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Direct synthesis of barium titanium oxyhydride for use as a hydrogen permeable electrode

Tasuku Uchimura,[ab] Fumitaka Takeiri,[abc] Kei Okamoto,[ab] Takashi Saito[de], Takashi Kamiyama[de], and Genki Kobayashi*[ab]

Barium titanium oxyhydride BaTiO$_{3-x}$H$_x$ is a promising functional material that exhibits H$^-$/e$^-$ mixed conduction. Here we firstly report a direct synthesis of BaTiO$_{3-x}$H$_x$ by a mechanochemical method. The prepared polycrystalline sample was able to work as hydrogen permeable electrodes.

Oxyhydrides, wherein hydride ions (H$^-$) stabilized in oxide frameworks, have recently become a new topic of materials science. Representative examples are the first case of transition-metal oxyhydride LaSrCoO$_3$H$_{0.7}$,[1] unusual pnictide superconductor LaFeAsO$_{1-x}$H$_x$,[2,3] and pure H$^-$ conductor La$_{2-x-y}$Sr$_{x+y}$LiH$_{1-x+y}$O$_{3-y}$.[4] In particular, perovskite-type BaTiO$_{3-x}$H$_x$ is an important piece that exhibits metallic electronic conduction,[5] H$^-$ diffusion,[6] and high anion exchangeability.[7,8] Such properties afford valuable chemical functions represented by catalytic activity for NH$_3$ synthesis and CO$_2$ reduction.[9,10] Furthermore, the H$^-$/e$^-$ mixed conducting nature should be promising for the use of electrodes capable of hydrogen transmission in electrochemical devices for chemical/energy conversion.

The polycrystalline titanium-based oxyhydrides, ATiO$_{3-x}$H$_x$ (A = Ba, Sr, Ca, Eu), are previously prepared by solid-state topochemical reactions, in which a mixture of the corresponding oxide precursors ATiO$_3$ and calcium hydride (CaH$_2$) are heated under vacuum.[5,11,12] The hydrogen concentration x can be varied depending on the reaction conditions including sintering temperature and period. However, preparation of a single phase ATiO$_{3-x}$H$_x$ with

controlled x value, which is a critical matter for the above-mentioned chemical functions, is still a challenge. It is because that not only thermodynamic but also kinetic factors, such as particle size of precursor oxides[11] and anion diffusivity in the lattice,[13,14] should be considered. Moreover, the washing process to remove the residual CaH$_2$ and byproduct CaO are inevitable in the topochemical reaction. Such a complex and multi-step process might result in less reproducibility of functional performance and be unsuitable for future applicable use.

Mechanochemical synthesis through dry milling without heating can use mechanical energy for chemical reactions, and thus is used for preparing nanoparticles[15], hydrogen storage materials,[16,17] and metastable phases such as glass-ceramics.[18,19] Herein, we show a direct preparation of BaTiO$_{3-x}$H$_x$ by only 90 minutes of ball-milling, which is the first report of mechanochemical synthesis of oxyhydrides.

Commercial reagents of BaH$_2$, BaO, TiO$_2$, and TiH$_2$ were used as starting materials. Those reagents were mixed in an Ar-filled glovebox using an agate mortar, following equation (1) with the nominal composition of x_{nom} = 0.1, 0.25, 0.5, 1.

$$x\text{BaH}_2 + (1-x)\text{BaO} + \text{TiO}_2 \rightarrow \text{BaTiO}_{3-x}\text{H}_x + 0.5x\text{H}_2 \quad (1)$$

For the nominal composition of x_{nom} = 2, TiH$_2$ was used instead of BaH$_2$ and TiO$_2$ as following the equation (2).

$$\text{BaO} + \text{TiH}_2 \rightarrow \text{BaTiOH}_2 \quad (2)$$

The mixtures of 1 g were sealed in a ZrO$_2$ container together with ZrO$_2$ balls. Mechanical activation was performed at 600, 800, and 1100 rpm for 90 min without intervals using high-energy ball milling equipment (Emax, Retsch).

