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Effect of Coexisting TiO₂ Powder on Ionic Conduction of Highly Concentrated LiTFSA Aqueous Electrolyte (20.5 mol kg⁻¹)

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The cover art is attributed to an article entitled "Effect of Coexisting TiO_2 Powder on Ionic Conduction of Highly Concentrated LiTFSA Aqueous Electrolyte (20.5 mol kg⁻¹)" by Jingchao Xu et al. This issue's Editor's Choice is an interesting study on the dependence of electrical conductivity on liquid-phase volume fraction in solidliquid coexistence systems consisting of a highly concentrated LiTFSA electrolyte and TiO_2 powder.

The authors investigated solid-liquid coexistence systems comprising TiO_2 powder and highly concentrated LiTFSA aqueous electrolytes using electrical conductivity measurements and various spectroscopic methods. In this article, solid-phase and liquid-phase interactions were analyzed, and the influence of LiTFSA concentration on electrical conductivity changes with respect to the liquid-phase volume fraction was discussed.

> See "J. Xu et al., *Electrochemistry*, **93(1)**, 017003 (2025)." [DOI: 10.5796/electrochemistry.24-00115]

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Article

Effect of Coexisting TiO₂ Powder on Ionic Conduction of Highly Concentrated LiTFSA Aqueous Electrolyte (20.5 mol kg⁻¹)[†]

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ABSTRACT

An electrical conductivity and its activation energy are measured for solid-liquid coexistence systems consisting of TiO_2 powder/highly concentrated LiTFSA aqueous electrolyte (20.5 mol kg⁻¹). The conductivity increases exponentially with an increase of the liquid content up to ca. 40 vol%, and the activation energy of the conductivity increases with a decrease of the liquid content below 35 vol%. Various spectroscopic measurement, such as Raman, near-infrared (NIR), and NMR spectra indicated that the presence of TiO_2 disrupts the nanoscale water channel structure in the water-enriched regions of the bulk solution in the TiO_2 powder/20.5 mol kg⁻¹ LiTFSA solid-liquid coexistence system with a liquid phase volume fraction below 40 vol%, resulting in an unusual decrease in the electrical conductivity. The strong influence of the solid phase on the electrical conduction of the highly concentrated LiTFSA electrolyte was found to be significant only in the region below 50 vol% in the liquid content, while in the region of the solid phase on electrical conduction.



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Keywords : Highly Concentrated LiTFSA Electrolyte, Solid/liquid Interface, Ionic Conductivity

1. Introduction

Much research has been studied on the diversification of aqueous energy storage devices due to their safety and ease of handling, which is not the case with conventional energy storage devices using flammable solvents.^{1–4} For example, overcoming the water decomposition voltage of 1.23 V is expected to be feasible through research using highly concentrated aqueous electrolyte solutions.⁵ Especially, battery systems using highly concentrated aqueous electrolyte solutions are expected to have features not found in conventional

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aqueous electrolytes, such as increased output voltage by taking advantage of the low activity of water as solvent and increased current capacity due to increased ionic concentration.

In particular, aqueous lithium bis(trifluoromethanesulfonyl)amide (LiTFSA; LiN(SO₂CF₃)₂) with concentrations exceeding 20 mol kg⁻¹ have a heterogeneous ionic distribution, with water-rich regions consisting of hydrated cation such as Li(H₂O)₄⁺ and anionrich regions consisting of Li(TFSA)_x^{(x-1)-} ionic aggregates, despite being 1 : 1 electrolytes simply consisting of cations, anions, and solvents. This has led to the term "water-in-salt" electrolyte, which has attracted much attention.^{6–9}

In general, in highly concentrated aqueous solutions, it is difficult to achieve the stable hydration structure and independent migration of ions observed due to the formation of ion pairs. For example, since the ratio of Li : H_2O is ca. 1 : 3 in the 20 mol kg⁻¹ LiTFSA system, complete hydration of Li⁺ ion is not expected. However, the ionic interaction between Li⁺ and TFSA⁻ is certainly enhanced between Li⁺ and O in TFSA⁻, which causes some Li⁺ ions to release water molecules. Therefore, it is suggested that coexisting Li⁺ ions that are not interacting with TFSA⁻ can hydrate with water

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molecules beyond their existence ratio, forming relatively stable hydrated ions.^{1,10,11} Consequently, aggregated hydrophobic $\text{Li}(\text{TFSA})_x^{(x-1)-}$ domains form disproportionate structures due to the presence of hydrophilic Li-rich domains in the gaps between them. Hydrated Li⁺ ions are avoided interaction with TFSA⁻ ions and maintain a high conductivity of $10 \,\mathrm{mS}\,\mathrm{cm}^{-1}$ despite high concentration and viscosity.⁹

We are interested in whether the enhanced conductive path of Li⁺ ions is maintained in various composite materials in electrochemical devices, because many electrolytes coexist with and are supported by separators or active materials made of various powders and gels resulting in the formation of numerous solid/liquid interfaces. The structural characteristics of these interfaces can significantly impact the performance of electrochemical devices. For example, Bhattacharyya et al. found that the addition of metal oxide powders to non-aqueous solutions enhances electrolyte dissociation due to the interactions between the solid and counterions (with charges opposite to those on the solid surface).¹²⁻¹⁴ They referred to such composites as "soggy sand" electrolyte. These results in an increased conductivity of the space charge region, leading to an overall conductivity increase by an order of magnitude. Suzuki et al. reported the heterogeneous distribution of a binary solvent solution of propylene carbonate-1,2-dimethoxyethane containing LiClO₄ on SiO₂ surfaces, indicating that such distributions can affect the conductivity within solid-liquid mixed systems.15 Moreover the structural changes of LiTFSA aqueous electrolyte with different concentration at solid-phase interfaces have been extensively studied using atomic force microscopy (AFM), surface force apparatus (SFA), and molecular dynamics simulations (MD).¹⁶⁻²⁰ However, the impact of these structural changes on the electrical conductivity has vet to be discussed, and there is a lack of experimental data exploring the influence of solids on the structure of 20.5 mol kg^{-1} LiTFSA electrolyte.

