

Dynamics of NaClO₄-ethylen glycol-water mixture

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In rechargeable batteries using an aqueous solution as the electrolyte, high voltage cannot be obtained due to the narrow potential window of water. With increasing the concentration of electrolytes, the potential window of water becomes wide [1]. However, the viscosity of the electrolyte is high at a high concentration. Recently, it was found that adding ethylene glycol (EG) to NaClO₄ aqueous solution expands the potential window of water even at a lower salt concentration. In this study, the liquid structure and dynamics of the sodium perchlorate-ethylene glycol-water system were investigated by X-ray diffraction, NMR relaxation time, and neutron quasi-elastic scattering in order to study the cause of the enlargement of the water potential window.

The sample solution is NaClO₄-ethylene glycol-water mixture. The concentration of NaClO₄ is 0, 1, and 13 m (mol/kg). The mole fractions of EG (x_{EG}) are 0 and 0.1. The sample solution was sealed in an aluminum cylindrical cell. Quasi-elastic neutron scattering (QENS) spectra were obtained using an AGNES spectrometer installed in the research reactor JRR-3 owned by the Japan Atomic Energy Agency (JAEA). The energy resolution is 120 μ eV, and the Q range is 0.38-2.63 \AA^{-1} . The spectrum of pure water (ice) at 3 K was used as a resolution function.

Dynamic structure factors obtained from QENS measurement were fitted with three Lorentzian functions. The slowest relaxation can be analyzed by a Jump-diffusion model. Faster relaxation is assigned by a local motion because there is no Q dependence on the relaxation.

Figure 1 shows the temperature dependence of the diffusion coefficients obtained from the jump-diffusion model. At $x_{EG} = 0$, the diffusion motion of water molecule showed a maximum at a salt concentration of 1

m, consistent with ¹⁷O NMR relaxation time result [1]. As ClO₄⁻ ion is known as a structure-breaking ion, ClO₄⁻ ion disrupts water structure for a dilute solution. With an increase in the salt concentration, the water structure is broken, and the water molecule strongly interacts with Na⁺ ion. This retarded water translational motion.

At $x_{EG} = 0.1$, the diffusion coefficient decreases monotonously with increasing temperature. It is reflected by not only the diffusion motion of water but also the diffusion motion of EG molecules. The rotational dynamics of water molecules investigated by ¹⁷O NMR relaxation becomes slow with increasing the mole fraction of EG [1]. These results show that EG interacts with water molecules through hydrogen bonding and disrupts water structure. Hence, water breaking effect of ClO₄⁻ is not seen as shown at $x_{EG} = 0.1$. With increasing the concentration of the salt, water molecules strongly interact with Na⁺ ion.

In the future, we plan to clarify the relationship between this change in liquid structure and the expansion of the water potential window by combining structural information revealed by X-ray diffraction and MD simulation.

[1] A. Kitajou et al., *Electrochemistry* 91 (11) 117002 (2023).

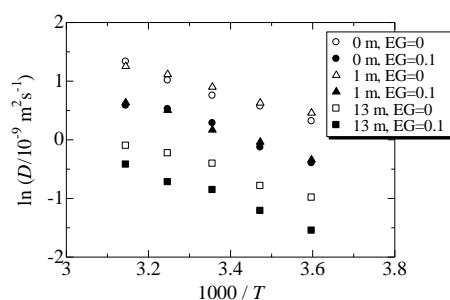


Fig.1 Temperature dependence of the diffusion coefficients of NaClO₄-EG-water mixture