Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Eutectic Solvent as Electrolytes for Rechargeable Proton Batteries

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Electrolyte Preparation:

1,1,1-trifluoro-*N*-[(trifluoromethyl)sulfonyl]methanesulfonamide (HTFSA) and 2,2,2-trifluoro-*N*-methylacetamide (MTFAA) were used as the hydrogen-bond donor and acceptor, respectively. Both reagents were purchased from Kanto Chemical Co., Inc. and Tokyo Chemical Industry Co., Ltd., and were used without further purification or dehydration. After purchase, all chemicals were stored in an argon-filled glovebox (dew point below −70 °C). The eutectic solvents were prepared by weighing HTFSA and MTFAA at stoichiometric molar ratios and mixing them in sealed sample vials.

Electrochemical Measurements:

α-MoO_3 was synthesized by the following procedure. Ammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 2.0010 g, 0.0324 mol) was dissolved in 50 mL of deionized water, followed by the addition of 20 mL of 3 mol dm^{-3} (M) nitric acid. The resulting solution was stirred for 10 min and then transferred to a 100 mL Teflon vessel, which was heated at 180 °C for 12 h. After heating, the obtained white precipitate was collected by centrifugation and washed three times with deionized water. The washed powder was finally dried under vacuum at 80 °C for 24 h. Amorphous TiO_x (EtOH) was prepared *via* hydrolysis of titanium tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$; TTIP), as reported in our previous paper.

Slurry mixtures consisting of 80 wt % active material (α-MoO_3 or a-TiO_x), 10 wt % acetylene black as the conductive additive, and 10 wt % polyvinylidene (PVDF) as the binder with *N*-methyl-2- pyrrolidone (NMP) were uniformly cast onto a Ti current collector (thickness: 18 µm) using a doctor blade and then dried at 120 °C under vacuum for 12 h to prepare composite electrodes as the working electrode. The loading mass of the active materials were 0.9−1.1 mg cm^{-2}. Protonation/deprotonation behavior was evaluated using a potentiostat (SP-300; Bio-Logic Science Instruments) and a three-electrode cell composed of the working electrode, an activated carbon electrode with a loading mass at least 4 mg cm^{-2} as the counter electrode, and an Ag/Ag^+ wire (0.1 M $AgNO_3$/0.1 M tetrabutylammonium perchlorate in acetonitrile) as the reference electrode, which was separated from the main electrolyte by porous Vycor glass. For the aqueous electrolytes of $[HTFSA]_x[H_2O]_{1-x}$, an Ag/AgCl (+0.197 V vs. SHE) wire immersed in a saturated NaCl solution was used as the reference electrode. Regardless of the electrolyte composition, a glass fiber separator (Whatman GF/A) was employed. Ref.) M. Shimizu, D. Nishida, T. Ichikawa, A. Kikuchi, S. Arai, *J. Phys. Chem. C*, 129 (2025) 5833−5839

Characterization:

Intermolecular hydrogen bonding interaction of $[HTFSA]_x[MTFAA]_{1-x}$ (x=0.3, 0.4, 0.5, 0.6, 0.7) was analyzed at room temperature by using an attenuated total reflection of Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iS5; Thermo Fisher Scientific) and a Raman spectroscopy system (LabRAMHR Evolution; HORIBA, Ltd.) with a 532 nm line of diode-pumped solid-state laser. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Fourier 300 spectrometer. NMR coaxial tubes consisting of two separate NMR tubes were used: a 4 mm insert, which narrows to 2 mm towards the measurement area, and a matching 5 mm outer tube. D_2O was used for a NMR lock shifts.

Viscosity measurements were carried out using a viscometer (EMS-1000 S; Kyoto Electronics). Thermal gravimetric analysis was performed by using a TG-DTA instrument (Thermo plus; TG8120, Rigaku) in the temperature range from room temperature to 300 ^{o}C under flowing N_2 (flow rate: 200 mL min^{-1}), and differential scanning calorimetry (DSC) was conducted using a calorimeter (Thermo plus; EVO2, Rigaku) with a sealed-aluminum ampoule at a ramp rate of 10 K min^{-1}. Ionic conductivity was measured using an airtight four-probe cell consisting of two inner Pt wire-electrodes for monitoring the potential difference and two outer Pt disk-electrodes for feeding an alternating current.

The structural changes of α-MoO_3 associated with proton insertion and extraction were investigated by X-ray diffractometry (XRD; SmartLab, Rigaku) with Cu-Kα radiation (λ=1.54 Å).