In this study, we investigated the electrical conductivity and its activation energy in solid/liquid mixed systems by mixing the 20.5 mol kg^{-1} LiTFSA electrolyte with anatase TiO₂ metal oxide powder. To explain the relationship between the electrical conductivity and ionic interaction for the effect of solid phase of TiO₂ powder, Raman spectra was measured in order to observe the state of the hydration structure by Raman spectroscopy.

However, the volume fraction of water is extremely low in the presence of a large portion of ionic species and in coexistence with solids, and little amount exceeding the limit of sensitivity of Raman spectra made the difficulty of the measurement. Therefore, we employed near-infrared (NIR) spectroscopy to detect the behavior changes in water molecules. Additionally, we turned our attention to the near-infrared (NIR) spectroscopy of water molecules. Due to the anharmonicity of molecular vibrations, vibrational spectra can be observed in the NIR range. Moreover, due to the significant anharmonicity of heterodiatomic OH bond in water solvent, these groups exhibit absorption peaks in the NIR region that are much stronger than those of other functional groups, giving NIR spectroscopy a natural advantage in detecting water molecules. Furthermore, because of the anharmonicity of the spectra, the NIR spectra of water molecules are highly sensitive to changes in hydrogen bonding environments. This makes it frequently used in studies related to changes in water structure. For instance, Dagade et al. conducted a detailed analysis of the NIR spectra of water molecules in aqueous solutions, subdividing the absorption peaks by the number of hydrogen bonds and studying the disturbance of water structure by ions.²¹ In this study, we employed diffuse reflectance NIR spectroscopy to investigate in detail the effects of TiO₂ solids on water molecules in high-concentration aqueous solutions by analyzing the changes in the distribution of water molecules with different hydrogen-bonding states as a function of solid-liquid mixing ratios. Additionally, because the nuclear spin-spin relaxation time (T_2) is highly sensitive to interactions surrounding the nuclei, we examined the behavior changes of water molecules in the presence of TiO₂ in water-in-salt electrolytes by measuring the T_2 of water molecules.

2. Experimental

2.1 Preparation of samples

For the material of solid phase, anatase TiO2 (FUJIFILM Wako Pure Chemical Corporation. 1st Grade) was dried in a vacuum oven at 180 °C for 20 hours. After drying, it was stored in a glove box filled with Ar atmosphere. The specific surface area of the dried TiO₂ was determined by BET analysis to be $9.39 \text{ m}^2 \text{ g}^{-1}$, with a true density of 3.9 g cm⁻³. LiCl (Nacalai Tesque Inc., GR) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSA) (KANTO CHEMICAL CO., INC. SP) can be used without further purification. LiCl and LiTFSA are stored in a glove box filled with Ar atmosphere, and the required mass is weighed out. The substances are dissolved in the corresponding mass of deionized water (conductivity $< 0.055 \,\mu\text{S}\,\text{cm}^{-1}$) to prepare solutions of concentrations from $1.0 \text{ mol } \text{kg}^{-1}$ to $20.5 \text{ mol } \text{kg}^{-1}$. Typically, studies on water-in-salt electrolyte focus on electrolyte solutions with a concentration of $21 \text{ mol kg}^{-1.6-8}$ According to the phase diagram obtained by Ding et al.,²² the electrolyte solution of 21 mol kg⁻¹ precipitates LiTFSA monohydrate (LiTFSA·H2O) crystals from the saturated solution, causing phase separation below 25 °C on the liquidus line. This crystallization causes problems of handling in sample preparation and storage. If the solution solidifies below the temperature at which crystal precipitation occurs, it can be easily and uniformly redissolved by heating in a system consisting only of liquid, allowing easy experimental operation even just below saturated solution concentration, i.e., 21 mol kg⁻¹ at 25 °C.

In performing experimental operations with a sample of concentrated solution mixed with the solid phase, it is expected that the liquid phase will separate within the solid-phase gap, resulting in a non-uniform distribution. Coagulation during experimental operation must be avoided as much as possible, because once heterogeneously separated, the hydrate does not return to its original homogeneous phase even if it is re-dissolved after heating among the solid particles. We confirmed that by using a LiTFSA electrolyte of 20.5 mol kg⁻¹, the solidification on the liquid phase line decreases from 25 °C to about 22.5 °C, thus enabling us to obtain results on temperature dependence with good reproducibility.

From a solution structure perspective, the $[H_2O]/[Li^+]$ ratio in a 21 mol kg⁻¹ LiTFSA aqueous solution is 2.65, whereas it is 2.71 at 20.5 mol kg⁻¹. This slight difference does not influence with the formation of nanometer-scale heterogeneity in the LiTFSA solution, as this nanostructure is still observable at 15 mol kg⁻¹,⁸ although with potentially slight effects on the nanometer dimensions of waterrich domains. Thus, it can be assumed that this minor difference in water content between 21 to 20.5 mol kg⁻¹ does not influence the structural behavior of the LiTFSA aqueous electrolyte in the presence of a solid phase very much.

Densities of electrolyte aqueous solutions are measured at room temperature using a densitometer (Anton Paar, DMA 5000 M) for all electrolyte samples. All solutions were stored at 30 °C to avoid the solidification of the concentrate solution. The concentration and relevant information for the prepared solutions are shown in Table 1.

