Electronic Supplementary Information

Electrochemical Protonation/Deprotonation of $TiNb_2O_7$ in Protic Ionic Liquids

Department of Materials Chemistry, Faculty of Engineering, Shinshu University

4-17-1 Wakasato, Nagano 380-8553, Japan

Masahiro Shimizu,* Takuya Kawai,
Tomonori Ichikawa, Susumu Arai

Dr. Masahiro Shimizu
Tel: +81-26-269-5627; Fax: +81-26-269-5432
E-mail: shimizu@shinshu-u.ac.jp

Table S1. Summary of ionic conductivities for $(AcOH)_x(Im)_{1-x}$, $(AcOH)_x(DBU)_{1-x}$, $(HTFSA)_x(Im)_{1-x}$, and $(HTFSA)_x(Im)_{1-x}$ (x=0.1, 0.2, 0.3, 0.4, 0.5).

Temperature / °C	Ionic conductivity / mS cm^{-1} (AcOH/Im)					Ionic conductivity / mS cm^{-1} (AcOH/DBU)				
	x=0.1	0.2	0.3	0.4	0.5	x=0.1	0.2	0.3	0.4	0.5
20	0.46	1.00	1.67	2.49	4.33	0.05	0.07	0.06	0.02	0.01
25	0.51	1.11	1.88	2.83	4.99	0.06	0.09	0.08	0.04	0.01
30	0.56	1.24	2.11	3.20	5.74	0.08	0.12	0.12	0.06	0.02
35	0.61	1.37	2.33	3.60	6.56	0.10	0.16	0.17	0.10	0.04
40	0.66	1.53	2.58	4.02	7.39	0.12	0.21	0.22	0.14	0.07
45	0.72	1.67	2.85	4.45	8.29	0.14	0.27	0.30	0.21	0.13
50	0.77	1.81	3.12	4.91	9.18	0.17	0.33	0.38	0.29	0.19
55	0.82	1.96	3.37	5.38	10.10	0.20	0.40	0.48	0.39	0.31
60	0.88	2.10	3.64	5.87	11.05	0.24	0.48	0.60	0.52	0.41
65	0.93	2.24	3.95	6.36	12.02	0.28	0.58	0.74	0.66	0.59
70	0.99	2.38	4.22	6.88	12.99	0.31	0.68	0.90	0.83	0.83
75	1.04	2.54	4.49	7.41	13.96	0.36	0.78	1.07	1.02	1.24

Temperature / °C	Ionic conductivity / mS cm^{-1} (HTFSA/Im)					Ionic conductivity / mS cm^{-1} (HTFSA/DBU)				
	x=0.1	0.2	0.3	0.4	0.5	x=0.1	0.2	0.3	0.4	0.5
20	15.04	10.17	7.09	3.83		0.76	0.63	0.29	0.35	
25	16.77	11.75	8.43	4.66		0.93	0.82	0.41	0.50	
30	18.58	13.74	9.93	5.62		1.15	1.07	0.58	0.69	1.15
35	20.47	15.72	11.42	6.77		1.39	1.35	0.80	0.93	1.49
40	22.39	17.82	13.19	7.98		1.65	1.67	1.06	1.22	1.88
45	24.35	20.01	15.07	9.29		1.94	2.03	1.37	1.56	2.34
50	26.39	22.34	17.06	10.73	6.56	2.26	2.44	1.74	1.95	2.85
55	28.42	24.70	19.16	12.16	7.59	2.59	2.88	2.16	2.40	3.43
60	30.48	27.10	21.41	13.79	8.71	2.94	3.36	2.63	2.89	4.09
65	32.59	29.92	23.76	15.54	9.92	3.31	3.89	3.17	3.45	4.80
70	34.99	32.56	26.10	17.40	11.21	3.71	4.47	3.77	4.07	5.60
75	37.09	35.38	28.50	19.34	12.60	4.13	5.07	4.43	4.73	6.46