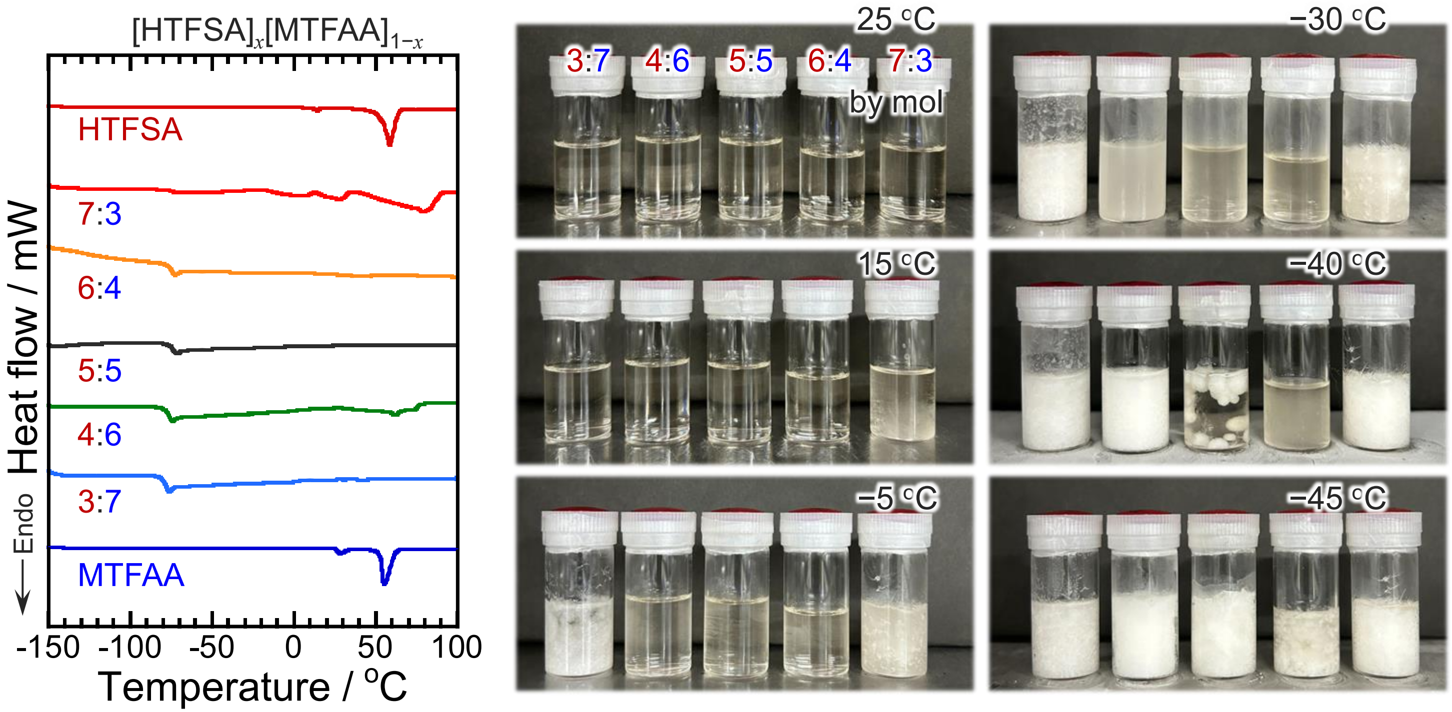

Figure S1. Differential scanning calorimetry curves of eutectic solvents prepared by mixing hydrogen-bond donor (HTFSA) and acceptor (MTFAA) in arbitrary molar ratios. Differential scanning calorimetry (DSC) did not show distinct endothermic peaks that would allow the melting points to be determined. Therefore, the phase states were visually inspected after equilibrating the mixtures for 30 min at selected temperatures. Solidification occurred at 15 °C for the 7:3 mixture, at −5 °C for 3:7, and at −30 °C for 4:6. In contrast, both 5:5 and 6:4 remained liquid down to −35 °C. Finally, all mixtures became fully solid at −45 °C.

