Reaction Mechanism Studies towards Effective Fabrication of Lithium-Rich Anti-Perovskites Li_3OX ($X = \text{Cl}, \text{Br}$)

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Abstract:

Lithium-rich Anti-perovskites (LiRAPs), with general formula Li_3OX ($X = \text{Cl}, \text{Br}$), recently reported as superionic conductors with 3-dimensional Li^+ migrating channels, are emerging as promising candidates for solid electrolytes in all-solid-state lithium-ion batteries (LIBs). However, great challenges remain in the fabrication of pure LiRAPs due to difficulties such as low yield, impurity phases, thermodynamic instabilities, and moisture-sensitivity. In this work, we thoroughly studied the formation mechanism of Li_3OCl and Li_3OBr using various solid state reaction routes. Different experimental strategies were developed to improve the syntheses, namely for the purposes of phase stability, phase purity, and large-scale production. One feasible method is to use the strong reducing agents Li metal or LiH to eliminate the OH species. The results show that LiH is more effective than Li metal, mainly due to negatively charged H^- and reaction uniformity. The other successful method employs a solid diffusion approach using Li_2O and LiX as the starting reagents, thereby avoiding OH entirely; ball milling of reagents under Ar atmosphere was utilized to decrease initial grain size and increase the reaction rate. **Fourier transform infrared spectroscopy (FTIR)**, thermal analyses and first-principles calculations were performed to give indications on the reaction pathway.

Keywords: solid electrolyte, lithium-ion battery, Lithium-rich Anti-Perovskite, solid state reaction

1. Introduction

Lithium-ion batteries (LIBs) are ubiquitous energy storage devices for their extensive use in applications including electric/hybrid vehicles, personal electronics, and other portable devices. [1-4] Conventional LIBs use lithium salts dissolved in organic solvents as the electrolyte. [5] However, the liquid electrolytes in these batteries are commonly toxic, corrosive and/or

flammable. [5,6] In addition, if using lithium metal as the anode, the dendrites resulted from non-uniform lithium deposition either becomes “dead” lithium, reducing the battery efficiency, [7] or even worse, breaks the separator, resulting in a short circuit. Recently developed solid state lithium ion batteries are expected to solve the safety and environmental issues related to conventional LIBs. [8-11] The solid state LIBs use inorganic compounds as electrolytes, which are non-toxic, non-flammable, environmental friendly and safe. Furthermore, because of their intrinsic mechanical properties, solid electrolytes can avoid the risk of lithium dendrite formation to a large degree. This enables solid state battery assemblies to make use of lithium metal as the anode, hence maximizing working potential, capacity, power density and energy density. As the key component in solid state LIBs, the solid electrolyte needs to possess qualities such as high ionic conductivity, low Li^+ migration activation energy barrier, negligible electronic conductivity, large electrochemical window, and compatibility with electrodes. [9] Several inorganic compounds having Li^+ superionic conductivity have been studied as solid electrolytes for use in LIBs, some showing good performance. [9,12-16] The recently developed lithium superionic conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, with a new three-dimensional framework, has a Li^+ conductivity of 1.2×10^{-2} S/cm at room temperature, which is the highest ionic conductivity reported for a solid electrolyte. [12] The garnet-type $\text{Li}_7\text{La}_3\text{ZrO}_{12}$ compound was also observed to have a Li^+ 3-dimensional diffusion pathway that facilitates Li^+ transport. [13,14] Nanoporous $\beta\text{-Li}_3\text{PS}_4$ was reported to have an ionic conductivity of 1.6×10^{-4} S/cm at room temperature, a wide electrochemical window, and stability against Li metal. [15] NASICON [16] and LISICON [17,18] compounds have also been widely studied as solid state superionic conductors over the past few decades. Solid state thin film batteries using LiPON as the electrolyte were demonstrated to show excellent performance with a high columbic efficiency >99.98% and stable cycling for 10 000 cycles. [19]