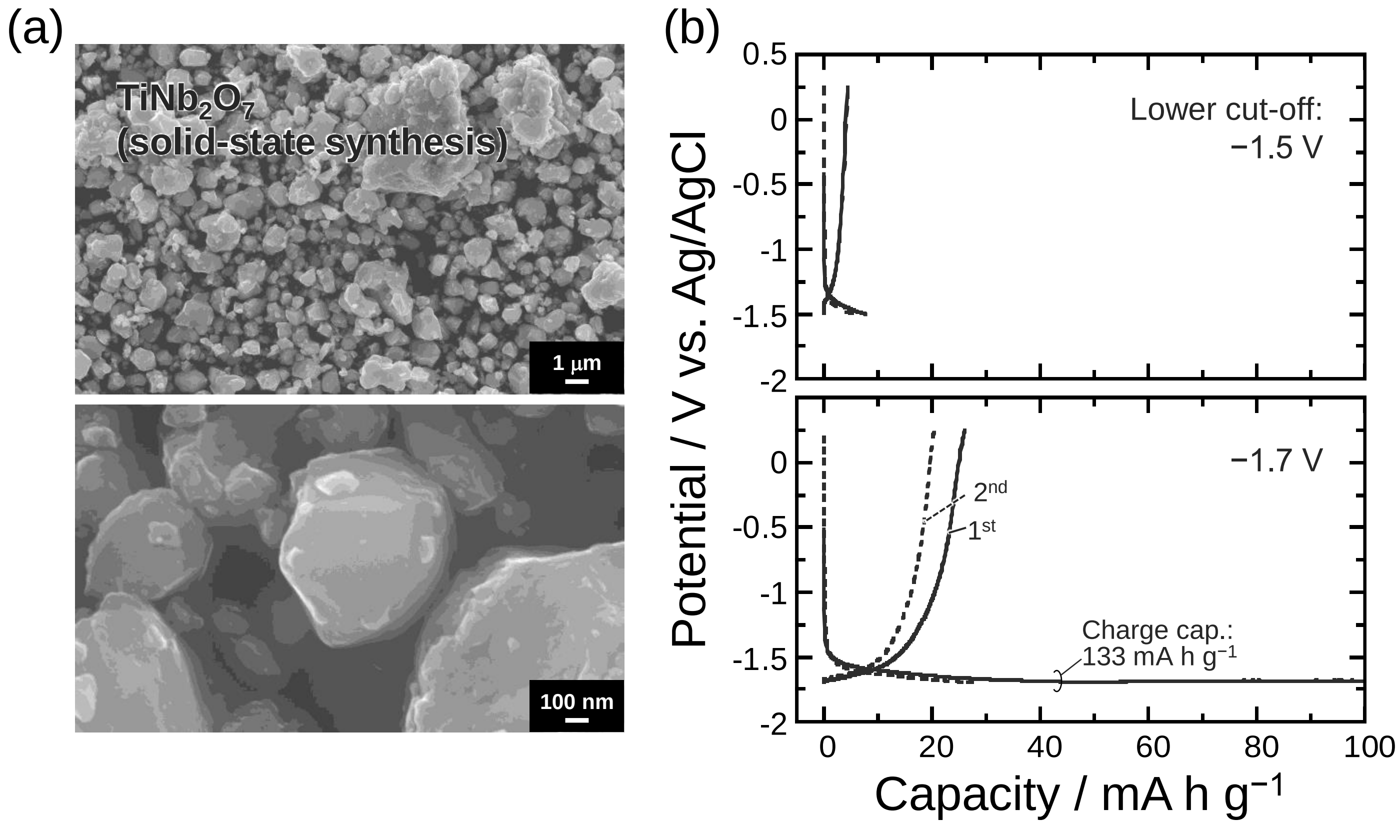

Figure S1. (a) SEM images of $TiNb_2O_7$ prepared by solid-state synthesis from anatase TiO_2 and Nb_2O_5. (b) Galvanostatic charge/discharge (protonation/deprotonation) curves of the $TiNb_2O_7$ in the electrolyte of $(HTFSA)_{0.4}(DBU)_{0.6}$. The lower cut-off potentials in the test are (upper) −1.5 and (lower) −1.7 V vs. Ag/AgCl, respectively. Regardless of the lower cut-off potential, the $TiNb_2O_7$ synthesized *via* the solid-state method (calcination) exhibited no electrochemical activity toward protonation.