2.2 Preparation of solid-liquid coexisting sample

 TiO_2 powder and the aqueous electrolyte were mixed in a volume ratio, with the liquid phase volume fraction ranging from 5 vol% to 50 vol% in an alumina mortar. After thorough mixing, the mixture was poured into a circular mold and compressed into cylindrical samples with a diameter of 10 mm by applying a pressure of 5 MPa for 30 minutes, as shown in Fig. S1.

Solution	Concentration			Density
	$/mol kg^{-1}$	$/mol L^{-1}$	$[H_2O]/[Li^+]$	$/\mathrm{g}\mathrm{cm}^{-3}$
I :Cl	1	0.98	55.6	1.021
LICI	20.5	14.27	2.7	1.301
LiTFSA	1	0.88	55.6	1.126
	5	2.91	11.1	1.417
	10	4.08	5.5	1.578
	15	4.71	3.7	1.665
	20.5	5.13	2.7	1.722

 Table 1. Various concentration indications and density for LiTFSA and LiCl aqueous solutions.

2.3 Electrical conductivity measurement and calculation of the activation energy

We measured the AC impedance for obtaining the electrical conductivity of the solid/liquid systems containing TiO₂ powder/ highly concentrated electrolyte. The prepared tablet samples were placed into a cell, as illustrated in Fig. S2, and AC impedance tests were conducted using a pair of platinum electrodes with a precision LCR meter (HP 4284A). An AC voltage of 0.6 V was applied, with a frequency range of 1 MHz to 25 Hz. To obtain the activation energy for ion transport, ΔE_a , the temperature inside the cell was controlled between 30 °C and 50 °C, with measurements taken every 2.5 °C. The activation energy for the conductivity, ΔE_a , was calculated by examining the dependency of conductivity on temperature. For cases where a linear relationship between these two variables was observed, the value of ΔE_a was determined by calculating the slope of the linear relationship between log σ and 1/T following the Arrhenius equation, as shown below:

$$\log \sigma = \frac{-\Delta E_{\rm a}}{2.303RT} + \log A \tag{1}$$

where R and A are the gas constant and an constant, respectively.

In the case that non-linear temperature dependence obtained in the Arrhenius plots, activation energy was calculated using the Vogel-Tammann-Fulcher (VTF) equation.^{23–25} This equation is commonly applied to describe the temperature dependence of conductivity in highly concentrated electrolyte solutions, as follows:

$$\sigma = AT^{-1/2} \exp[-B/(T - T_0)]$$
(2)

where *A* and *B* are constants, and T_0 is ideal glass transition temperature in free-volume theory. Mizuhata et al. provided a detailed description of the method for calculating the parameters in the VTF equation.^{26,27} The VTF parameters were determined with a nonlinear Gauss-Newton inverse matrix optimizing method.²⁷ The calculation was carried out on $\ln \sigma$ vs. *T* plots with respect to the following equation, which is the logarithmic function of Eq. 3:

$$\ln \sigma(T) = A' - (\ln T)/2 - B(T - T_0)$$
(3)

where $A' = \ln A$ in Eq. 2. Three partial derivative functions with respect to parameters, A', B, and T_0 were introduced for this operation as follows

$$\frac{\partial}{\partial A'} \left[\ln \sigma(T) \right] = 1 \tag{4}$$

$$\frac{\partial}{\partial B} \left[\ln \sigma(T) \right] = -\frac{1}{T - T_0} \tag{5}$$

$$\frac{\partial}{\partial T_0} \left[\ln \sigma(T) \right] = -\frac{B}{\left(T - T_0\right)^2} \tag{6}$$

The data processing was carried out by the BASIC program, which includes the functions of Eqs. 4–6, with emulator ANEX86 in

personal computer. The calculation was processed until the relative error became within 10^{-3} %. After these parameters were determined, ΔE_a was calculated from the differential coefficient at 30 °C in Eq. 7;

$$\frac{\mathrm{d}(\ln\sigma)}{\mathrm{d}(1/T)} = -\frac{\Delta E_{\mathrm{a}}}{R} = -\frac{1}{2}T - B\left(\frac{T}{T-T_{0}}\right)^{2} \tag{7}$$

2.4 Spectroscopy measurement

Raman spectra were recorded using a T-64000 Raman spectrometer (HORIBA, Ltd.) equipped with a Nb: YVO_4 laser and a chargecoupled device cooled using liquid nitrogen as a detector. The 532 nm line was used for excitation. The solution samples were loaded into glass tubes and spectra were recorded in the backscattering geometry. The monochromator was calibrated using the CCl_4 peak at 459 cm⁻¹. All experiments were performed at room temperature.

To further understand the behavior of water molecules in solidliquid coexistence systems, we employed diffuse reflectance spectroscopy to analyze the near-infrared spectra of water molecules. The near-infrared spectra of water molecules in pure solution were measured using total internal reflection. The ZnSe prism was employed at an incidence angle of 45°, with three reflections. In contrast, the near-infrared spectra of water molecules in a solidliquid coexistence system were measured using a diffuse reflectance attachment (DR-600B) in an N2 atmosphere. All near-infrared spectra were obtained using a JASCO FT-IR-615 spectrometer, with a resolution of 2 cm⁻¹, and averaged over 64 scans. The O-H stretching vibrations of water molecules are highly sensitive to changes in surrounding interactions, such as the formation or disruption of hydrogen bonds. Therefore, we examined the combination frequency of the OH symmetric and antisymmetric stretching vibrations of water molecules in the range of 6000-8000 cm⁻¹.^{21,28} Using Gaussian functions and referencing the deconvolution results of pure water, we attributed the four components obtained from the deconvolution to different hydrogen bonding states of water molecules.²¹ To enhance the signal-to-noise (S/N) ratio, the Savitzky-Golay smoothing method was applied to the near-infrared spectra of all water samples.