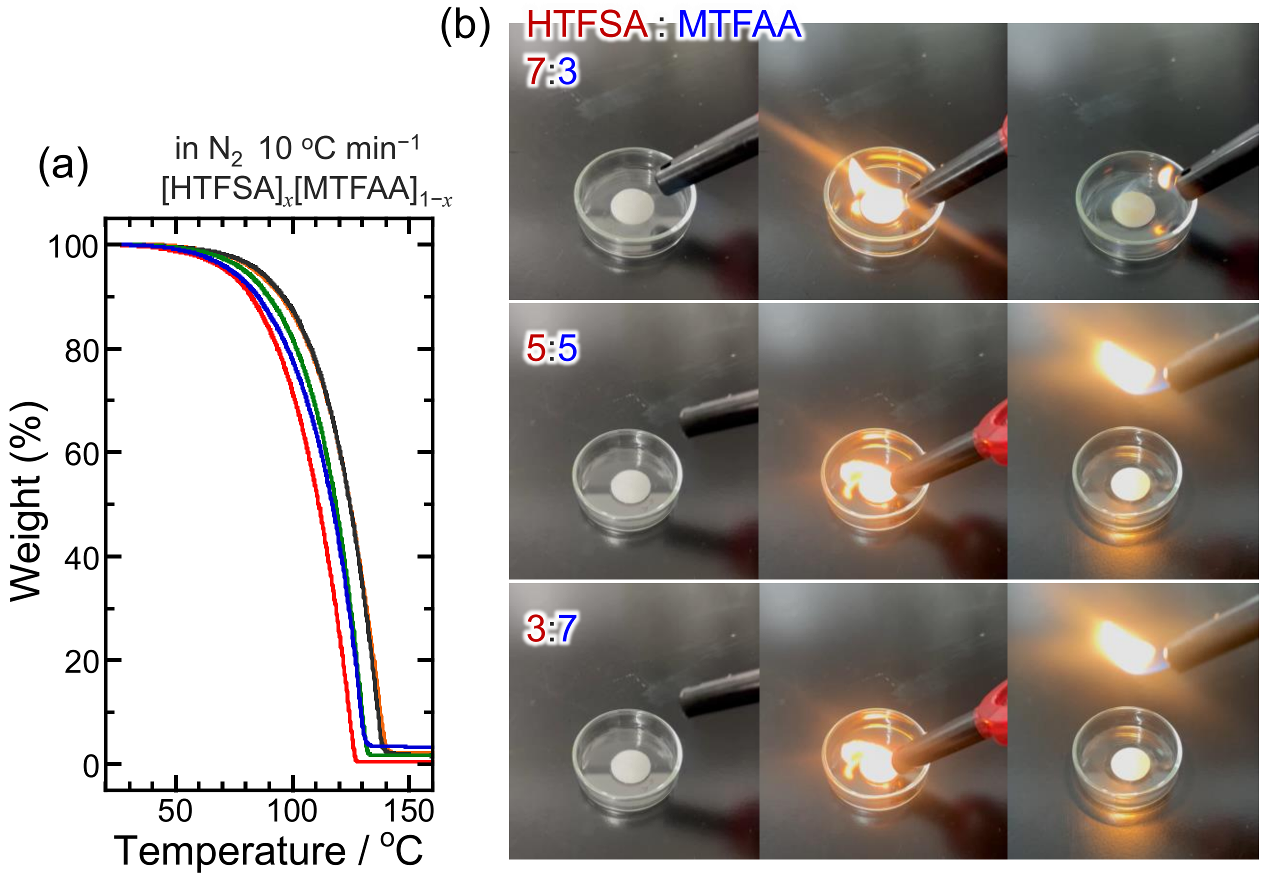

Figure S2. (a) Thermogravimetric traces of eutectic solvents in the temperature range from room temperature to 500 °C under flowing N_2 (flow rate: 200 mL min^{-1}). (b) Simplified flammability test. The eutectic solvents were exposed to a flame for 5 s, after which ignition behavior was visually examined upon flame removal. Regardless of the molar ratio of hydrogen-bond donor (HTFSA) and acceptor (MTFAA), none of the eutectic solvents exhibited flammability.