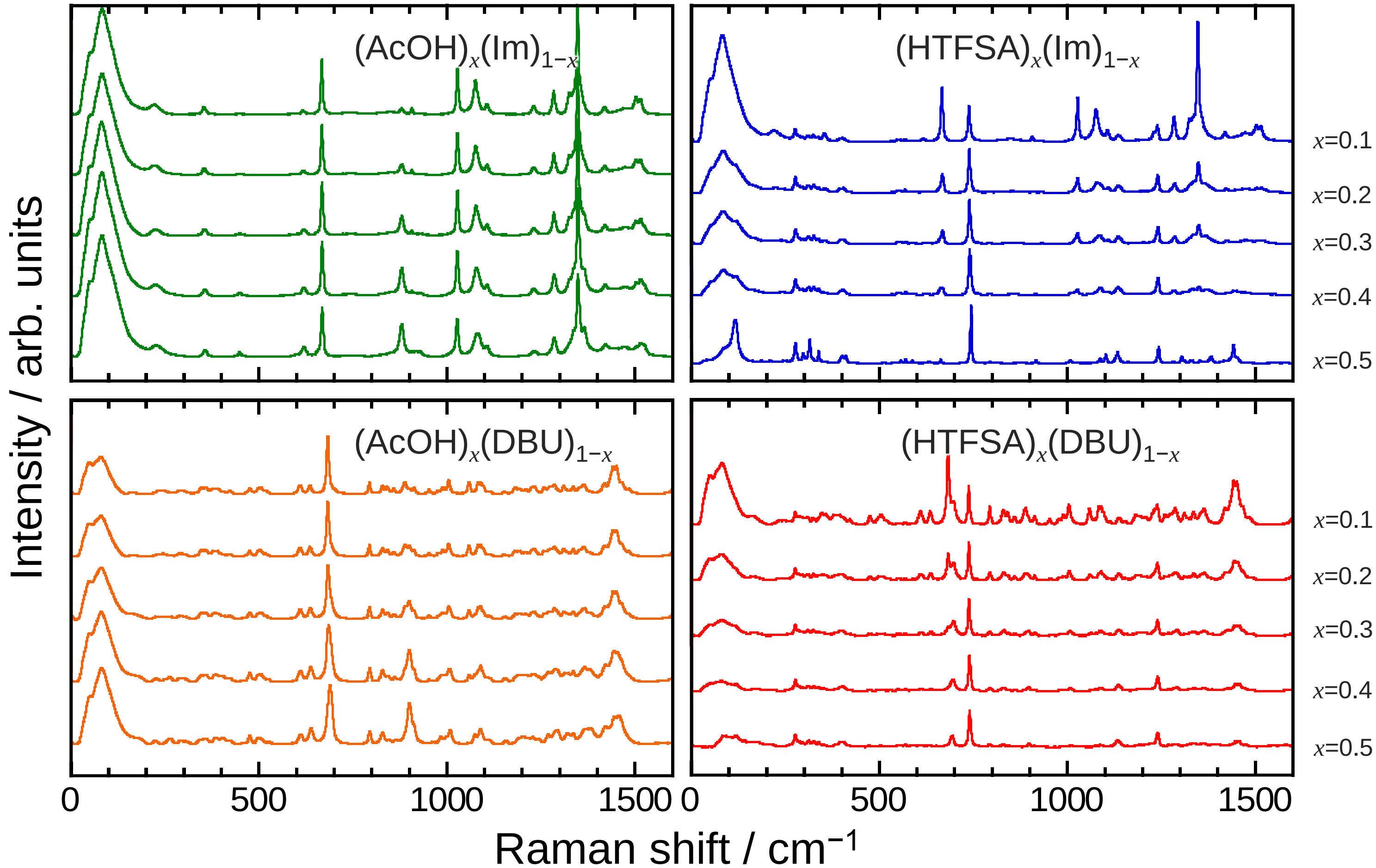

Figure S2. Raman spectra of $(AcOH)_x(Im)_{1-x}$, $(AcOH)_x(DBU)_{1-x}$, $(HTFSA)_x(Im)_{1-x}$, and $(HTFSA)_x(Im)_{1-x}$ (x=0.1, 0.2, 0.3, 0.4, 0.5). We tightly sealed the electrolyte solution in a quartz cell in an argon-filled glove box to prevent exposure to water vapor.