The spin-spin relaxation time T_2 of ¹H NMR in both pure solution and solid-liquid coexistence samples was measured using Acorn Area (Xigo Nanotools). The magnetic field strength was set to 0.3 T, with a measurement frequency of 13 MHz, a time of integrations of 4 times, and the measurement temperature was maintained at 30 °C. All samples were measured 10 times, and the average of these 10 results was taken. Due to instrument precision, the volume fraction of the liquid phase in the tested samples ranged from 40 vol% to 100 vol%.

3. Results and Discussion

3.1 The conductivity of lithium electrolyte solutions in solidliquid coexisting systems

Figure 1 display the Nyquist plots of the electrochemical impedance for 1 mol kg⁻¹ and 20.5 mol kg⁻¹ LiTFSA electrolyte at 30 °C. All samples exhibit a semicircular feature at high frequencies and a linear portion at low frequencies in their Nyquist plots. Additionally, as the liquid phase volume fraction decreases, the diameter of the semicircular part increases. In the case of 20 vol% liquid content, TiO₂ powder/20.5 mol kg⁻¹ LiTFSA aqueous electrolyte system showing a resistance of ca. $8 \times 10^5 \Omega$, normal polarization in the low frequency range is unlikely to occur, and there is little impedance indicative of solution diffusion, as shown in Fig. 1b. All Nyquist plots at high frequency range are considered as the resistance of the electrical conductivity of the solid-liquid coexistence system caused by ionic conduction of the aqueous liquid



Figure 1. Nyquist plots obtained by impedance measurement of (a) TiO_2 powder/1 mol kg⁻¹ LiTFSA-H₂O electrolyte; (b) $TiO_2/20.5 \text{ mol kg}^{-1}$ LiTFSA-H₂O electrolyte coexisting system at the liquid phase volume fraction of 20 vol%; (c) $TiO_2/20.5 \text{ mol kg}^{-1}$ LiTFSA-H₂O electrolyte coexisting system at the liquid phase volume fraction of 20 vol%; (c) $TiO_2/20.5 \text{ mol kg}^{-1}$ LiTFSA-H₂O electrolyte coexisting system at the liquid phase volume fraction of 20 vol%. The italicized numbers in the three figures indicate the measurement frequencies for AC impedance.

phase. In TiO₂ powder/20 vol% 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte system, the excessively high resistance value leads to an inability to accurately detect results as the low frequency approaches the DC region. The electrical conductivity in each solid-liquid coexistence system is calculated using the following formula:

$$\sigma = L/RS \tag{8}$$

Where *L* represents the thickness of the sample, *R* is the resistance of the sample obtained through Nyquist analysis, and *S* is the crosssectional area of the sample. The results of the conductivity of the solid-liquid coexistence systems as a function of the liquid phase volume fraction are shown in Fig. 2. For both LiTFSA aqueous electrolyte solutions of the concentrations of 1 mol kg^{-1} and the 20.5 mol kg⁻¹, the electrical conductivities increase with the liquid content exponentially, so to assess the effect of TiO₂ on the conductivity of the 20.5 mol kg⁻¹ LiTFSA electrolyte, we introduced Archie's empirical formula.²⁹ Archie's empirical formula is widely recognized in geology and is typically used to evaluate the relationship between the porosity of rocks and the conductivity of the interstitial water, as shown in Eq. 9:

$$\sigma/\sigma_{\rm liq.} = a\varphi_{\rm l}^{m} \tag{9}$$

that is:



Figure 2. The variation of the electrical conductivity with the liquid content of the TiO_2 powder/LiTFSA aqueous electrolyte solid-liquid coexistence system. The concentration notations in the figure are for LiTFSA electrolyte solution.

$$\log(\sigma/\sigma_{\text{liq.}}) = m\log\varphi_1 + \log a \tag{10}$$

where σ is the measured conductivity of the solution in the solidliquid coexistence system, $\sigma_{\text{liq.}}$ is the conductivity of the bulk solution, *a* is a constant, φ_1 is the volume fraction of the liquid phase in the solid-liquid coexistence system, and m, known as the cementation index, is typically considered to be a constant related to the intrinsic properties of the solid phase. However, due to the limitations of Archie's equation, it is typically used to discuss aqueous solutions with concentrations similar to that of seawater. In these solutions, the electrolyte concentration is low, and the interactions between ions, as well as between ions and solids, are relatively weak, resulting in minimal influence from the solid phase. In this regard, Deki et al. found that the cementation index, m, indicates the interactions between the solid and liquid phases, as well as by changes in the structure of the liquid phase solution, when studying the conductivity of solid-liquid coexistence systems with varying concentrations, temperatures, and ionic species.³⁰ Figure 3a illustrates the effect of changes in the volume fraction of the liquid phase on the conductivity of $1\,mol\,kg^{-1}$ and $20.5\,mol\,kg^{-1}$ LiTFSA aqueous electrolyte coexisting with TiO2, corresponding to the relationship described in Eq. 10. For ease of comparison, Fig. 3b shows the influence of the TiO₂ solid phase on the conductivity of 1 mol kg⁻¹ LiCl and 20.5 mol kg⁻¹ LiCl aqueous solutions. Values of a and m in Archie's equation for the TiO_2 powder/Li⁺ electrolyte systems are shown in Table 2. The conductivity for the 20.5 mol kg⁻¹ LiTFSA solution are shown to decrease by a factor of about 1/1000 as the liquid phase volume fraction decreases from 45 vol% to 15 vol%, which indicates a significant decrease compared to results for other systems.30 This indicates that the influence of TiO₂ on the 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte is much greater than that on other aqueous solutions of the same concentration, such as LiCl solutions.

