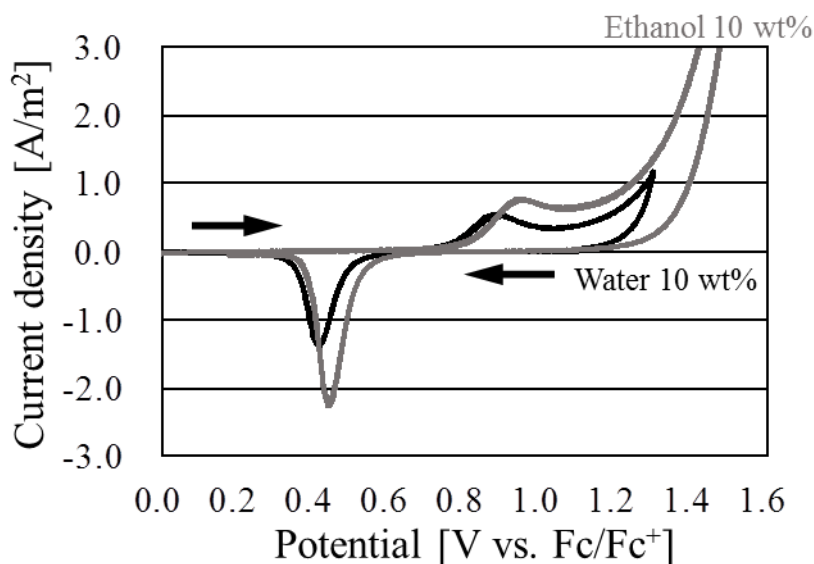


Fig. 3 Cyclic voltammograms measured in ionic liquid-solvent mixing solutions

As a result, the similar oxidation peak was appeared around 0.9 V, whereas the peak height is higher than that for water mixture. Again the onset potential of this peak is almost constant with that for water mixture. These result indicate that the oxidation peaks found in IL-water and IL-ethanol mixed solutions were resulted from the same reaction which should be the bond formation between the hydrogen sulphate ions, the constituent anion of the ionic liquid and the gold atoms of the electrodes (anion adsorption). It is worth noting that there is still a possibility that this peak is originated from oxidation of gold electrode to form Au-OH or Au-O due to residual water content. The water content in ethanol is very low, but residual water in IL can be concentrated near the electrode surface as indicated in the literatures [2]. We believe this is not the case because the peak for ethanol mixture is higher than water mixture.

The viscosity of the IL with different amount of water(2-10 wt%) at 22 °C were shown in Fig. 4. The drastic decrease of the viscosity can be found for increased water concentrations.

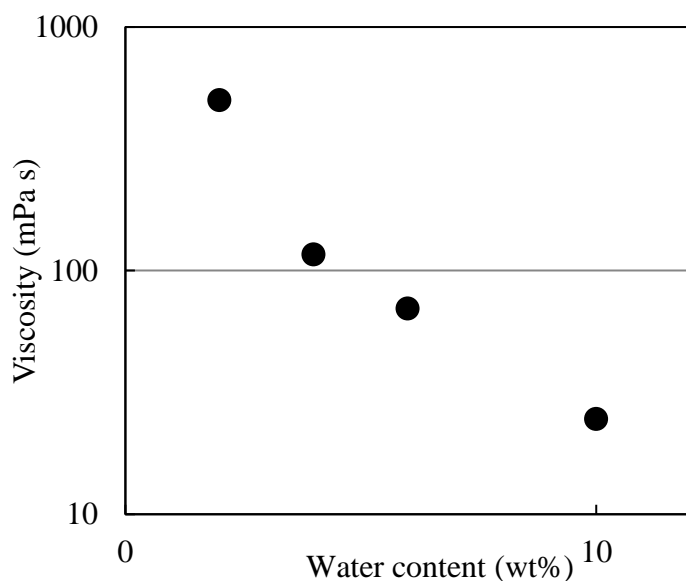


Fig. 4 Viscosity of ionic liquid-water mixing solutions

The oxidation peaks found in CVs due to anion adsorption can be affected by the viscosity change shown here. The peak shows negative peak shift with constant onset for increased water concentrations (Fig. 2). It was indicated that the potential for anion adsorption was not change, but the rate of anion adsorption was accelerated. The decrease in viscosity, on the other hand, indicated the acceleration of the transport kinetics in the bulk IL solutions. The kinetics at the vicinity of the electrode surface and the bulk sometimes show different tendency, but in general show similar tendency for slight perturbation such as addition of slight water. Thus, the decrease in the viscosity supports the interpretation of the origin of the peak shift as acceleration of adsorption kinetics.

The total charge for the oxidation peak is also increased for higher water concentration (Fig. 2). This can be interpreted as the increase in the amount of adsorbed anions completed before start of decomposition of the IL molecules, due to acceleration of anion adsorption. The reduction peaks at negative-going potential scans also increase its intensity correlated with that for the oxidation peaks. This indicated that this peak is due to the desorption of anions.

The acceleration of anion adsorption kinetics by water addition has been already directly observed in a hydrophobic IL 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [2]. Time-resolved surface-enhanced infrared absorption spectroscopy (SEIRAS) measured during potential step experiment obviously showed accelerated anion adsorption kinetics for IL with slight amount of water. The present results for the hydrophilic IL is consistent with the previous results on the hydrophobic IL. Such spectroscopic observation will lead to more convincing evidence on the above interpretation on the hydrophilic IL obtained only by electrochemical observations.

4. CONCLUSIONS

The electrochemical behavior of an Au electrode in the hydrophilic IL mixed with water and ethanol were studied. CV measurements showed the current peak around 0.9 V vs. Fc/Fc⁺ in both IL-water and IL-ethanol mixture. This indicated that the peaks were originated from common reactions, that is, adsorption of hydrogen sulphate anions. The negative peak shift with constant onset for higher water concentration can be explained by acceleration of anion adsorption kinetics due to dilution of ILs which is suggested by decreased viscosity.

References

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