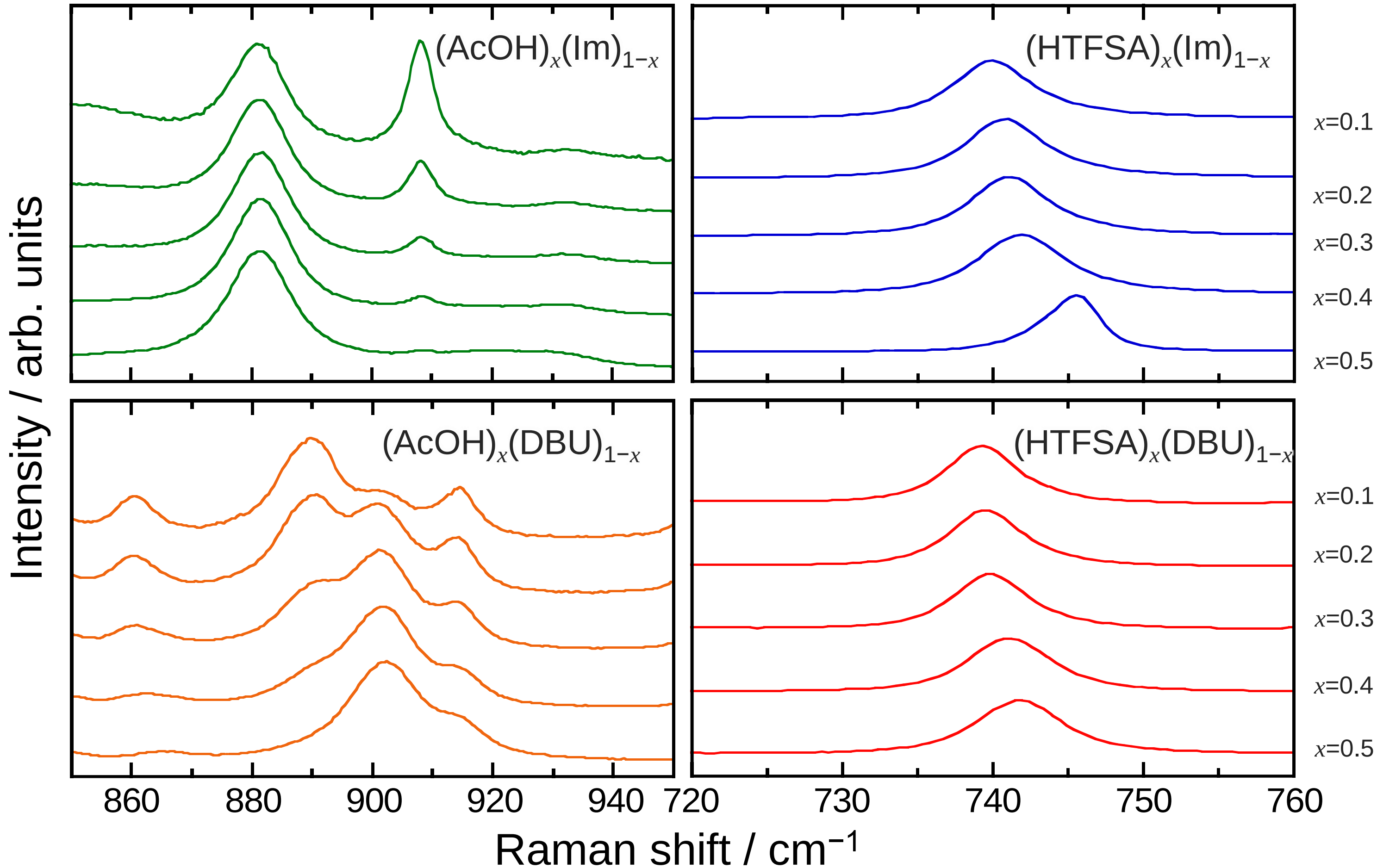

Figure S3. Enlarged views of Raman spectra. In the case of $(AcOH)_x(Im)_{1-x}$, no band shift is observed, indicating the absence of AcO^- regardless of the molar ratio of the Brønsted acid/base. In contrast, band shifts are recognized for $(AcOH)_x(DBU)_{1-x}$, suggesting that proton transfer to DBU occurs, leading to ionization into AcO^-.