On the other hand, the activation energy of ion mobility in the solution, ΔE_{a} , typically reflects the energy barrier for ion transport. Therefore, to obtain the activation energy of ion mobility in the solid-liquid coexistence system, the conductivity of the samples was measured at different temperatures, as shown in Fig. 4. Since the relationship between conductivity and temperature for all samples exhibited nonlinearity, the relationship between the conductivity and temperature of all samples was fitted using the VTF equation given in Eqs. 2 and 7, with the results shown in Fig. 5. Whereas the value of activation energy is ca. 24 kJ mol^{-1} in 20.5 mol kg^{-1} LiTFSA aqueous solution, it can be observed that the activation energy for the conductivity at the liquid phase of 45 vol% in the 20.5 mol kg^{-1}



Figure 3. Archie's plots for the system of (a) TiO_2 powder/LiTFSA aqueous electrolyte solution coexistence system and (b) TiO_2 powder/LiCl aqueous electrolyte solution coexistence system. The concentration notations in the figure are each electrolyte solution.

Table 2. Values of *a* and *m* in Archie's equation, $\sigma/\sigma_{\text{liq.}} = a\varphi_1^m$, for TiO₂ powder/Li electrolyte solution coexisting systems.

Electrolyte	а	т
1.0 mol kg ⁻¹ LiTFSA	0.110	1.86
$20.5 \mathrm{mol}\mathrm{kg}^{-1}$ LiTFSA	5.54	6.26
$1.0 \mathrm{mol}\mathrm{kg}^{-1}$ LiCl	0.45	2.83
$20.5 \text{mol} \text{kg}^{-1} \text{LiCl}$	0.572	2.88

LiTFSA aqueous electrolyte is ca. $35 \text{ kJ} \text{ mol}^{-1}$ and higher than that in the 1 mol kg⁻¹ solution (ca. $28 \text{ kJ} \text{ mol}^{-1}$). These differences are observed across all liquid phase volume fractions. Furthermore, when the liquid phase volume fraction is below 35 vol%, i.e., the apparent average thickness of the liquid phase of ca. 15 nm, the ΔE_a value increases rapidly, which corresponds well with the anomalous decrease in the conductivity for the system using 20.5 mol kg^{-1} LiTFSA. To discuss the influence of the solid phase on the solution, we considered an ideal model in which all TiO₂ particles can be approximated as uniformly sized spheres. Under the assumption of homogeneous mixing of the solid and liquid phases, the thickness of the liquid phase distributed on each particle's surface remains



Figure 5. Variations of the activation energy of the electrical conductivity with the apparent average thickness of the liquid phase for the system of TiO_2 powder/LiTFSA aqueous electrolyte coexistence system.



Figure 4. Temperature dependence of the electrical conductivity of TiO_2 powder/LiTFSA aqueous electrolyte coexistence system. Concentration of LiTFSA: (a) 1 mol kg⁻¹ and (b) 20.5 mol kg⁻¹ at various liquid contents.



Figure 6. Raman spectrum of the S-N-S bending vibration in TFSA⁻. (a) Raman spectral changes in the S-N-S bending vibration of TFSA⁻ in LiTFSA aqueous electrolyte solutions at different concentrations. The deconvoluted spectra are shown in Fig. S4. (b) The deconvolution ratios in Raman spectra (a) using Gaussian functions. The deconvolution was performed with two Gaussian components: the high-frequency component is assigned to TFSA⁻ involved in the Li⁺ solvation shell, and the low-frequency component is assigned to free TFSA⁻ not interacting with Li⁺. (c) Raman spectra of the S-N-S bending vibration of TFSA⁻ in the TiO₂/20.5 mol kg⁻¹ LiTFSA aqueous electrolyte solution coexistence system at different liquid phase volume fractions. (d) The change in the wavenumber of the maximum Raman signal of the S-N-S bending vibration of the liquid phase volume fraction.

consistent, referred to as the apparent average thickness. The detailed model and calculation formulas are provided in the supporting information, as shown in Fig. S3. Figure 5 illustrates the variation of activation energy at different apparent average thicknesses calculated based on the mixing ratio of the liquid and solid phases, as well as the specific surface area of the solid phase. Compared to the 1 mol kg⁻¹ LiTFSA solution, which shows a significant increase in activation energy at an apparent average thickness of ca. 7.5 nm, 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte begins to exhibit a significant influence from the solid phase at a liquid thickness of ca. 15 nm. This observation contrasts with the trend noted by Mizuhata in CaCl₂ aqueous solutions.²⁶ Considering the structural changes reported at the electrode interface¹⁶ and the mica surface²⁰ in 21 mol kg⁻¹ LiTFSA aqueous electrolyte, we further propose that the anomalous decrease in the conductivity of the 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte is closely related to its interaction with the TiO₂ solid phase, which leads to significant alterations in the solution structure at the solid phase interface compared to the bulk solution. This change disrupts the original ionic transport mechanism in the bulk 20.5 molkg⁻¹ LiTFSA electrolyte, ^{7–9,31–34} making ion transport significantly more difficult.

