Direct synthesis of barium titanium oxyhydride promising for electrode material with hydrogen permeability

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Abstract

Barium titanium oxyhydride $BaTiO_{3-x}H_x$ is a promising functional material that exhibits H^-/e^- mixed conduction and catalytic activity. 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 electrodes exhibiting hydrogen pearmeability.

Introduction

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 $LaSrCoO_3H_{0.7}$,[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, titanium perovskite $BaTiO_{3-x}H_x$ is an important piece that exhibits metallic electronic conduction and high anion exchangeability.[5–7] Such properties afford valuable chemical functions represented by catalytic activity for NH_3 synthesis and CO_2 reduction.[8,9] 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 samples of 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.[5,10,11] The hydrogen concentration x can be varied depending on the reaction conditions including sintering temperature and period. However, controlling x value, that is a critical factor for the above-mentioned chemical functions, is still a challenge. It is because that not only thermodynamic but also kinetic factor, such as anion diffusivity in the lattice, should be considered.[12,13] For example, BaTiO$_{3-x}$H$_x$ in single phase was obtained from the precursors of nano size (~ 170 nm) particles, while the multi-phases wherein hydrogen concentration differs generated from those of larger particles (10-30 mm).[10] In addition, the long reaction period for a week and washing process to remove the residual CaH$_2$ and the byproduct CaO are inevitable in topochemical reactions. 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. Especially among research fields of catalyst and battery, it has become one of the effective methods for materials synthesis. For instance, mechanochemical prepared CaO-ZnO mixed oxides show more catalytic activity for biodiesel production compared to those prepared by the coprecipitation method[14]. Li$_2$S-P$_2$S$_5$ glass-ceramics exhibits high ionic conductivity at room temperature.[15,16] 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.

Results and Discussion

Mechanochemical synthesis of polycrystalline samples of $BaTiO_{3-x}H_x$ were performed as below. 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.

$$xBaH_2 + (1 - x)BaO + TiO_2 \rightarrow BaTiO_{3-x}H_x + 0.5xH_2 \qquad (1)$$
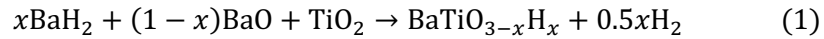
For the nominal composition of x_{nom} = 2, TiH_2 was used instead of BaH_2 and TiO_2 as following the equation (2).

$$BaO + TiH_2 \rightarrow BaTiOH_2 \qquad (2)$$

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 reduced partial Ti^{4+} to Ti^{3+}, and the obtained cubic phase was stable in air. Those 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 check the presence of hydrogen in the sample. Figure 2 (inset) shows the obtained spectrum corresponding to desorbed H_2 molecule (m/z = 2) upon heating. The desorption gradually occurred above 200 ºC and sharply increased around 480 ºC. The total amount of hydrogen overall temperature range was estimated by integrating the peak area, giving the hydrogen content x of 0.427 for $BaTiO_{3-x}H_x$. Scanning electron microscopy (SEM) image of the obtained powder indicates a broad particle size distribution of 0.1-2 mm (Fig. S1), possibly inducing the H_2 desorption at a wide range of temperatures.

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 and Z-Rietveld program, respectively.[17,18] ND refinement assuming a cubic perovskite $BaTiO_{3-x}H_x$ converged well and gave x = 0.3900(14) (Fig. 2 and Table S1). The estimated composition is consistent with both the SXRD refinement yielding

a sizable amount of anion vacancy of d = 0.423(4) for $BaTiO_{3-d}$ (Fig. S2 and Table S2) and the

TDS result. A slight decrease of hydrogen 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.

Laboratory XRD patterns of x_{nom} = 0.1, 0.25, 0.5, 1, and 2 after ball-milling at 1100 rpm are

summarized in Fig. 3a, both showing a formation of cubic perovskites. Byproducts mainly

indexed for BaH_2 appeared in x_{nom} = 2. As x_{nom} increases, the cubic profiles were shifted toward

lower angles, e.g. 112 peaks highlighted 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, the

observed trend indicates that hydrogen concentration in mechanochemically prepared

oxyhydrides could be tuned by appropriate setting of nominal compositions. 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) that is the

most hydrogen-exchanged composition prepared by CaH_2 reaction,[5] possibly implying that the

mechanochemical method could expand the hydrogen solubility limit in the titanium oxyhydrides.