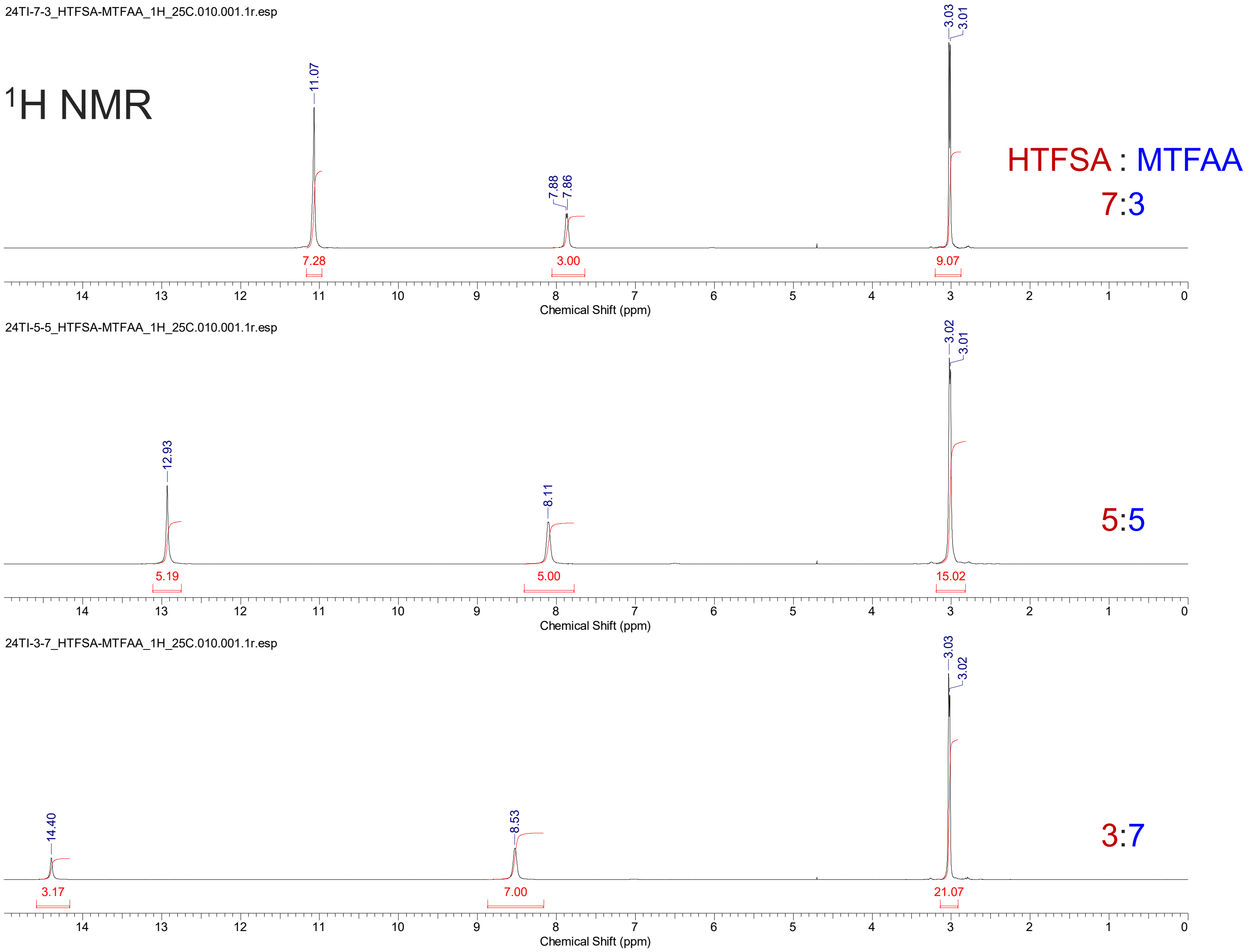

Figure S3. ^{1}H NMR spectra of eutectic solvents consisting of HTFSA and MTFAA.