3.2 The behavior of TFSA⁻ in solid-liquid coexistence systems To further understand the effect of TiO₂ on the solution structure of 20.5 mol kg⁻¹ LiTFSA aqueous solution, we analyzed the molecular vibrations of water molecules and TFSA- under the influence of the TiO₂ solid phase within the solid-liquid coexisting system. Figure 6 presents the Raman spectral peak changes of the S-N-S bending vibration, $\delta_{SNS},$ of TFSA $^-$ at different concentrations and liquid phase volume fractions.^{35,36} According to Suo et al., the S-N-S vibration near 749 cm⁻¹ in 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte is highly sensitive to the anion environment and is thought to be related to the formation of a permeable TFSA⁻ anionic network.⁶ As shown in Fig. 6a, with increasing bulk LiTFSA concentration, the peak wavenumber of the bending vibration shifts from 746 cm^{-1} at 1 mol kg^{-1} to 749 cm^{-1} at 20.5 mol kg^{-1} . The deconvolution of the S-N-S bending Raman peak into two Gaussian components is shown in Fig. 6b. We assign the component at 750 cm⁻¹ to TFSA⁻ in ion pairs, including CIP and AGG, and the component at 746 cm⁻¹ to free TFSA⁻, the deconvoluted spectra are shown in Fig. S4. The results indicate that no significant Li⁺-TFSA- interaction is observed in LiTFSA solutions below 5 mol kg⁻¹. At concentrations above 5 mol kg⁻¹, TFSA⁻ begins to participate in Li⁺ solvation, forming CIP or AGG, with increasing ion-ion interactions at higher concentrations. This observation aligns well with the findings of Borodin et al.⁷

When the liquid phase volume fraction in the solid-liquid coexisting system is reduced to 10 vol%, as shown in Figs. 6c and



Figure 7. The deconvolution results of the Raman spectra of the S-N-S bending vibration of TFSA⁻ ion at different liquid contents in Fig. 6c.

6d, the peak wavenumber of the S-N-S bending vibration shifts from 749.3 cm^{-1} to 746.7 cm^{-1} . The deconvolution results reveal that as the liquid phase volume fraction decreases, interaction between TFSA⁻ and Li⁺ is weakened, resulting in an increase in free TFSA⁻, as illustrated in Fig. 7. Results of changes in conductivity and activation energies with the amount of HTFSA added to LiTFSA aqueous electrolyte solution of $1 \mod kg^{-1}$ and $20.5 \mod kg^{-1}$ at a liquid phase volume fraction of 30 vol% as shown in Fig. S5. The horizontal axis indicates the logarithmic opposite of the HTFSA added to the bulk solution. Results for conductivity and activation energies without HTFSA addition are shown at " ∞ " on the right side of the graph. The electrical conductivity and the apparent activation energy calculated from the temperature dependence of the electrical conductivity of TiO2 powder/LiTFSA solution systems with a liquid phase volume fraction of 30 vol% are shown as a function of HTFSA addition. In the system without HTFSA, the pH of the 1.0 mol kg⁻¹ and 20.5 mol kg⁻¹ solutions had pH values of 6.3 and 2.4, respectively, indicating that H⁺ is released from water molecules between TFSA- ions and the pH decreases with increasing LiTFSA concentration, as indicated by Han et al.³⁷ The fact that the pzc of TiO₂ in commonly used Li salts, e.g. LiCl and LiClO₄, shows a pzc of ca. 6^{38} suggests that the surface charge becomes negative (in a base side) at low concentrations and positive (in an acid side) at high concentrations with increasing concentration in LiTFSA solutions. In this case, the specifically adsorbed ions are H⁺ or OH⁻ in aqueous systems, whereas Li⁺ and TFSA⁻ are not specifically adsorbed ions and the effect of electrostatic interactions with the surface charge must be considered. As shown in Fig. S5a, when small amount of HTFSA (log [HTFSA] = -3.6, i.e., $2.5 \times$ 10^{-4} mol L⁻¹) is added in a 1.0 mol kg⁻¹ LiTFSA solution, the surface charge is neutralized, which mean the surface charge of LiTFSA is mostly neutral. On the other hand, as shown in Fig. S5b, when HTFSA is added to a solution of 20.5 mol kg^{-1} , the surface charge becomes even more positive when HTFSA is added, the electrical conductivity falls. If the decrease in electrical conductivity is due to viscous effects, then the activation energy should increase in this case, but in fact the activation energy decreases. This suggests that the TFSA- ions is adsorbed on the solid phase, and that the activation energy is further lowered because the Li⁺ ions with low activation energy are the major conducting species.

From these results, the influence of the solid phase on the addition of TiO_2 at each concentration can be considered as follows: in a solution system of 1.0 mol kg⁻¹ with a solution pH close to pzc, the activation energy hardly increases even with a high content of

solid phase until the average thickness decreases to about 7 nm, as shown in Fig. 5, and the solid phase is considered to be very insensitive to the effect of the solid phase. However, in the 20.5 mol kg⁻¹ solution system, the addition of the solid phase causes the activation energy to increase from about 15 nm, Deki et al. found that the increase in activation energy due to electrostatic interactions depends on the thickness of the electric double layer, so that at higher concentrations the activation energy increases at a greater distance from the solid surface. They stated that the activation energy rises from a closer distance.²⁶ In contrast, the results of Fig. 3 suggest that the decrease in the solid-phase dependence of the electrical conductivity is caused by a significant decrease in the pH of the high-concentration solution, which increases the surface charge of the solid phase.

3.3 The behavior of H₂O in solid-liquid coexistence systems

The NIR spectra for TiO_2 powder/20.5 mol kg⁻¹ LiTFSA aqueous solution coexisting systems are shown in Fig. 8a, each component is assigned as following items.

- I_0 : Free water molecules with no hydrogen bond.
- I_1 : Water molecules with one hydrogen bond.
- I_2 : Water molecules with two or three hydrogen bond.
- *I*₃: Water molecules with four hydrogen bonds.

We further categorize the four types of water molecules into two major classes: I_0 and I_1 are considered as water molecules interacting with ions, while I_2 and I_3 are those are not influenced by ion interactions. The results of the peak intensity ratios as a function of liquid phase volume fraction are shown in Fig. 8b. It can be observed that the addition of solids increases the number of hydrogen-bonded water molecules on the low-frequency side, while the number of water molecules with fewer hydrogen bonds decreases.