In order to evaluate the electrode property for $BaTiO_{3-x}H_x$ (x_{nom} = 0.5), we constructed the

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 flow in the temperature

range of 150 – 325 ºC. The electrolyte, $LaSrLiH_2O_2$, was prepared by sintering under ambient

pressure, according to the previous report.[19] 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 is obtained. The validity of this model was also

confirmed by analyzing the spectrum of the cell with a thicker electrolyte using the same

equivalent circuit (Fig. S3).

Temperature dependence of H^- conductivity of the electrolyte ($LaSrLiH_2O_2$) estimated from

the bulk and grain boundary resistance is comparable to reported one (grey dashed line) using

deposited Au as hydrogen blocking electrodes,[19] as shown in Fig. 4b. Notably, the pressed

polycrystalline $BaTiO_{3-x}H_x$ sintered at a relatively low temperature (400 ºC) exhibits an electronic

conductivity enough for electrode use. The activation energy for ion diffusion was estimated as

66.9 kJ/mol, which is smaller than the reported one of 80.7 kJ/mol, probably derived from the

reduced grain boundary resistance owing to hot pressing. Furthermore, observation of the clear

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.[20] 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 heterointerface of the powder samples, including the contact area and compositional distribution.

Conclusion

In conclusion, 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. This is the first case of mechanochemical synthesis of oxyhydrides and should be applied for other known compounds. Furthermore, the reaction condition without external heating might offer a route to new metastable oxyhydrides. It is 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 electrodes in electrochemical chemical/energy conversion devices.

Acknowledgement

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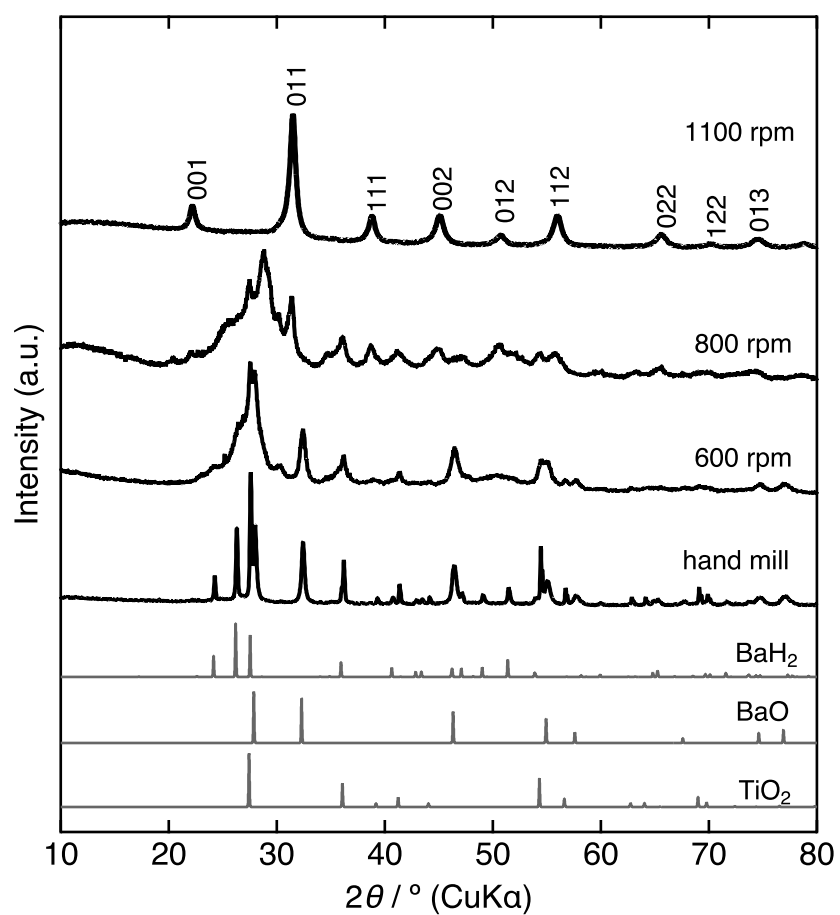20   M. C. Verbraeken, C. Cheung, E. Suard and J. T. S. Irvine, *Nat. Mater.*, 2015, **14**, 95–100.

