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# Electrochemical protonation/deprotonation of TiNb<sub>2</sub>O<sub>7</sub> in protic ionic liquids†

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In recent years, there has been growing interest in rechargeable batteries utilizing protons or hydronium ions as charge carriers, driven by the rapid ionic conduction enabled by the proton-specific Grötthuss mechanism. However, the use of acidic aqueous electrolytes introduces side reactions, such as irreversible hydrogen evolution and the dissolution of active materials into the electrolyte, which are influenced by the reaction potential of the active materials. These challenges complicate the identification and development of active materials. While some combinations of Brønsted acids and bases may potentially compromise the advantages of the Grötthuss mechanism, this study successfully demonstrated the electrochemical protonation of TiNb<sub>2</sub>O<sub>7</sub> using protic ionic liquids as electrolytes. Acetic acid (AcOH) and 1,1,1-trifluoro-*N*-(trifluoromethyl)sulfonyl)methanesulfonamide (HTFSA) were employed as Brønsted acids, while 1-methylimidazole (Im) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) were utilized as Brønsted bases. Irreversible hydrogen evolution was dominant in an aqueous buffer solution consisting of citric acid and trisodium citrate. The AcOH/DBU system showed negligible charge/discharge capacities within the cut-off potential range of −1.5 to +0.25 V. In contrast, AcOH/Im and HTFSA/Im systems exhibited reversible capacities of 61 and 55 mA h g<sup>−1</sup>, respectively, during the first cycle. However, their Coulomb efficiencies were significantly low below 20%. Meanwhile, HTFSA/DBU, despite a lower reversible capacity of 40 mA h g<sup>−1</sup> (corresponding to H<sub>0.5</sub>TiNb<sub>2</sub>O<sub>7</sub>), achieved a Coulomb efficiency exceeding 90%. Notably, it maintained an average Coulomb efficiency of 96% over 50 cycles without any capacity degradation.

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## Introduction

With the growing significance of storage batteries, recent years have seen active research on not only divalent (Zn<sup>2+</sup>, Mg<sup>2+</sup>)<sup>1–7</sup> and trivalent (Al<sup>3+</sup>)<sup>8–10</sup> metal cations but also anions, such as fluoride ions (F<sup>−</sup>),<sup>11–13</sup> as carrier ions. On the other hand, there are not enough studies on proton/hydronium ions as charge carriers. If the fast ionic conduction specific to proton based on the Grötthuss mechanism can be utilized, rapid charge–discharge performance can be offered. However, in the case of acidic aqueous solutions, which are typical proton conductors, irreversible hydrogen or oxygen evolution occurs dominantly depending on reaction potentials of active materials, and there is a concern that proton-insertion/deinsertion into/from host materials do not proceed. From this point of view, buffer solutions<sup>14–18</sup> are used and molecular crowding electrolytes<sup>19,20</sup> are being actively considered. The electrolytes also contribute to suppressing the dissolution of active materials into acidic

aqueous solutions. Veronica *et al.* succeeded in suppressing the dissolution of Ti<sup>3+</sup> from H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> and improving the reversible capacity by using phosphate buffer as the electrolyte.<sup>21</sup> The suppression of Ti<sup>3+</sup> dissolution (generation of surface pitting) associated proton adsorption is also evident from SEM observation after electrochemical tests. On the other hand, as an attempt to adjust the reaction potential based on the crystal structure, we have focused on rutile TiO<sub>2</sub>.<sup>22</sup> The rutile TiO<sub>2</sub> synthesized by the hydrothermal method allows electrochemical protonation at a higher potential compared to anatase TiO<sub>2</sub>, thereby mitigating irreversible hydrogen evolution and improving cycle performance. As outlined above, the complexity of developing active materials for proton rechargeable batteries arises from side reactions such as the dissolution of active materials and irreversible hydrogen evolution. These issues make it inherently challenging to determine whether the synthesized samples can electrochemically accommodate protons.