It is generally known that the electric double layer at the oxide/ aqueous solution interface and the surface potential based on it depend on the pH value due to the potential-determining ions, i.e., H^+ and $OH^{-.39,40}$ However, the contribution of dissolved ions cannot be ignored for the surface potential in highly concentrated aqueous solutions. For example, studies have shown that TFSA⁻ ions exhibit physisorption due to electrostatic interactions with solid surfaces. Additionally, a series of investigations on the structure of a 21 mol kg⁻¹ LiTFSA aqueous electrolyte at the interface have reported that, under positive potentials, water molecules are excluded from the layer closest to the electrode surface.^{16–18,36}



Figure 8. Near-infrared spectrum of water molecules in the TiO₂/LiTFSA aqueous electrolyte solid-liquid coexistence system, featuring the absorption peak associated with the combination frequency of the symmetric stretching and antisymmetric stretching vibrations of OH groups. (a) After deconvoluting the near-infrared absorption peak of OH, four Gaussian components were obtained, attributed to: the component I_0 on the high wavenumber side represents free water molecules with no hydrogen bonding, I_1 represents water molecules with one hydrogen bond, I_2 corresponds to water molecules with two or three hydrogen bonds, and I_3 denotes water molecules with four hydrogen bonds. (b) Dependence of the relative peak area of water molecules with fewer hydrogen bonds ($I_0 + I_1$) and water molecules with more hydrogen bonds. ($I_2 + I_3$) on liquid phase volume fraction.

The decrease in ion-ion interactions near the solid surface obtained from the Raman scattering results described in Section 3.2 is a result that supports the promotion of phase separation between the domains of TFSA⁻ ions forming the hydrophobic phase and the hydrophilic phase formed by Li+ hydration structure. In this situation, the Li⁺ ions originally interacting with TFSA⁻ would migrate to the hydrophilic phase, forming a more concentrated domain of hydrated Li⁺ ions. However, in stoichiometric condition of $[H_2O]/[Li^+] = ca. 2.7$ in 20.5 mol kg⁻¹ LiTFSA aqueous solution, the water molecules are under the influence of multiple Li⁺ ions. In Fig. 7, it is suggested that the interaction between anions and cations is weakened as they coexist with the solid phase, while Fig. 8 shows that a hydrogen bonding network is partially formed. If coexistence with the solid phase leads to adsorption of water molecules to the solid phase or to the development of a hydration structure, the values of $I_2 + I_3$ should decrease and the space where water can assemble, which does not contribute to solid phase adsorption or orientation to ions, should be taken into account.

The results of electrical conductivity suggest that TFSA⁻ ions are in a state where they can easily assemble near the solid phase. It follows that Li⁺ ions excluded from the TFSA⁻ domain can only be incompletely hydrated, and water molecules gather to form hydrogen bonding networks in the repulsive field among Li⁺ ions, resulting in an increase in $I_2 + I_3$ already when the liquid phase volume fraction is reduced to 50 %.

In bulk 21 mol kg⁻¹ LiTFSA aqueous electrolyte, the presence of nanoscale water channels results in a conductivity of nearly 10 mS cm⁻¹ even at high concentrations and viscosities.⁹ Consequently, the behavior of water molecules in the solid-liquid coexistence system plays a decisive role in ionic transport. Studies utilizing proton nuclear magnetic resonance (¹H NMR) to detect the spin-spin relaxation time (T_2) of water molecules in the aqueous solution have been widely reported.⁴¹ Since the spin-spin relaxation process of hydrogen nuclei is a dipolar relaxation process, T_2 of the hydrogen nuclei is highly sensitive to changes in the dipole interactions surrounding the water molecules.⁴² Therefore, we aim to clarify the behavioral changes of water molecules by measuring T_2 in the solid-liquid coexistence system. Due to the different interactions between various electrolytes and water molecules, the T_2 relaxation times of hydrogen in these bulk aqueous solutions vary. Therefore, to discuss the effect of TiO₂ solids on the T_2 relaxation times of H₂O in each solution more intuitively, all T_2 times measured at various liquid volume fractions were normalized using the values result of each bulk solution as a reference. The unnormalized T_2 results for all conditions are provided in Supplementary Information, Fig. S6.

Due to the typical strong hydrophilicity of TiO₂, water molecules readily interact with TiO₂, leading to their ordering structure at the surface and the formation of hydrogen bonds, which restricts the thermal motion of the water molecules. Consequently, as the volume fraction of TiO_2 increases, a significant decrease in the T_2 relaxation time of water molecules in all solutions can be observed, as shown in Figs. S6a and S6b. This indicates that the mobility of water molecules in the electrolyte is reduced due to confinement by the solid phase. Figure 9a compares the relative changes in T_2 relaxation times of 20.5 mol kg⁻¹ LiCl-H₂O and 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte, highlighting their liquid volume fraction dependency. Notably, although LiCl and LiTFSA have the same number of ions per water molecule, the relative T_2 relaxation times of water molecules in the 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte vary with volume fraction more similarly to pure water than those in LiCl. By examining the changes in the relative T_2 relaxation times of H nuclei in LiCl solutions of different concentrations, we conclude that increasing concentration leads to more water molecules participating in interactions with cations or anions. This electrostatic interaction is evidently stronger than that between water molecules and TiO₂, resulting in a limited interaction with TiO₂. Consequently, water molecules in highly concentrated solutions are less influenced by the solid phase, yielding a more gradual change in T_2 relaxation times compared to dilute solutions, as shown in Fig. 9b. In the 21 mol kg⁻¹ bulk LiTFSA aqueous electrolyte, the water molecules in the hydrophilic regions are less influenced by contact ion pairs and exhibit weaker interactions with TFSA- and Li+ concentration being significantly lower than the apparent concentration of the solution. Therefore, we believe that the addition of TiO₂ causes water molecules in the hydrophilic regions to aggregate on the TiO₂ surface, resulting in relative T_2 relaxation time changes that resemble those of water molecules in dilute solutions.



