Scaling Relation between Electrochemical Seebeck Coefficient and Viscosity

The electrochemical Seebeck coefficient \( \alpha \) (= d\( V \)/d\( T \); \( V \) is redox potential) is a key parameter for thermal energy harvesting. We systematically investigated \( \alpha \) for Fe\(^{2+}/Fe^{3+} \) in 16 organic solvents. \( \alpha \) showed remarkable solvent dependence and was distributed from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. We further found a scaling relation between \( \alpha \) and viscosity \( \eta \) of the solvent as \( \alpha \sim \eta^{-0.4} \), which is interpreted in terms of the configuration entropy of the solvent molecules. In addition, we found that the \( O_h \)-type octahedral coordination of the solvent molecules showed \( D_{4h} \)-type deformation with increase in \( \eta \).

To realize a zero-emission society, it is necessary to develop highly efficient and low-cost thermal energy harvesting devices that produce electric energy from human body heat or waste heat near room temperature. An energy harvesting thermocell consisting of hot/warm or cold electrodes of identical type and solution with redox couple was proposed in the 1950s and 1960s and is still undergoing active research and development. Similarly to a solid thermoelectric device, the thermocell converts temperature difference (\( \Delta T \)) between the two electrodes to electric energy. An energy harvesting thermocell was observed to produce electric energy from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. We further found a scaling relation between \( \alpha \) and \( \eta \) of the solvent as \( \alpha \sim \eta^{-0.4} \) and interpreted the relation in terms of the enhanced \( \Delta S_{\text{config}} \) in the low-\( \eta \) solution. Furthermore, \( \alpha \) showed strong solvent dependence and was widely distributed from 0.14 mV/K for glycerin to 3.60 mV/K for acetone. Based on the pre-edge spectra at the Fe K-edge around Fe\(^{2+} \), the solvent dependence is ascribed to \( D_{4h} \)-type deformation of the Fe\(_6 \) octahedra.

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\alpha \sim \eta^{-0.4}
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Figure 1: Electrochemical Seebeck coefficient \( \alpha \) against viscosity \( \eta \) of solvent. Squares and triangles represent protic and aprotic solvents, respectively.

Figure 2: Pre-edge spectra at the Fe K-edge around Fe\(^{2+} \) in several solutions: EG, 1Pr, and 1Bu denote ethylene glycol, 1-propanol, and 1-butanol, respectively. Physical quantities in parentheses indicate \( \eta \) of the solvent.