Fig. 1 XRD patterns for preparation composition BaTiO$_{2.5}$H$_{0.5}$ at hand mill, 600 rpm, 800 rpm, and 1100 rpm. Selected *hkl* reflections with relatively intense peaks are indexed.
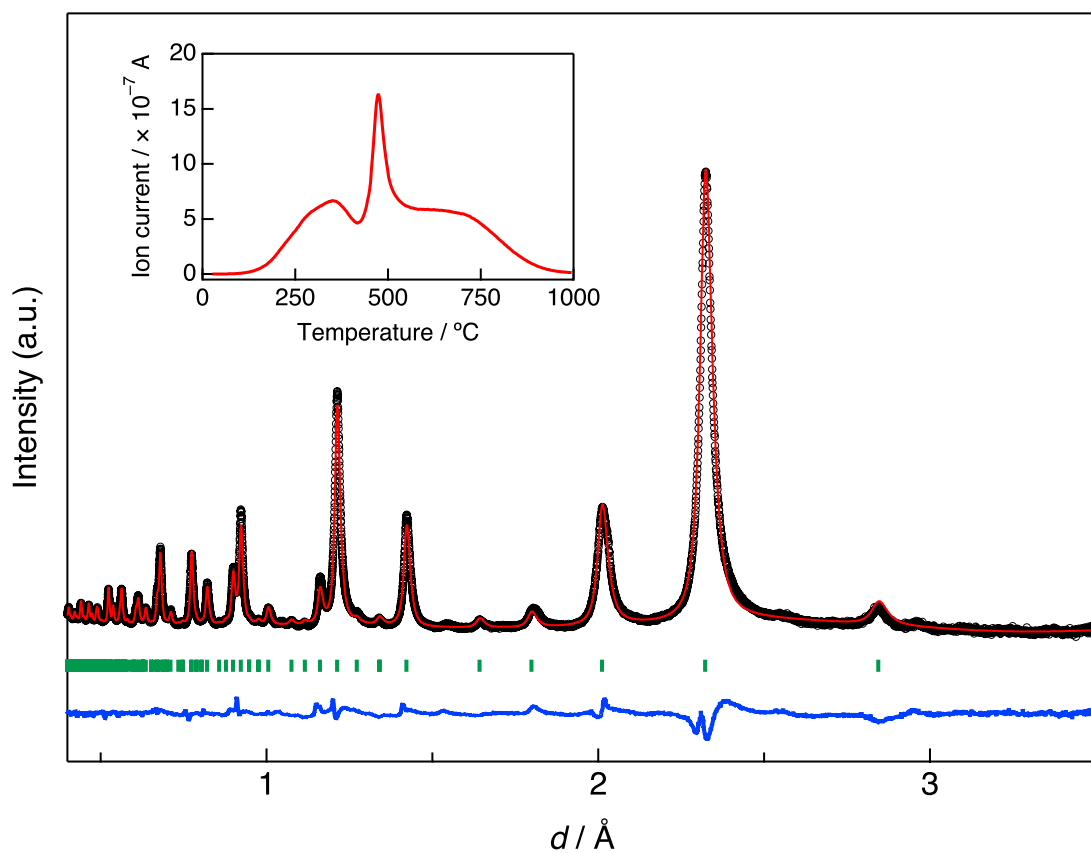
Fig. 2 Rietveld refinements for ND data of x_{nom} = 0.5 product. Circles (black) and lines (red) indicate observed and calculated data, respectively. The vertical marks (green) indicate the Bragg reflection positions. The inset shows TDS curve corresponding to H_2 desorption upon heating.