Figure 9. Variation of the T_2 relaxation time of hydrogen nuclei in water molecules within the solid-liquid coexistence system. To compare the results of different electrolyte, the T_2 relaxation times for all liquid phase volume fractions were normalized using the respective bulk solution T_2 relaxation times as a reference, expressed as $T_2/T_{2,\text{bulk}}$. (a) T_2 relaxation time dependence on liquid phase volume fraction for pure water, 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte, and 20.5 mol kg⁻¹ LiCl aqueous solution in conjunction with TiO₂ powder. (b) Dependence of the T_2 relaxation time of hydrogen nuclei in water molecules on liquid phase volume fraction in TiO₂/LiCl aqueous solution coexistence systems with different concentration. (c) Dependence of the T_2 relaxation time of hydrogen nuclei in water molecules on LiCl aqueous solution and LiTFSA aqueous electrolyte at a liquid phase volume fraction of 40 vol%.

Additionally, at a liquid phase volume fraction of 40 vol%, we investigated the effect of solution concentration on the T_2 relaxation times of water molecules. As mentioned earlier, increasing the solution concentration reduces the impact of the solid on the water molecules, causing $T_2/T_{2, \text{ bulk}}$ to approach 1, as illustrated for LiCl (blue) in Fig. 9c. However, as the concentration increases, a decrease in $T_2/T_{2,\text{bulk}}$ is observed in LiTFSA aqueous electrolyte. At low concentrations, the ionic interactions are weak, so the LiTFSA solution does not exhibit significant differences compared to LiCl. Han et al. indicated that phase separation in concentrated LiTFSA aqueous solution over ca. 5 mol kg⁻¹, ionic aggregates form leading to hydrophilic(water) and hydrophobic(ionic) domains.³⁷ Consequently, more water molecules are excluded from the hydrophobic regions, making them more susceptible to the influence of TiO₂, resulting in a slight decrease in T_2 . As the concentration continues to increase, the expanding interface between the hydrophilic and hydrophobic regions raises the proportion of interfacial water, thereby inhibiting the interaction between water molecules and TiO₂. However, overall, the inhibitory effect of Li⁺ and TFSA⁻ on the interaction between water molecules and TiO₂ is still significantly less than that of LiCl.

4. Conclusions

In order to discuss the influence from solid phase on ionic conduction in highly concentrated aqueous solutions, we measured the electrical conductivity and its activation energy of solid-liquid coexistence systems consisting of 20.5 mol kg^{-1} LiTFSA aqueous electrolyte and TiO₂ powder and correlated them with various spectroscopic results indicating interactions between dissolved species.

The electrical conductivity of the 20.5 mol kg⁻¹ LiTFSA aqueous electrolyte increased exponentially with an increase of the volume fraction of the liquid phase up to ca. 40 vol%, and the activation energy of electrical conductivity increased with a decrease of the liquid phase below 35 vol%.

S-N-S bending mode in TFSA⁻ anions at ca. 750 cm⁻¹ in Raman spectra shifts toward to lower wave number, which indicates weakened ion-ion interactions with TFSA⁻ and Li⁺ due to the coexistence of a solid phase. In the near-infrared spectra ($v_1 + v_3$) of water molecules in the 6500–7500 cm⁻¹ region, which indicate the hydrogen-bonding network state, the intensity at lower wave-

numbers, indicating the formation of hydrogen-bonding network structure among water molecules, increases with the coexistence of the solid phase. These results suggest that the ion-water interaction is weakened and Li+ ions are released from the hydrophobic TFSAanions and concentrated in the hydrophilic region. As a result, water molecules form hydrogen bonds with each other in the repulsive field of high concentration of Li⁺ ion, and the near-infrared band at lower wavenumber side is considered to increase. As for the spin-spin relaxation in ¹H-NMR measurement in the electrolyte coexisting with the solid phase, the relaxation time (T_2) is significantly reduced due to the reduced mobility of water molecules, which is more pronounced in the order of H₂O > LiTFSA > LiCl. This may be due to the hydration structure of LiCl which weakens the solid effect relatively, while LiTFSA, due to the high hydrophobicity of TFSA, has a less pronounced effect on water molecule dynamics, leading to a more pronounced effect from the solid phase. These results indicate that in the $TiO_2/20.5 \text{ mol kg}^{-1}$ LiTFSA solid-liquid coexistence system with a liquid phase volume fraction below 40 vol%, the presence of TiO₂ disrupts the nanoscale water channel structure in the water-enriched regions of the bulk solution, resulting in an unusual decrease in electrical conductivity. The strong influence of the solid phase on the electrical conduction of the highly concentrated LiTFSA electrolyte was found to be significant only in the region below 50 vol% in the liquid content, while in the region above 50 vol%, there were no differences due to electrolyte concentration and ion species, indicating the influence of the solid phase on electrical conduction.

CRediT Authorship Contribution Statement

Jingchao Xu: Conceptualization (Lead), Data curation (Lead), Investigation (Lead), Methodology (Lead), Validation (Lead), Writing – original draft (Lead)

- Hideshi Maki: Investigation (Supporting), Methodology (Supporting)
- Hiro Minamimoto: Investigation (Supporting), Methodology (Supporting)
- Minoru Mizuhata: Conceptualization (Lead), Funding acquisition (Lead), Investigation (Supporting), Methodology (Supporting), Supervision (Lead), Writing review & editing (Equal)

Data Availability Statement

The data that support the findings of this study are openly available under the terms of the designated Creative Commons License in J-STAGE Data listed in D1 of References.

Conflict of Interest

The authors declare no conflict of interest in the manuscript.

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