Figure 1 shows laboratory X-ray diffraction patterns of x_{nom} = 0.5 samples with various milling conditions. For the sample after hand-milling, only profiles derived from the raw materials of BaO, BaH$_2$, and TiO$_2$ were detected. After ball-milling at 600 rpm, the peaks were broadened, and new peaks appeared at 800 rpm with a relatively high background. In contrast, at 1100 rpm, clear peaks indexable with a cubic unit cell of a = 4.0252 Å

were observed without any other peaks, indicating a formation of simple perovskite in a single phase. The powder color changed from white to black, suggesting the presence of reduced Ti^{3+} from Ti^{4+}, and the obtained cubic phase was stable in air. Such features are the same with those for previous reported $BaTiO_{3-x}H_x$ prepared by topochemical reaction using CaH_2.[5] Thermal desorption spectroscopy (TDS) measurement was performed to estimate hydrogen content in the obtained sample. Figure 2 (inset) shows the spectrum corresponding to desorbed H_2 molecule (m/z = 2) upon heating. The H_2 desorption gradually occurred above 200 ºC and sharply increased around 480 ºC. The hydrogen content x in $BaTiO_{3-x}H_x$ estimated by integrating the total peak area was $x = 0.427$ in $BaTiO_{3-x}H_x$. Scanning electron microscopy (SEM) image of the obtained powder indicates a broad particle size distribution of 0.1-2 μm (Fig. S1), possibly inducing the H_2 desorption at a wide range of temperatures.
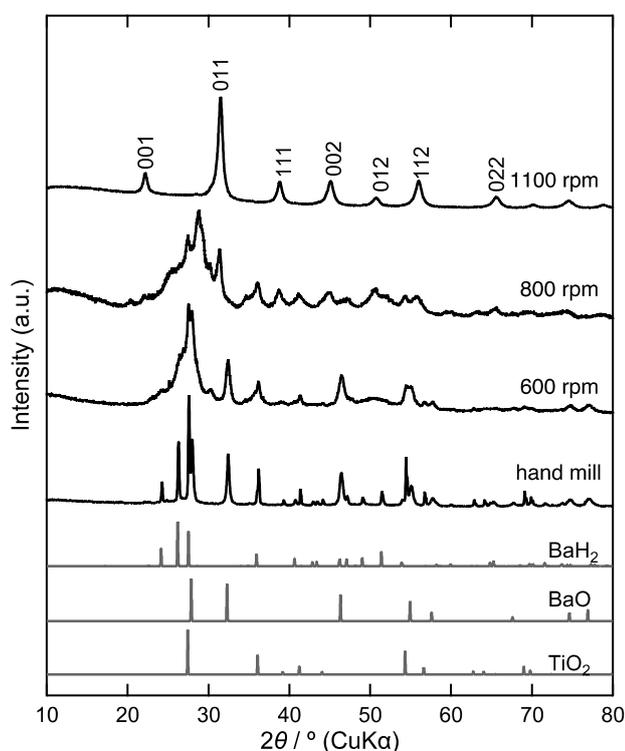

Fig. 1 XRD patterns of the products of $BaTiO_{3-x}H_x$ (x_{nom} = 0.5) at hand mill, 600 rpm, 800 rpm, and 1100 rpm. Selected *hkl* reflections with relatively intense peaks are indexed.

The crystal structure and composition of the x_{nom} = 0.5 product were estimated by Rietveld refinement. Powder synchrotron X-ray and neutron diffraction (SXRD and ND) data collected at room temperature were refined using RIETAN-FP[20] and Z-Rietveld program,[21] respectively. ND refinement assuming a cubic perovskite $BaTiO_{3-x}H_x$ converged well with H and O occupancies of g(H) = 0.1413(18) and g(O) = 0.8588(12), yielding the composition of $BaTiO_{2.58}H_{0.42}$ with no significant anion vacancies. This result is consistent with both the SXRD refinement yielding a sizable amount of anion vacancy of $\delta \approx$ 0.42 for $BaTiO_{3-\delta}$ (Fig. S2 and Table S2) and hydrogen content estimated by TDS. A slight decrease of hydrogen concentration from the nominal composition (x_{nom} = 0.5) could be derived