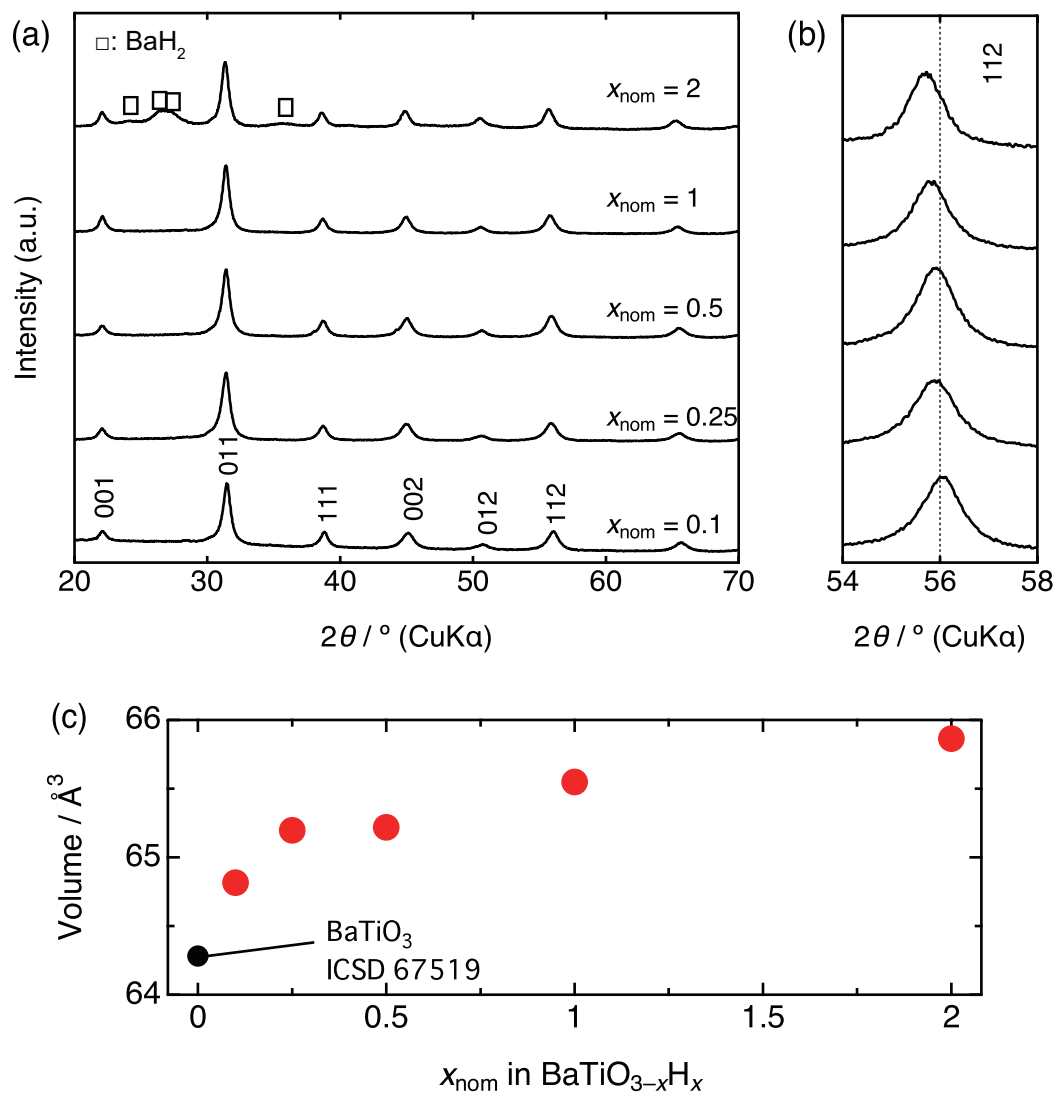
Figure 3 (a) XRD patterns of mechanochemically prepared $BaTiO_{3-x}H_x$ and (b) the enlargedview at $2\theta = 54\text{-}58°$ wherein the (112) peak exists. Arrows in $x_{nom} = 2$ indicates peaks derived from BaH_2. (c) Volume of the unit cell estimated from lab-XRD depending on x_{nom} (red circles). Black circle is that of $BaTiO_3$ (ICSD 67519).
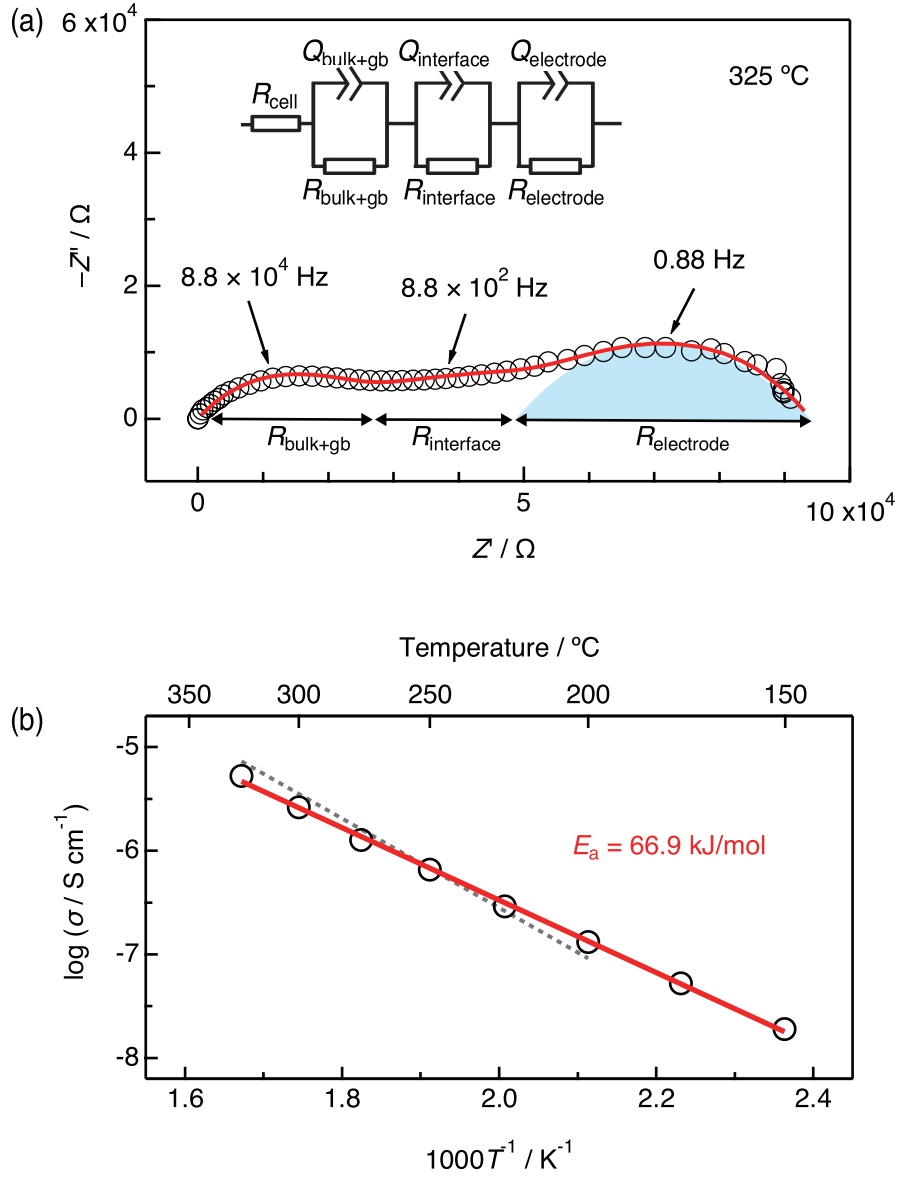
Figure 4 (a) Impedance spectrum of a three-layered symmetric cell composed of electrolyte LaSrLiH$_2$O$_2$ sandwiched by BaTiO$_{2.5}$H$_{0.5}$ electrodes at 325 °C. The Equivalent circuit used for fitting the spectrum is shown in (a). R and Q represent resistance and constant phase element (CPE). The red solid line is fitting result. (b) Arrhenius plots for the total conductivity of LaSrLiH$_2$O$_2$ (open circle) and its linear fitting (red solid line). Grey dashed line indicates the reported data using deposited Au electrodes[19].