Supporting Information

Unlimiting Ionic Conduction:

Manipulating Hydration Dynamics through Vibrational Strong Coupling of Water

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Experimental section

Materials.

Au and Pt metals were purchased from Tanaka Precious Metals, Japan. The CaF$_2$ windows were purchased from the Specac Ltd., UK. All the aqueous electrolyte solutions were prepared using Milli-Q water (Millipore; 18.2 MΩ cm resistivity). LiCl, NaCl, KCl, RbCl LiF, LiBr H$_2$O, and LiI were purchased from Wako. CsCl was purchased from Tokyo Chemical Institute.

Preparation of the Fabry–Pérot cavity.

The Fabry–Pérot cavity consisting of two parallel mirrors was prepared according to our previous works.[1] The holes for liquid insertion were used to position the two platinum wire electrodes for electrochemical measurements. The mirrors were fabricated by sputtering an 2-nm-thick layer of Ti, 8-nm-thick layer of Au on 2-mm-thick CaF$_2$ windows, followed by sputtering a 20-nm-thick top layer of SiO$_2$. The mirrors were sandwiched to create a home-made cell, and the cavity thickness (L) was tuned using a screw. The cavity modes were determined using the following equations: $\omega_{cav}(i) = ik_0$ and $k_0 = (2nL)^{-1}$, where $\omega_{cav}(i)$ is the frequency of the i-th cavity mode, i is an integer, k_0 is the free spectral range (FSR) corresponding to the peak-to-peak separation of cavity modes, n is the refractive index of the cavity medium, and L is the cavity thickness. These mirrors were sandwiched within a homemade cell, and the cavity thickness was mechanically controlled by the screw. The homogeneity of the cavity thickness was verified based on the Newton ring as a result of interference structural color

of the cavity.[1] The cavity modes can be determined by the fringe observed in the peak-to-peak separation of cavity modes. The cavity thickness was controlled between 1 and 5 μm without using a spacer. Refractive index of water was used as 1.33. The progression of cavity modes was confirmed from the interference characteristic of the cavity. The two mirrors had to be positioned in parallel within the cavity to accurately observe changes in the electrochemical properties of the electrolyte solutions, as described later.

IR measurements.

IR spectroscopic measurements were recorded using a JASCO FT-IR 4200. The resolution was set as $4\,cm^{-1}$, and the spot size was typically 2.5 mm in diameter. The quality of the cavity cell was confirmed based on the infrared spectra and the structural color in the cavity cell.

Electrochemical impedance measurements.

The established methods were utilized for the evaluation of the ionic conductivities.[1,2] All electrochemical impedance measurements were conducted using a Biologic VSP-150 potentiostat. The frequency range was set between the range of 1 MHz to 1 Hz. The potential bias was set as 0 V, and the amplitude was 300 mV. To perform the measurements, two Pt electrodes (ϕ = 0.3 mm) were introduced into the two holes in the window, and the ionic conductivity was measured parallel to the window. Bulk ion conductivity values were evaluated from the control experiment by using CaF_2

window without Au mirror. The values were compared to the literature values for the validation of the measurement's accuracy. The bulk ionic conductivities were shown in Figure 2.

Temperature control

Temperature control cell was hand-made. Temperature-controlled ethanol was flow within the copper jacket (Figure S1) by using the piezo-based micropumps (Takasago electric, Japan). The temperature was calibrated with the control experiment with the KCl ionic conductivity with the literature values[3] (Figure S2). For the cavity cell, first, the third order of cavity mode was adjusted to the OH stretching mode by adjusting cavity thickness to 3.3 μm. After the electrochemical measurements at various given temperatures, the coupling state and the good stability of the cavity cell were confirmed again after the measurements. The Arrhenius type behavior were verified through the experiments.
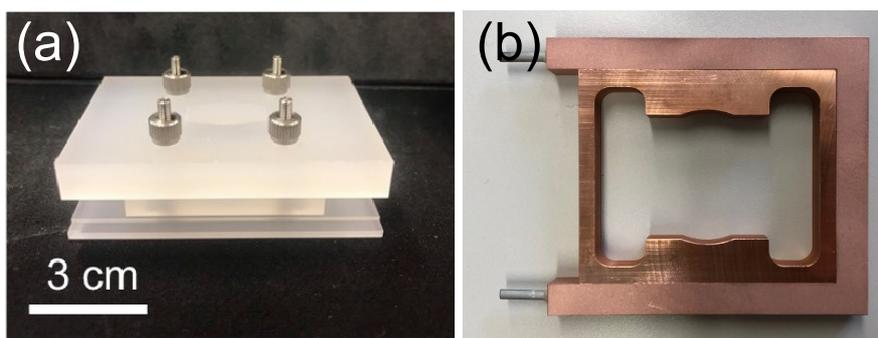
Figure S1. (a) The structure of the cell. (b) The temperature-controlled copper jacket.
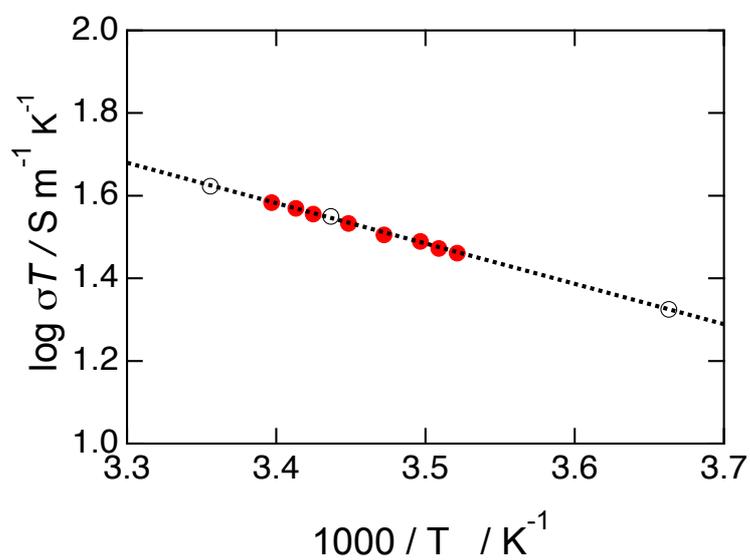
Figure S2. Representative Arrhenius plots for the verification of the experimental cell setup. Open symbol represents the literature value of the 0.01 M KCl electrolyte. Closed red symbols represent the obtained data of 0.01 M KCl electrolyte in our cell.

Table 1. The representative parameters for the physicochemical properties of electrolyte solutions.

	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ref.
R_{ion} / nm	0.141	0.071	0.097	0.141	0.150	0.173	Marcus[4]
Molar volume / cm³ mol⁻¹	-5.41	-6.29	-6.62	3.61	8.66	15.93	Marcus[5]
ΔH_{hyd} / kJ mol⁻¹	-1103	-531	-416	-334	-308	-283	Marcus[6]
ΔS_{hyd} / J mol⁻¹ K⁻¹		-103	-74	-38	-29	-23	Marcus[7]
ΔG_{hyd} / kJ mol⁻¹	-1050	-475	-365	-295	-275	-250	Marcus[8]
Number of hydration shell	12	5.2	3.5	2.6	2.4	2.1	Marcus[8]
B-coefficient	0.068	0.146	0.085	-0.009	-0.033	-0.047	Marcus[9]

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