from oxygen contamination in the raw material BaH_2 or/and during milling using a ZrO_2 pot and balls. From these results, we conclude that barium titanium oxyhydride $BaTiO_{3-x}H_x$ was successfully synthesized by mechanochemical reaction without significant hydrogen loss.
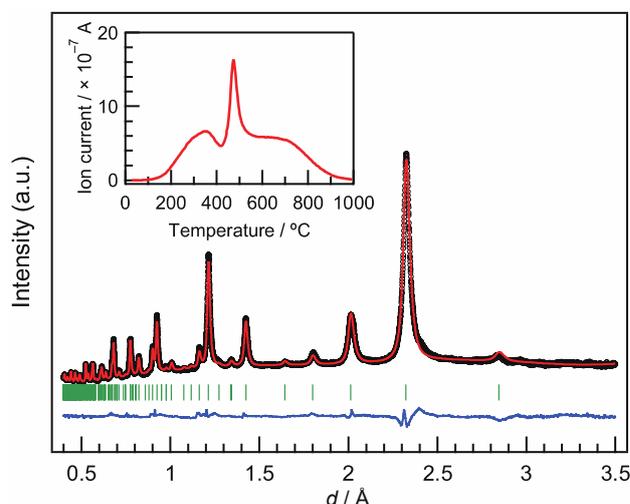

Fig. 2 Rietveld refinement profile for ND data of x_{nom} = 0.5 product. Final observed, calculated, and residual differences are shown in black circles, red solid line, and blue solid line, respectively. Green vertical marks indicate the positions of Bragg reflections. The inset shows TDS curve corresponding to H_2 desorption upon heating.

Laboratory XRD patterns of products for x_{nom} = 0.1, 0.25, 0.5, 1.0, 2.0 after ball-milling at 1100 rpm are summarized in Fig. 3a. Although byproducts mainly indexed for BaH_2 appeared in x_{nom} = 2.0, cubic perovskites were observed in all compositions. As x_{nom} increases, the XRD profiles were shifted toward lower angles, e.g. 112 peaks magnified in Fig. 3b. Figure 3c plots the calculated lattice volumes for each nominal composition x_{nom}, showing a nearly linear correlation. Given the previous studies on $BaTiO_{3-x}H_x$ with a roughly positive correlation between the lattice constants and x,[8] hydrogen concentration in mechanochemically prepared oxyhydrides could be tuned by appropriate settings of nominal compositions. In fact, the product of x_{nom} = 0.25 was estimated to be $BaTiO_{2.71}H_{0.29}$ from Rietveld analysis (Fig. S3-4 and Table S3-4). The lattice constant of 4.0384 Å for x_{nom} = 2 is somewhat larger than that for $BaTiO_{2.40}H_{0.60}$ (4.0321 Å), which is a heavily hydrogen-exchanged composition prepared by CaH_2 reduction.[7] The hydrogen solubility limit in the titanium oxyhydrides might be expanded by the mechanochemical method.

In order to evaluate the electrode property for $BaTiO_{3-x}H_x$ prepared by the mechanochemical method, we constructed a symmetric cell where H^- conductor, $LaSrLiH_2O_2$, sandwiched by $BaTiO_{3-x}H_x$ and performed electrochemical impedance spectroscopy (EIS) measurements under H_2 gas flow in the temperature range of 150 − 325 ºC. The x_{nom} = 0.5 product ($BaTiO_{2.58}H_{0.42}$) was selected for electrodes since metallic electronic conductivity was reported in 0.35 ≤ x ≤ 0.58 for $BaTiO_{3-x}H_x$.[22] We checked the electrical resistivity of the hot-pressed $BaTiO_{3-x}H_x$ (x_{nom} =0.5) and obtained a value of 17.9 Ω·cm^{-1} at room temperature (Fig. S5). The electrolyte, $LaSrLiH_2O_2$, was prepared by sintering under ambient pressure,

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according to the previous report.[23] The cell was prepared by sintering a three-layered pellet composed with $BaTiO_{3-x}H_x$|$LaSrLiH_2O_2$|$BaTiO_{3-x}H_x$ at 400 ºC under uniaxial pressure of 300 MPa.

