Electronic Supplementary Information

Electrochemical Protonation/Deprotonation of TiNb₂O₇ 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

Temperature / °C	Ionic conductivity / mS cm ⁻¹ (AcOH/Im)					Ionic conductivity / mS cm ⁻¹ (AcOH/DBU)				
	<i>x</i> =0.1	0.2	0.3	0.4	0.5	<i>x</i> =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 / ºC	Lonia conductivity / mS cm ⁻¹ /UTESA/lm)					Ionia conductivity / mS cm ⁻¹ (HTESA/DDL)				
									000)	
00	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		() () ()			~ - ~	
30	18 58	10 71	0.00	5 00		0.93	0.82	0.41	0.50	
35	10.50	13.74	9.93	5.62		1.15	1.07	0.41	0.50	1.15
	20.47	13.74 15.72	9.93 11.42	5.62 6.77		0.93 1.15 1.39	0.82 1.07 1.35	0.41 0.58 0.80	0.50 0.69 0.93	1.15 1.49
40	20.47 22.39	13.74 15.72 17.82	9.93 11.42 13.19	5.62 6.77 7.98		0.93 1.15 1.39 1.65	0.82 1.07 1.35 1.67	0.41 0.58 0.80 1.06	0.50 0.69 0.93 1.22	1.15 1.49 1.88
40 45	20.47 22.39 24.35	13.74 15.72 17.82 20.01	9.93 11.42 13.19 15.07	5.62 6.77 7.98 9.29		0.93 1.15 1.39 1.65 1.94	0.82 1.07 1.35 1.67 2.03	0.41 0.58 0.80 1.06 1.37	0.50 0.69 0.93 1.22 1.56	1.15 1.49 1.88 2.34
40 45 50	20.47 22.39 24.35 26.39	13.74 15.72 17.82 20.01 22.34	9.93 11.42 13.19 15.07 17.06	5.62 6.77 7.98 9.29 10.73	6.56	1.15 1.39 1.65 1.94 2.26	0.82 1.07 1.35 1.67 2.03 2.44	0.41 0.58 0.80 1.06 1.37 1.74	0.50 0.69 0.93 1.22 1.56 1.95	1.15 1.49 1.88 2.34 2.85
40 45 50 55	20.47 22.39 24.35 26.39 28.42	13.74 15.72 17.82 20.01 22.34 24.70	9.93 11.42 13.19 15.07 17.06 19.16	5.62 6.77 7.98 9.29 10.73 12.16	6.56 7.59	0.93 1.15 1.39 1.65 1.94 2.26 2.59	0.82 1.07 1.35 1.67 2.03 2.44 2.88	0.41 0.58 0.80 1.06 1.37 1.74 2.16	0.50 0.69 0.93 1.22 1.56 1.95 2.40	1.15 1.49 1.88 2.34 2.85 3.43
40 45 50 55 60	20.47 22.39 24.35 26.39 28.42 30.48	13.74 15.72 17.82 20.01 22.34 24.70 27.10	9.93 11.42 13.19 15.07 17.06 19.16 21.41	5.62 6.77 7.98 9.29 10.73 12.16 13.79	6.56 7.59 8.71	0.93 1.15 1.39 1.65 1.94 2.26 2.59 2.94	0.82 1.07 1.35 1.67 2.03 2.44 2.88 3.36	0.41 0.58 0.80 1.06 1.37 1.74 2.16 2.63	0.50 0.69 0.93 1.22 1.56 1.95 2.40 2.89	1.15 1.49 1.88 2.34 2.85 3.43 4.09
40 45 50 55 60 65	20.47 22.39 24.35 26.39 28.42 30.48 32.59	13.74 15.72 17.82 20.01 22.34 24.70 27.10 29.92	9.93 11.42 13.19 15.07 17.06 19.16 21.41 23.76	5.62 6.77 7.98 9.29 10.73 12.16 13.79 15.54	6.56 7.59 8.71 9.92	0.93 1.15 1.39 1.65 1.94 2.26 2.59 2.94 3.31	0.82 1.07 1.35 1.67 2.03 2.44 2.88 3.36 3.89	0.41 0.58 0.80 1.06 1.37 1.74 2.16 2.63 3.17	0.50 0.69 0.93 1.22 1.56 1.95 2.40 2.89 3.45	1.15 1.49 1.88 2.34 2.85 3.43 4.09 4.80
40 45 50 55 60 65 70	10.30 20.47 22.39 24.35 26.39 28.42 30.48 32.59 34.99	13.74 15.72 20.01 22.34 24.70 27.10 29.92 32.56	9.93 11.42 13.19 15.07 17.06 19.16 21.41 23.76 26.10	5.62 6.77 7.98 9.29 10.73 12.16 13.79 15.54 17.40	6.56 7.59 8.71 9.92 11.21	0.93 1.15 1.39 1.65 1.94 2.26 2.59 2.94 3.31 3.71	0.82 1.07 1.35 1.67 2.03 2.44 2.88 3.36 3.89 4.47	0.41 0.58 0.80 1.06 1.37 1.74 2.16 2.63 3.17 3.77	0.50 0.69 0.93 1.22 1.56 1.95 2.40 2.89 3.45 4.07	1.15 1.49 1.88 2.34 2.85 3.43 4.09 4.80 5.60

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).

1



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.