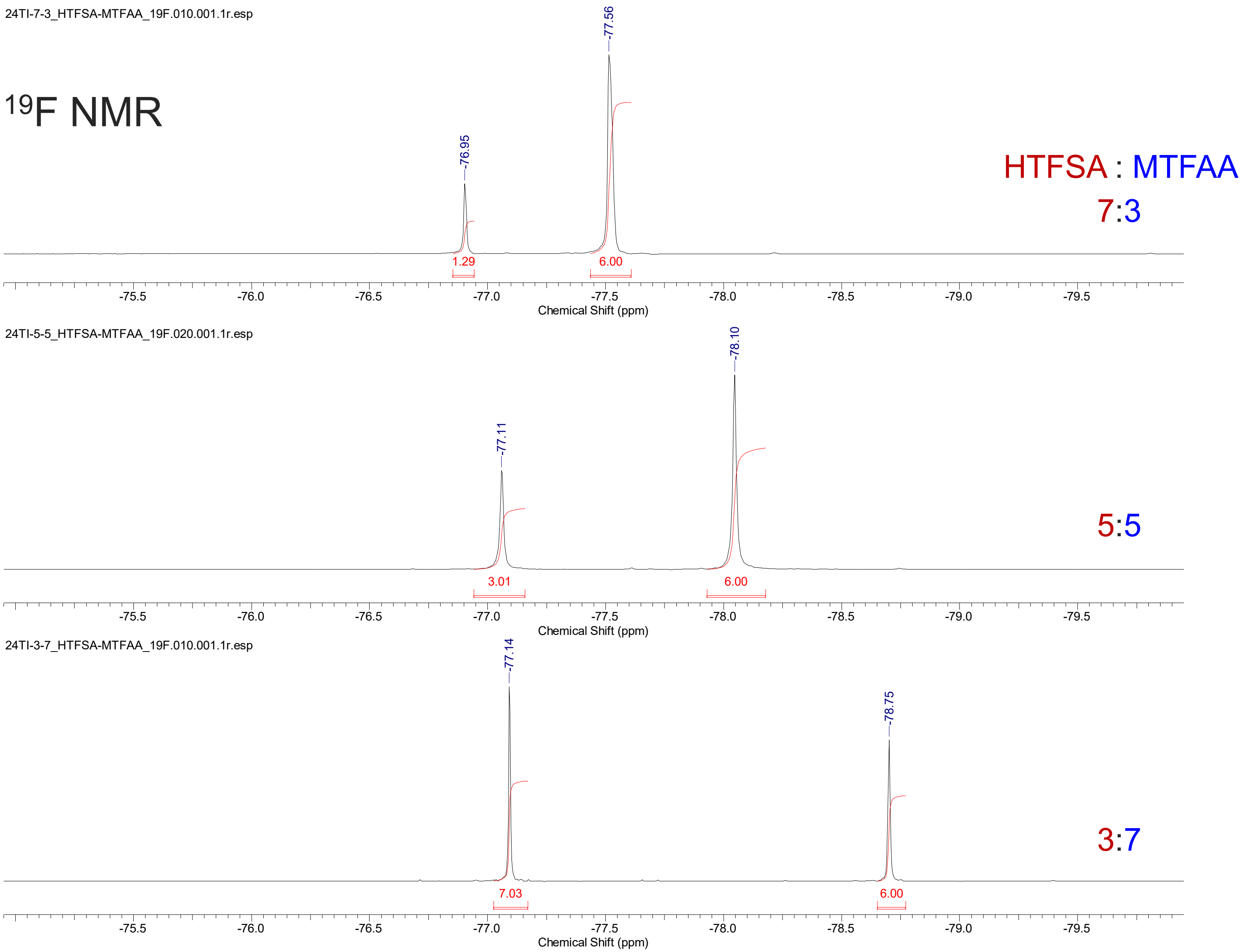

Figure S4. ^{19}F NMR spectra of eutectic solvents consisting of HTFSA and MTFAA.