Figure 4a presents a typical impedance spectrum obtained at 325 ºC, composed of at least three semicircles that can be attributed to responses from the sum of bulk and grain boundary ("bulk+gb"), electrolyte/electrode interface ("interface"), and electrode, respectively at high-, middle-, and low-frequency regions. The spectrum was analyzed by fitting with the equivalent circuit shown in Fig. 4a, and an acceptable fit was obtained. The validity of this model was confirmed by analyzing the spectrum of the cell with a thicker electrolyte using the same equivalent circuit (Fig. S6). It should be noted that $BaTiO_{3-x}H_x$ was stable without significant side reactions such as H_2 desorption during EIS measurements (see XRD patterns for the product of x_{nom} = 0.5 before and after EIS as shown in Fig. S7).
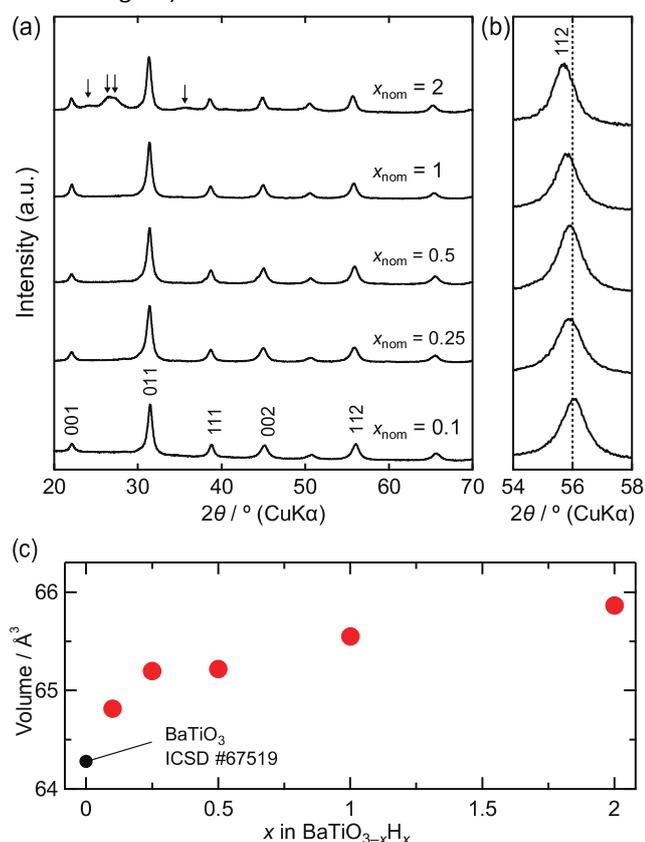

semicircle corresponding to electrode response, i.e., hydrogen charge transfer ($H_2 + 2e^- \Leftrightarrow 2H^-$), is similar to the EIS measurement of H^--conducting BaH_2 with hydrogen permeable Pd film electrodes.[24] This result firstly and clearly shows a capability of $BaTiO_{3-x}H_x$ as a hydrogen-permeable electrode derived from its H^-/e^- mixed conducting property. The relatively large and broad semicircle for the electrolyte/electrode interfacial resistance might reflect the intrinsic complexity of the solid-heterointerface of the powder samples, including the variable contact area and compositional distribution.[25]
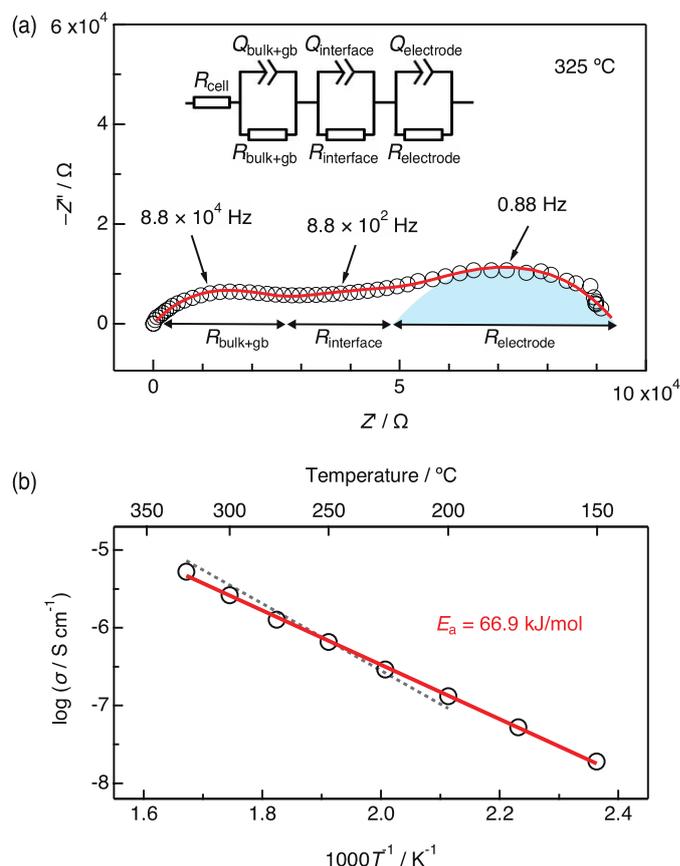