Since these undesirable side reactions predominantly occur in electrolytes using water as the solvent, this study focused on proton conduction in non-aqueous solvents, specifically exploring protic ionic liquids<sup>23,24</sup> as electrolyte candidates. Protic ionic liquids are formed through proton transfer from Brønsted acid to Brønsted base.<sup>25</sup> Angel *et al.* classified them into good and poor categories based on their ΔpK<sub>a</sub>, with a threshold of

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10.<sup>26,27</sup> Good ionic liquids exhibit high boiling points and ionic conductivities comparable to those of aprotic ionic liquids, whereas poor ionic liquids are characterized by lower boiling points and reduced ionic conductivities due to incomplete proton transfer. Protic ionic liquids have been extensively studied for their potential applications in electrochemical devices, serving as proton conductors in a new class of fuel cells<sup>28–33</sup> and as alternatives to alkaline aqueous electrolytes in nickel-metal hydride batteries.<sup>34</sup> N. Chaabene and J. Monnier were the first to demonstrate the phase transition of AB<sub>5</sub>-type alloys (A: rare earth, B: 3d late transition metal) into the hydride phase using the protic ionic liquid consisting of pyrrolidine (Pyr) and acetic acid (AcOH). Recently, a pseudo-protic ionic liquid exhibiting proton conductivity facilitated by a Grötthuss-like mechanism, as proposed by Umebayashi *et al.*,<sup>35–38</sup> has been reported to enhance the electrochemical protonation of VO<sub>2</sub>.<sup>39</sup> Unlike the aqueous electrolyte (12 M H<sub>3</sub>PO<sub>4</sub> aq.), the pseudo-protonic ionic liquid (AcOH/C<sub>1</sub>Im = 8 : 1) demonstrated remarkable cycling stability, retaining 75% of reversible capacity even after 200 cycles.

In this study, we report electrochemical protonation/deprotonation of TiNb<sub>2</sub>O<sub>7</sub> in protic ionic liquids. Wadsley-Roth phase TiNb<sub>2</sub>O<sub>7</sub> with a crystallographic shear structure is a promising candidate for energy storage of Li ions.<sup>40–43</sup> We hypothesized that TiNb<sub>2</sub>O<sub>7</sub> could accommodate protons inside the structure and subsequently investigated its electrochemical behavior. To suppress undesirable side reactions, protic ionic liquids were employed as electrolytes. This study examines the correlation between the  $\Delta pK_a$  of the Brønsted acid/base, the activation energy, the protonation potential, and the reversible capacity.

## Experimental section

### Preparation and characterization of protic ionic liquids as electrolytes

Protic ionic liquids were prepared by mixing of the following combinations of Brønsted acid/base (Fig. 1a) in an Ar-filled glovebox: acetic acid (AcOH; FUJIFILM Wako Pure Chemical Corporation, 99%), 1,1,1-trifluoro-*N*-((trifluoromethyl)sulfonyl)methanesulfonamide (HTFSA; Kanto Chemical Co., Inc., 98%), 1-methylimidazole (Im; Sigma-Aldrich, 99%), and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; Sigma-Aldrich, 99%). Thermogravimetric analysis was conducted using a TG-DTA instrument (Thermo Plus TG8120, Rigaku) from room temperature to 500 °C under flowing N<sub>2</sub> at a rate of 200 mL min<sup>-1</sup>. Differential scanning calorimetry (DSC) was performed with a calorimeter (Thermo Plus EVO2, Rigaku) using a sealed aluminum ampoule at a cooling/heating rate of 10 °C min<sup>-1</sup>. Ionic conductivity was evaluated by an electrochemical impedance analyzer (SP-300; Bio-Logic Science Instruments) using an airtight four-probe cell.

### Synthesis of TiNb<sub>2</sub>O<sub>7</sub> and electrochemical tests

TiNb<sub>2</sub>O<sub>7</sub> was synthesized by the hydrothermal methods, as detailed below.<sup>42</sup> Niobium pentachloride (NbCl<sub>5</sub>; Sigma-Aldrich, 99%) was dissolved in ethanol and mixed with titanium (iv) oxysulfate