Recently, a family of lithium-rich anti-perovskites (LiRAPs), with the formula of Li_3OX ($X = \text{Cl}, \text{Br}$), was reported as a Li^+ superionic conductor, and may be a candidate for a solid electrolyte in LIBs. [20] The inspiration for LiRAPs stems from the NaMgF_3 perovskite material, reported to have F^- superionic conductivity. [21] With electronic inversion (cations and anions switching crystallographic positions), Li_3OX was postulated to be a Li^+ superionic conductor. The anti-perovskite Li_3OX is lithium rich, with 60 at. % Li atoms in the perfect lattice. Theoretical calculations indicate that Li ions migrate via Li vacancies in a 3-dimensional channel. [22,23] Via cation- and/or anion-doping, Li^+ depleting, or other structural manipulation methods to introduce Li vacancies into the lattice, the ionic conductivity of this class of materials has reached 10^{-3} S/cm, with low activation energy barrier. [20] Additionally, theoretical calculations gave some indications that LiRAP has a large electrochemical window and low electronic conductivity. [22,23]. Furthermore, in experiments, Li_3OCl was also reported to be stable against Li metal, showing self-stabilization behavior [24]. These properties make LiRAP a promising candidate as a solid electrolyte for LiBs.

At the outset of our battery research and development, it is essential to get pure and stable phases of LiRAP compounds, so that the performance may be attributed to a single material, and not a phase mixture. In the previous report, Li_3OCl synthesis involved heating LiCl and LiOH mixture for a few days under vacuum with the purpose of actively removing H_2O . [20] Recently, Li_3OCl solid electrolyte films were fabricated via pulsed laser deposition (PLD) using a Li_3OCl compound target. [24] LiRAPs were also synthesized via a high-pressure high-temperature method [25], a quaternary ammonium salt method, and a wet chemistry method. [26] However, none of these methods can meet the criteria for both phase purity and large scale manufacture.

In this work, Li_3OX ($X = \text{Cl}, \text{Br}$) was synthesized using solid state reactions with slightly different approaches to obtain the pure phase LiRAP without undesired OH in the compounds. Our synthesis approaches are also time and cost effective, Two main techniques were employed: 1. reducing agents, such as Li-metal and LiH , were used to remove -OH that may exist in the products; 2. ball milling the Li_2O and LiX starting reagents to lower the kinetic reaction barriers increase the reaction rate. Thermogravimetry (TG), differential scanning calorimetry (DSC) Fourier transform infrared spectroscopy (FTIR), and first principles calculations were employed to clarify the reaction mechanism.

2. Experimental

2.1 Sample Preparation

LiRAP samples were synthesized with Li_2O (Alfa Aesar, 99.5 %), LiCl (Alfa Aesar, anhydrous, 99 %), LiBr (Alfa Aesar, anhydrous, 99 %), LiOH (Alfa Aesar, anhydrous, 98 %), Li metal (Sigma) and LiH (Alfa Aesar, 97 %) as starting materials. Other than the lithium metal, all starting reagents were in powder form. The materials were stored, weighed, mixed, ground and heated inside of an argon atmosphere glovebox ($\text{H}_2\text{O} < 5 \text{ ppm}$, $\text{O}_2 < 20 \text{ ppm}$). For a given reaction, the powder mixtures were placed in alumina crucibles, then placed in a compact furnace inside the glovebox for sintering. As for the ball milling process, the raw materials were initially loaded into sealed ball milling jars inside glovebox and then transferred to ball milling machine, and ball milled for 2 hours before sintering.

2.2 Sample characterization

The X-ray powder diffraction (XRD) patterns were recorded on an X-ray diffractometer (Bruker D8 Advance) with Bragg-Brentano scattering geometry. The as synthesized powders were placed either on a traditional sample holder with parafilm stretched over the sample area, or in a zero background air tight sample holder. Protection from atmosphere is necessary as the samples readily react with moisture in the air.