Fig. 4 (a) Impedance spectrum of a three-layered symmetric cell composed of electrolyte $LaSrLiH_2O_2$ sandwiched by $BaTiO_{2.5}H_{0.5}$ electrodes at 325 ºC. The Equivalent circuit used for fitting the spectrum is shown in (a). R and Q represent resistance and constant phase element (CPE). The red solid line is fitting result. (b) Arrhenius plots for the total conductivity of $LaSrLiH_2O_2$ (open circle) and its linear fitting (red solid line). Grey dashed line indicates the reported data using deposited Au electrodes.[19]

Fig. 3 (a) XRD patterns of mechanochemically prepared $BaTiO_{3-x}H_x$ and (b) the enlarged view at 2θ = 54-58º wherein the (112) peak exists. Arrows in x_{nom} = 2 indicate peaks derived from BaH_2. (c) Volume of the unit cell estimated from lab-XRD depending on x_{nom} (red circles). Black circle is that of $BaTiO_3$ (ICSD 67519).

Temperature dependence of H^- conductivity of the electrolyte ($LaSrLiH_2O_2$) estimated from the bulk and grain boundary resistance is comparable to the reported one (grey dashed line) using deposited Au as hydrogen blocking electrodes,[23] as shown in Fig. 4b. The activation energy for H^- diffusion was estimated as 66.9 kJ/mol, which is smaller than the reported one of 80.7 kJ/mol,[23] probably derived from the effect of hot-pressing. Furthermore, observation of the clear

In summary, we have succeeded in direct synthesis of barium titanium oxyhydride $BaTiO_{3-x}H_x$ by mechanochemical reaction, allowing gram-scale and speedy preparation of the functional material. Its unique reaction condition without external heating might be suitable for materials exploration of oxyhydrides. We also confirmed that the prepared polycrystalline $BaTiO_{3-x}H_x$ worked as a hydrogen-permeable electrode. This result suggests that H^-/e^- mixed conducting oxyhydrides are promising for electrode use in electrochemical chemical/energy conversion devices.

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were approved by JASRI (2019A1084, 2020A1659) and IMSS, KEK (2019S10).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1   M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall and F. L. Pratt, *Science (80-.).*, 2002, **295**, 1882–1884.

2   S. Iimura, S. Matuishi, H. Sato, T. Hanna, Y. Muraba, S. W. Kim, J. E. Kim, M. Takata and H. Hosono, *Nat. Commun.*, , DOI:10.1038/ncomms1913.

3   M. Hiraishi, S. Iimura, K. M. Kojima, J. Yamaura, H. Hiraka, K. Ikeda, P. Miao, Y. Ishikawa, S. Torii, M. Miyazaki, I. Yamauchi, A. Koda, K. Ishii, M. Yoshida, J. Mizuki, R. Kadono, R. Kumai, T. Kamiyama, T. Otomo, Y. Murakami, S. Matsuishi and H. Hosono, *Nat. Phys.*, 2014, **10**, 300–303.

4   G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science (80-.).*, 2016, **351**, 1314–1317.

5   Y. Kobayashi, O. J. Hernandez, T. Sakaguchi, T. Yajima, T. Roisnel, Y. Tsujimoto, M. Morita, Y. Noda, Y. Mogami, A. Kitada, M. Ohkura, S. Hosokawa, Z. Li, K. Hayashi, Y. Kusano, J. E. Kim, N. Tsuji, A. Fujiwara, Y. Matsushita, K. Yoshimura, K. Takegoshi, M. Inoue, M. Takano and H. Kageyama, *Nat. Mater.*, 2012, **11**, 507–511.