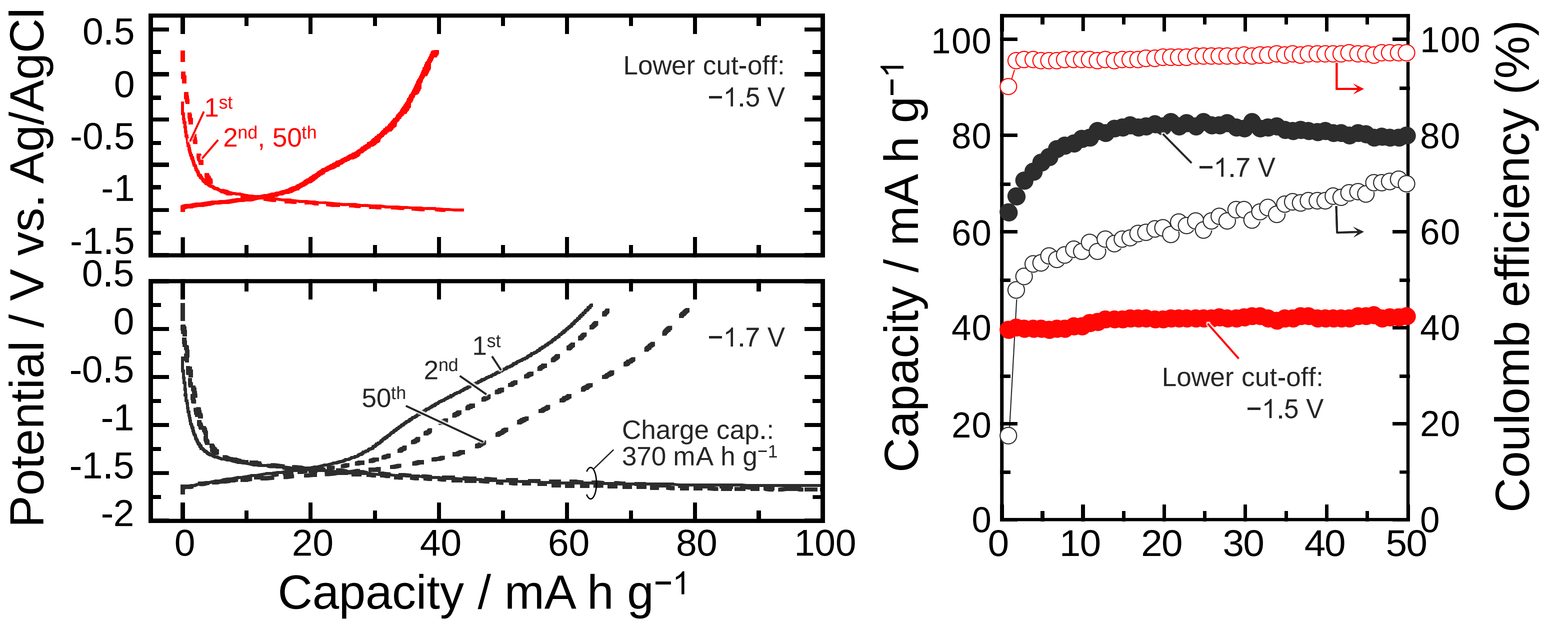

Figure S4. Galvanostatic charge/discharge (protonation/deprotonation) profiles of $TiNb_2O_7$ electrodes in $(HTFSA)_{0.4}(DBU)_{0.6}$. The lower cut-off potentials are (upper) −1.5 and (lower) −1.7 V, respectively. We attempted to store protons by setting the lower cut-off potential to the negative side of −1.7 V. The reversible capacity at the first cycle increased from 40 to 64 mA h g^{-1}, while the Coulomb efficiency decreased from 90 to 17%. The charge capacities at the cut-off potential in first charge cycle are 44 and 370 mA h g^{-1}.