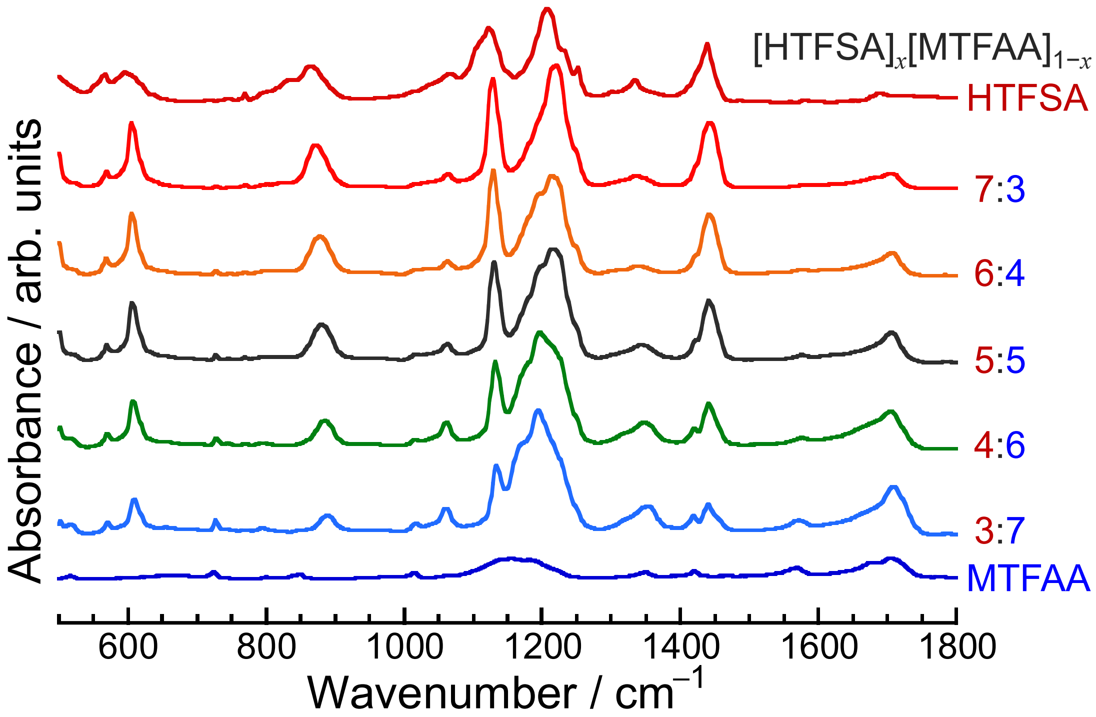

Figure S5. FT-IR spectra of eutectic solvents consisting of HTFSA and MTFAA.

Table S1. (a) Ionic conductivities and (b) viscosities of eutectic solvents composed of $[HTFSA]_x[MTFAA]_{1-x}$ (x=0.3 0.4, 0.5, 0.6, 0.7).

Temperature / ^{o}C	Ionic conductivity / mS cm^{-1}					Viscosity / mPa s				
	x=0.3	0.4	0.5	0.6	0.7	x=0.3	0.4	0.5	0.6	0.7
20	1.50	1.13	0.82	0.70	0.45	19.9	26.9	31.3	34.8	34.1
25	1.78	1.42	0.99	0.79	0.52	15.8	23.2	25.6	26.7	26.1
30	2.13	1.70	1.19	0.96	0.70	12.7	18.5	19.0	20.9	20.4
35	2.50	2.00	1.38	1.09	0.89	10.5	15.0	15.4	16.7	16.2
40	2.87	2.31	1.63	1.27	1.07	8.65	12.2	12.5	13.6	13.1
45	3.28	2.65	1.90	1.48	1.23	7.30	10.2	10.5	11.2	10.7
50	3.71	3.01	2.10	1.61	1.39	6.19	8.59	8.78	9.40	8.92