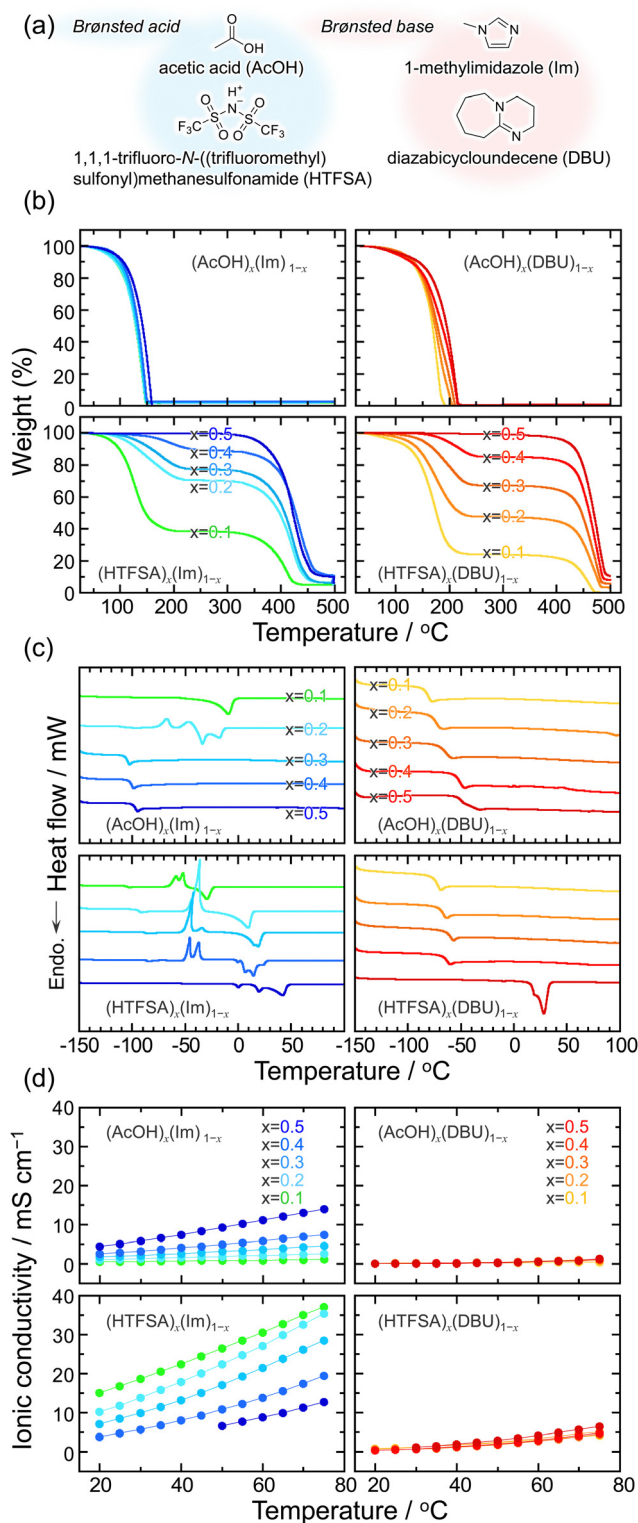


Fig. 1 (a) Chemical structures of Brønsted acid and base used in this study. (b) Thermogravimetric traces, (c) differential scanning calorimetry curves, and (d) ionic conductivities of (AcOH)<sub>x</sub>(Im)<sub>1-x</sub>, (HTFSA)<sub>x</sub>(Im)<sub>1-x</sub>, (AcOH)<sub>x</sub>(DBU)<sub>1-x</sub>, and (HTFSA)<sub>x</sub>(DBU)<sub>1-x</sub> ( $x = 0.1, 0.2, 0.3, 0.4, 0.5$ ).

solution (15 wt% TiOSO<sub>4</sub> in dilute sulfuric acid; Sigma-Aldrich, 99.99%) in a stoichiometric ratio. Ammonia solution (28–30%