FTIR spectra of the products were collected on a Nicolet IS5 Mid-infrared FT-IR spectrometer. OH in the crystal lattice is easily detected by a strong absorption around 3600 cm^{-1}

due to the OH stretch. FTIR was used as a qualitative probe to determine whether or not OH was present in the final product.

Thermal properties of the LiRAPs were tested on Netzsch STA 449 C DSC. Samples were placed in alumina crucibles with lids inside the glovebox. Ar was used as a carrier gas during each test. TG-DSC measurements were recorded with heating/cooling rate of 10 K/min.

For impedance measurements, the sample powders were melted and pressed between two pieces of gold foil before loading into a sealed sample holder. The whole assemble was transferred to a tube furnace with protecting Ar gas. The electrochemical impedance spectroscopic (EIS) measurement was carried out on an Solartron 1260 instrument (10 mV perturbation voltage and between 1 MHz and 100 mHz) as function of temperature from 25 °C to 175 °C.

2.3 Theoretical calculation

The crystal structures of Li₂O, LiCl and Li₃OCl from the ICSD database were employed for the initial structure model to study the total energy as a function of cell volume. The calculations were performed by using CASTEP software [27] at the GGA level of theory and energy cutoff of 380 eV. The total energies of the reactants (Li₂O + LiCl) were added by their individual formation energy with decreased or increased cell volumes with the same percentages.

3. Results and Discussion

3.1. Reducing agents as starting materials

As reported in our previous work [20], Li₃OCl was synthesized by heating LiCl and LiOH mixture under vacuum at 330 - 360 °C for several days, as shown in equation (1).

Long time heating under vacuum is necessary to remove water and hence drives the reaction going forward. However, this method has the requirements of high vacuum condition and long synthesis times. Therefore, reducing agents were used to break the O-H bond and hence drive the reaction to completion.

3.1.1. Lithium metal as a reducer

Lithium metal was adopted as a reducing agent. It reacts with LiOH and LiX (X = Cl, Br) via equation (2). The starting materials, Li metal, LiOH and LiX, were mixed by 1.05:1:1 molar ratio. Experience dictated that a slight excess of lithium metal (roughly 5 mol. %) was necessary in order to fully complete the reaction because of the lithium evaporation loss during sintering. The mixture was heated at 600 °C for 10 hours under vacuum. After cooling, the product was ground and reheated multiple times to get the pure phase anti-perovskite Li₃OX. Fig. 1a shows

the XRD pattern of the as synthesized Li_3OCl . It was indexed into cubic structure with space group $Pm-3m$, and with lattice parameter $a = 3.9161 \text{ \AA}$.

Fig. 1 Powder X-ray diffraction pattern of Li_3OCl synthesized via $\text{Li} + \text{LiOH} + \text{LiCl} \rightarrow \text{Li}_3\text{OCl} + 1/2\text{H}_2 \uparrow$ (a), Li_3OCl via $\text{LiH} + \text{LiOH} + \text{LiCl} \rightarrow \text{Li}_3\text{OCl} + \text{H}_2 \uparrow$ (b), Li_3OBr via $\text{LiH} + \text{LiOH} + \text{LiBr} \rightarrow \text{Li}_3\text{OBr} + \text{H}_2 \uparrow$ (c), and Li_3OBr via ballmilling and sintering method $\text{Li}_2\text{O} + \text{LiBr} \rightarrow \text{Li}_3\text{OBr}$ (d). Indexing was performed by using space group $Pm-3m$, $a = 3.9161 \text{ \AA}$ for Li_3OCl and $a = 4.0468 \text{ \AA}$ for Li_3OBr . Peaks marked by solid green squares are contributed by parafilm, and red arrows are ascribed to Li_2O .