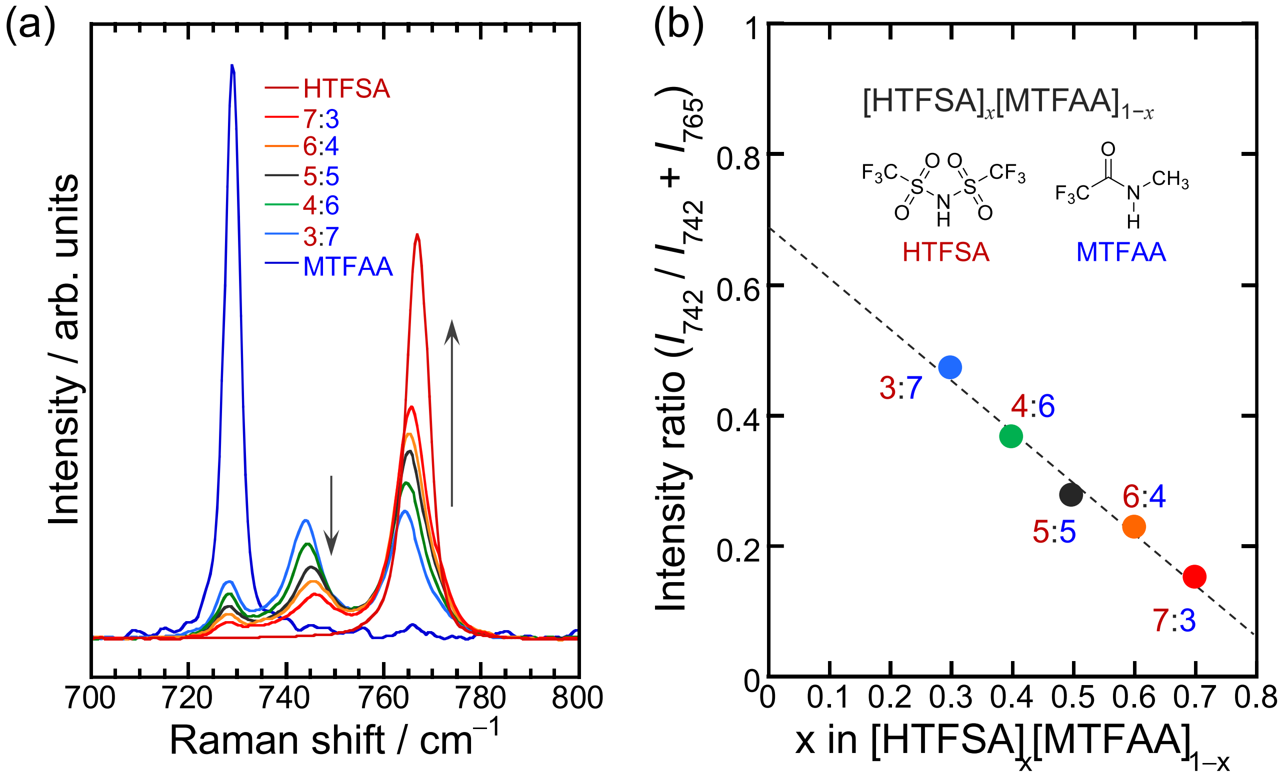

Figure S6. (a) Raman spectra of eutectic solvents composed of HTFSA and MTFAA. (b) Plots of $I_{742}/(I_{742}+I_{765})$ as a function of the concentration ratio of HTFSA (hydrogen-bond donor). The dissociation degree eutectic solvents was analyzed using a Raman spectroscopy system (LabRAM HR Evolution; HORIBA, Ltd.) using the 532-nm line of a diode-pumped solid-state laser at room temperature. The electrolytes were tightly sealed in a quartz cell in the glove box to prevent exposure to water vapor.

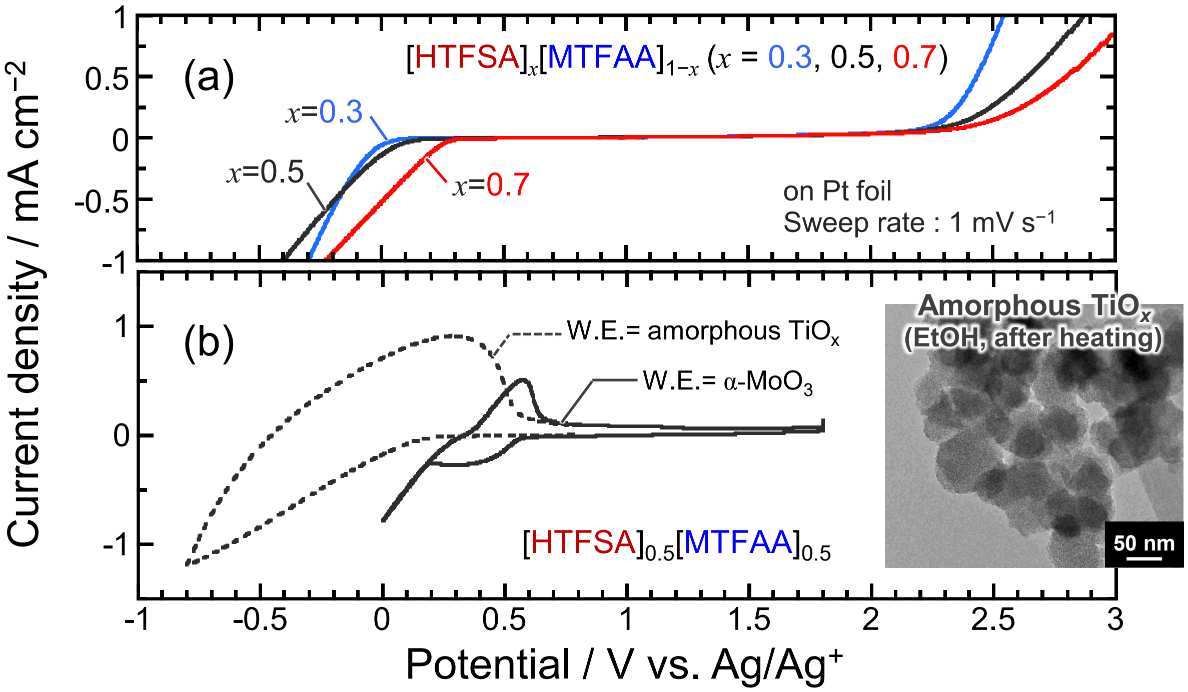

Figure S7. (a) Linear sweep voltammograms of Pt foils in eutectic solvents composed of HTFSA and MTFAA at a sweep rate of 1 mV s^{-1}. (b) Cyclic voltammograms of α-MoO$_3$ and amorphous TiO$_x$ electrodes in the equimolar eutectic solvent. Inset: TEM image of the amorphous TiO$_x$ powder. Electrochemical stability measurements on Pt electrodes revealed that all of the examined systems exhibited an electrochemical window exceeding 1.8 V, which is broader than the stability range of an acidic aqueous solution.