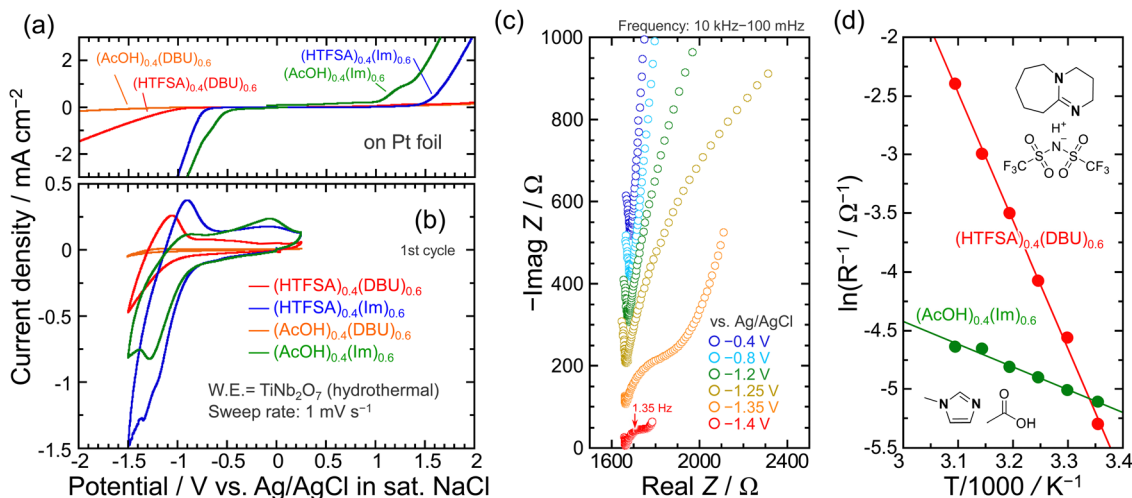


Fig. 3 (a) Linear sweep voltammograms of a Pt foil and (b) cyclic voltammograms of  $\text{TiNb}_2\text{O}_7$  (hydrothermal) electrodes in protic ionic liquids (electrolytes) at a sweep rate of  $1 \text{ mV s}^{-1}$ . (c) Nyquist plots of the  $\text{TiNb}_2\text{O}_7$  electrodes. (d) Temperature dependence of the inverse of charge transfer resistances ( $1/R_{\text{ct}}$ ). In the Nyquist plots, each spectrum is shifted by  $100 \Omega$  toward  $-Z$ -axis for clarity. Activation energies were estimated from the slopes.

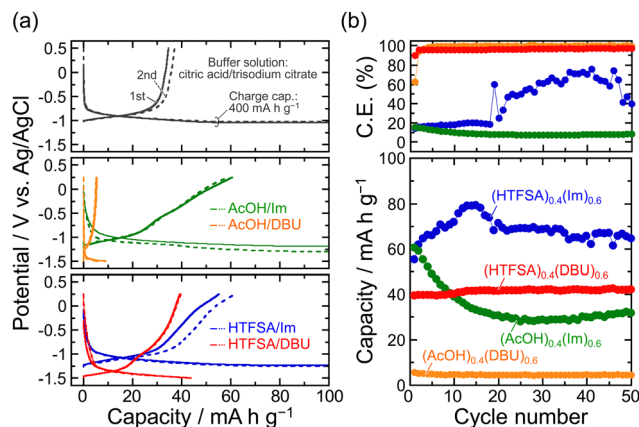
because the stability of the protonated cation is higher in DBU than in Im, and protons are less likely to be transferred to  $\text{TiNb}_2\text{O}_7$ . When HTFSA was used as the Brønsted acid, the reversibility was improved from 33% to 69% by using DBU as Brønsted base compared to Im. However, the reduction/oxidation responses associated with proton-insertion/deinsertion were decreased, and the onset potential of protonation was also shifted to the negative side. These findings highlight that the combination of Brønsted acids/bases is a highly important factor in regulating reaction potentials. As an overall trend, as the cathodic limit on the electrolytes becomes more negative, the protonation potential for the  $\text{TiNb}_2\text{O}_7$  also shifted in a more negative direction. Fig. 3c displays Nyquist plots of the  $\text{TiNb}_2\text{O}_7$  electrodes in the electrolyte of HTFSA/DBU. One distinct semicircle was recognized below  $-1.35 \text{ V}$ , and the dimension of the semicircle became smaller at  $-1.40 \text{ V}$ , which is assigned to charge transfer resistance ( $R_{\text{ct}}$ ) involved with protonation. The lack of semicircle due to interfacial resistance, as observed in a graphite electrode used in Li-ion batteries, suggests that the solid electrolyte interphase (SEI) is either not present or has negligible resistance in the HTFSA/DBU system. The temperature dependence of  $R_{\text{ct}}$  was measured from 298 to 323 K to examine the kinetics of protonation. The inverse of the charge transfer resistances as a function of reciprocal temperature obeyed the following Arrhenius equation (Fig. 3d):<sup>47</sup>