6   X. Liu, T. S. Bjørheim and R. Haugsrud, *J. Mater. Chem. A*, 2017, **5**, 1050–1056.

7   T. Yajima, F. Takeiri, K. Aidzu, H. Akamatsu, K. Fujita, W. Yoshimune, M. Ohkura, S. Lei, V. Gopalan, K. Tanaka, C. M. Brown, M. A. Green, T. Yamamoto, Y. Kobayashi and H. Kageyama, *Nat. Chem.*, 2015, **7**, 1017–1023.

8   N. Masuda, Y. Kobayashi, O. Hernandez, T. Bataille, S. Paofai, H. Suzuki, C. Ritter, N. Ichijo, Y. Noda, K. Takegoshi, C. Tassel, T. Yamamoto and H. Kageyama, *J. Am. Chem. Soc.*, 2015, **137**, 15315–15321.

9   Y. Tang, Y. Kobayashi, N. Masuda, Y. Uchida, H. Okamoto, T. Kageyama, S. Hosokawa, F. Loyer, K. Mitsuhara, K. Yamanaka, Y. Tamenori, C. Tassel, T. Yamamoto, T. Tanaka and H. Kageyama, *Adv. Energy Mater.*, , DOI:10.1002/aenm.201801772.

10   Y. Tang, Y. Kobayashi, C. Tassel, T. Yamamoto and H. Kageyama, *Adv. Energy Mater.*, , DOI:10.1002/aenm.201800800.

11   T. Sakaguchi, Y. Kobayashi, T. Yajima, M. Ohkura, C. Tassel, F. Takeiri, S. Mitsuoka, H. Ohkubo, T. Yamamoto, J. E. Kim, N. Tsuji, A. Fujihara, Y. Matsushita, J. Hester, M. Avdeev, K. Ohoyama and H. Kageyama, *Inorg. Chem.*, 2012, **51**, 11371–11376.

12   T. Yamamoto, R. Yoshii, G. Bouilly, Y. Kobayashi, K. Fujita, Y. Kususe, Y. Matsushita, K. Tanaka and H. Kageyama, *Inorg. Chem.*, 2015, **54**, 1501–1507.

13   F. Takeiri, T. Yajima, T. Yamamoto, Y. Kobayashi, T. Matsui, J. Hester and H. Kageyama, *J. Solid State Chem.*, 2017, **256**, 33–37.

14   F. Takeiri, K. Aidzu, T. Yajima, T. Matsui, T. Yamamoto, Y. Kobayashi, J. Hester and H. Kageyama, *Inorg. Chem.*, 2017, **56**, 13035–13040.

15   Ž. Kesić, I. Lukić, D. Brkić, J. Rogan, M. Zdujić, H. Liu and D. Skala, *Appl. Catal. A Gen.*, 2012, **427–428**, 58–65.

16   E. Jeon and Y. W. Cho, *J. Alloys Compd.*, 2006, **422**, 273–275.

17   Y. Kim, E. K. Lee, J. H. Shim, Y. W. Cho and K. B. Yoon, *J. Alloys Compd.*, 2006, **422**, 283–287.

18   A. Hayashi, S. Hama, T. Minami and M. Tatsumisago, *Electrochem. commun.*, 2003, **5**, 111–114.

19   H. Yamane, M. Shibata, Y. Shimane, T. Junke, Y. Seino, S. Adams, K. Minami, A. Hayashi and M. Tatsumisago, *Solid State Ionics*, 2007, **178**, 1163–1167.

20   F. Izumi and K. Momma, in *Solid State Phenomena*, Trans Tech Publ, 2007, vol. 130, pp. 15–20.

21   R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2009, **600**, 94–96.

22   G. Bouilly, T. Yajima, T. Terashima, W. Yoshimune, K. Nakano, C. Tassel, Y. Kususe, K. Fujita, K. Tanaka, T. Yamamoto, Y. Kobayashi and H. Kageyama, *Chem. Mater.*, 2015, **27**, 6354–6359.

23   A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry*, 2017, **85**, 88–92.

24   M. C. Verbraeken, C. Cheung, E. Suard and J. T. S. Irvine, *Nat. Mater.*, 2015, **14**, 95–100.

25   J. Haruyama, K. Sodeyama, L. Han, K. Takada and Y. Tateyama, *Chem. Mater.*, 2014, **26**, 4248–4255.