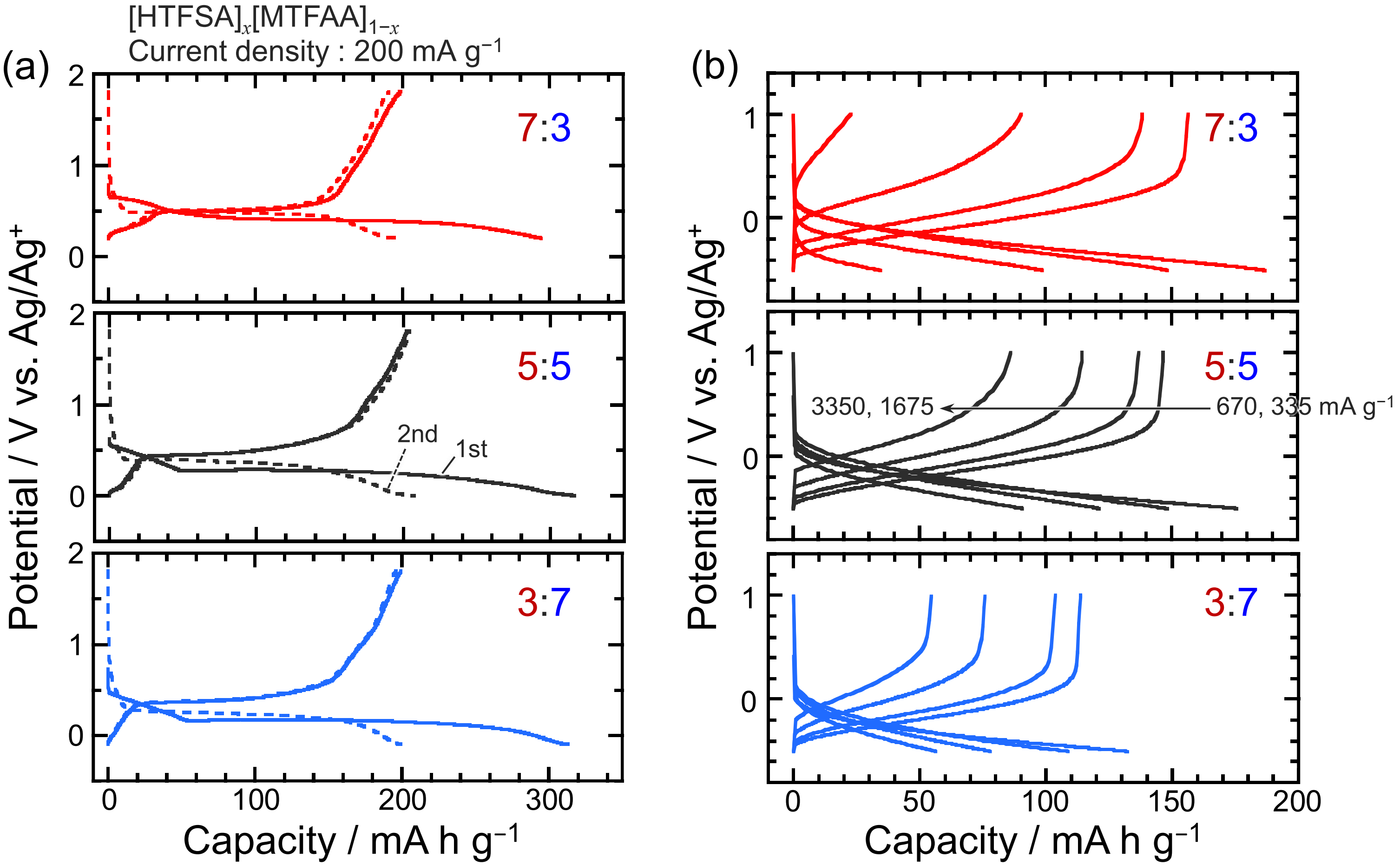

Figure S8. (a) Galvanostatic charge/discharge (protonation/deprotonation) profiles of α-MoO_3 electrodes in eutectic solvents at a current density of 200 mA g^{-1}. (b) Rapid charge−discharge properties of amorphous TiO_x electrode in eutectic solvents composed of HTFSA and MTFAA.