$$\frac{1}{R_{\text{ct}}} = A \exp\left(-\frac{E_{\text{a}}}{RT}\right) \quad (1)$$

where the symbols  $A$ ,  $E_{\text{a}}$ ,  $R$  and  $T$  denote the frequency factor, activation energy, gas constant, and absolute temperature, respectively. The impedance measurements for the evaluation of activation energy were conducted at potentials of  $-1.1 \text{ V}$  and  $-1.4 \text{ V}$  for Brønsted acids AcOH and HTFSA, respectively. The  $E_{\text{a}}$  for the protonation of  $\text{TiNb}_2\text{O}_7$  in  $(\text{HTFSA})_{0.4}(\text{DBU})_{0.6}$  calculated from the slope of the Arrhenius plot was  $90 \text{ kJ mol}^{-1}$ .

The  $E_{\text{a}}$  in the electrolyte systems for  $(\text{AcOH})_{0.4}(\text{Im})_{0.6}$ ,  $(\text{AcOH})_{0.4}(\text{DBU})_{0.6}$ , and  $(\text{HTFSA})_{0.4}(\text{Im})_{0.6}$  are 16, 31, and  $40 \text{ kJ mol}^{-1}$ , respectively, and these values became large according to the  $\Delta pK_{\text{a}}$ . In the case of large  $\Delta pK_{\text{a}}$ , the protonated Brønsted base remains stable, making proton transfer to an active material unlikely. This is probably the reason why the activation energy increased with  $\Delta pK_{\text{a}}$ .

Fig. 4a exhibits galvanostatic charge–discharge profiles of the  $\text{TiNb}_2\text{O}_7$  electrodes at a current density of  $387 \text{ mA g}^{-1}$  in the potential range between  $-1.5$  and  $+0.25 \text{ V vs. Ag/AgCl}$ . At this stage, we have not yet determined the theoretical capacity of  $\text{TiNb}_2\text{O}_7$ . The current density of  $387 \text{ mA g}^{-1}$  was chosen based on this theoretical capacity when  $\text{TiNb}_2\text{O}_7$  is used as the negative electrode in Li-ion batteries.<sup>40–43</sup> When the aqueous-based buffer solution consisting of  $1 \text{ M}$  citric acid and  $1 \text{ M}$  trisodium citrate was applied, the potential did not reach the lower cut-off limit and remained at *ca.*  $1 \text{ V}$ . After the charge capacity reached  $400 \text{ mA h g}^{-1}$ , the switch to discharge process resulted in a reversible capacity of  $35 \text{ mA h g}^{-1}$ . Most of the charge capacity is attributed to the consumption for hydrogen evolution as a side reaction. As inferred from the results of the CV measurements, the AcOH/DBU system provided little charge/discharge capacity. The stagnation of potential was also observed in AcOH/Im and HTFSA/Im and should be due to the decomposition of electrolytes. Considering the activation energy for protonation of  $\text{TiNb}_2\text{O}_7$  in the AcOH/DBU system, it should exhibit a charge–discharge capacity comparable to that of HTFSA/Im. However, it shows almost no electrochemical activity. One possible explanation is the formation of a surface layer on  $\text{TiNb}_2\text{O}_7$  due to the decomposition of the electrolyte. However, at this stage, we have not yet identified the underlying cause of the uniquely inactive charge–discharge behavior of AcOH/DBU. Nevertheless, AcOH/Im and HTFSA/Im showed  $61$  and  $55 \text{ mA h g}^{-1}$ , respectively at the first cycle (Fig. 4b). After 50 cycles, the deprotonation capacities are  $32$  and  $65 \text{ mA h g}^{-1}$



**Fig. 4** (a) Galvanostatic charge/discharge (protonation/deprotonation) curves and (b) dependence of reversible capacities and coulombic efficiencies on cycle numbers for  $\text{TiNb}_2\text{O}_7$  (hydrothermal) electrodes at a current density of  $387 \text{ mA g}^{-1}$  in the cut-off potential between  $-1.5$  and  $+0.25 \text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  in sat.  $\text{NaCl}$ . For comparison, the electrochemical behavior in the aqueous buffer solution of  $1 \text{ M}$  citric acid and  $1 \text{ M}$  trisodium citrate is also shown.

for  $\text{AcOH}/\text{Im}$  and  $\text{HTFSA}/\text{Im}$ , respectively. In both systems, the Coulomb efficiency was notably low, indicating the accumulation of electrolyte-decomposition products on the surface of  $\text{TiNb}_2\text{O}_7$ . The differences in the capacity retention observed after 50 cycles are presumed to originate from the composition of the surface layers; however, this aspect was not further examined in this study. On the other hand, at the first cycle,  $\text{HTFSA}/\text{DBU}$  yielded a relatively smaller reversible capacity of  $40 \text{ mA h g}^{-1}$  compared to the two mentioned above but demonstrated a higher Coulomb efficiency of 90%. Furthermore,  $\text{HTFSA}/\text{DBU}$  exhibited stable cycling performance up to 50 cycles without any capacity loss, maintaining an average Coulomb efficiency of 96%. Based on the obtained reversible capacity, the stored protons are 0.5 moles per  $\text{TiNb}_2\text{O}_7$ . We attempted to store protons by setting the lower cut-off potential to the negative side of  $-1.7 \text{ V}$  (Fig. S4, ESI<sup>†</sup>). The reversible capacity at the first cycle increased to  $64 \text{ mA h g}^{-1}$ , while the Coulomb efficiency decreased to 17%. For the electrolytes except  $\text{AcOH}/\text{DBU}$ , the protonation potential shifted to the negative side as the  $\Delta pK_a$  is larger. The combination of Brønsted acid and Brønsted base, defined by their  $\Delta pK_a$ , serves as a key factor in tuning the protonation potential of the active material. The obtained results should greatly contribute to the design of electrolytes for proton rechargeable batteries. Some combinations of Brønsted acid/base lose the advantage of fast proton conduction by Gröthuss mechanism, the use of protic ionic liquids allows proton storage in active materials that could not function in aqueous electrolytes due to dominant hydrogen evolution.

## Conclusions

This study demonstrated the electrochemical protonation/deprotonation of  $\text{TiNb}_2\text{O}_7$  in protic ionic liquids. The relationship between  $\Delta pK_a$  and the activation energy for protonation of  $\text{TiNb}_2\text{O}_7$  was examined using four different combinations for

Brønsted acid/base. AC impedance measurements revealed an activation energy of  $16 \text{ kJ mol}^{-1}$  in the  $\text{AcOH}/\text{Im}$  system, which exhibited the smallest  $\Delta pK_a$  (2.4), whereas the activation energy increased to  $90 \text{ kJ mol}^{-1}$  in the  $\text{HTFSA}/\text{DBU}$  system (23.4). These results suggest that a larger  $\Delta pK_a$  stabilizes the protonated Brønsted base, thereby hindering proton transfer to the active material. The  $\text{HTFSA}/\text{DBU}$  system achieved a high Coulombic efficiency of 90% and a deprotonation capacity of  $40 \text{ mA h g}^{-1}$  during the first cycle. In contrast, the aqueous-based buffer solution composed of  $1 \text{ M}$  citric acid and  $1 \text{ M}$  trisodium citrate showed dominant irreversible hydrogen evolution during charging. Moreover, the  $\text{HTFSA}/\text{DBU}$  system maintained an average Coulombic efficiency exceeding 96%, with no observable capacity loss over 50 cycles.

## Data availability

The data that support the findings of this study are openly available in SOAR-RD at <https://soar-rd.shinshu-u.ac.jp/search/detail.html?systemId=gCkVbUkh&lang=ja&st=researcher>, ref. 1.

## Conflicts of interest

The authors declare no conflict of interest.

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