For this method, we considered two possible reaction pathways. The first possibility is that lithium metal reacts with LiOH to form Li_2O and release H_2 ; then highly active Li_2O reacts with LiX to form Li_3OX , as shown in equations (3) and (4). The second possibility is that LiOH and LiX react together, and then the product $\text{Li}_2(\text{OH})\text{X}$ reacts with the Li metal, as shown in equations (5) and (6).

To clarify the reaction mechanism, thermal analysis was used to determine the reaction process. **Fig. 2** shows the TG-DSC curves of $\text{Li} + \text{LiOH}$ (a), $\text{Li} + \text{Li}_2(\text{OH})\text{Cl}$ (b), $\text{Li} + \text{LiOH} + \text{LiCl}$ (c), $\text{Li}_2\text{O} + \text{LiCl}$ (d) mixtures, and DSC curves of Li_3OCl and $\text{Li}_2(\text{OH})\text{Cl}$ (e). It is clear in **Fig. 2a** that for the reaction between LiOH and Li metal (equation (3)), the Li metal melts at 179°C , and the Li and LiOH react significantly near 460°C , indicated by the strong exothermic peak and mass loss (H_2 release). However, the reaction of $\text{Li} + \text{LiOH} + \text{LiCl}$ mixture behaves differently (**Fig. 2b**). Energy is absorbed near 273°C (small endothermic peak starting at 273°C and peaking at 290°C), followed by a strong exothermic reaction at 303°C , coinciding with the release of H_2 gas. Compared to the reaction of the Li - LiOH mixture, the presence of LiCl alters the reaction pathway and causes the mass loss event to occur at a significantly lower temperature. This result indicates that the first possibility mentioned above is not the correct reaction pathway.

Further thermal analysis on the $\text{Li}_2(\text{OH})\text{Cl}$ compound and its mixture with Li-metal gives further indication about the reaction pathway. In reference to the TG-DSC curves in Fig. 2c, the thermal behavior of the Li- $\text{Li}_2(\text{OH})\text{Cl}$ mixture was similar to that of the Li-LiOH-LiCl mixture. The endothermic shoulder begins at 270 °C and peaks near 285 °C, corresponding to the melting temperature of $\text{Li}_2(\text{OH})\text{Cl}$. This is confirmed clearly by the DSC curves of Li_3OCl and $\text{Li}_2(\text{OH})\text{Cl}$ in Fig. 2e. It is apparent from these results that the Li- $\text{Li}_2(\text{OH})\text{Cl}$ system undergoes a similar (if not the same) reaction pathway as the Li-LiOH-LiCl system in regards to the release of H_2 gas.

Using the results from the TG-DSC experiments, we propose the reaction pathway of the Li-LiOH-LiCl system. With Li metal, LiOH and LiCl as the starting reagents, as temperature increases, the first event recorded is that of Li metal melting around 180 °C. Then, LiOH and LiCl react to form $\text{Li}_2(\text{OH})\text{Cl}$, which subsequently melts. Immediately following, Li and $\text{Li}_2(\text{OH})\text{Cl}$ react strongly, indicated by the large exothermic peak. This results in the formation of Li_3OCl and H_2 , suggesting the second reaction pathway is the correct one.

Fig. 2 TG-DSC curves of Li + LiOH (a), Li + LiOH + LiCl (b), Li + $\text{Li}_2(\text{OH})\text{Cl}$ (c) and Li_2O + LiCl (d) mixtures, and DSC curves of Li_3OCl and $\text{Li}_2(\text{OH})\text{Cl}$ (e). The solid green circles at 180 °C in DSC curve in a, b and c represent Li-metal melting.

Using Li metal to facilitate the release of H_2 gas is effective approach in the synthesis of Li_3OX ($\text{X} = \text{Cl}, \text{Br}$). However, it is difficult to control the reaction as the soft and light nature of the lithium metal make it difficult to attain reaction uniformity. Additionally, not all the hydrogen is completely removed, thereby leaving measureable amounts of OH behind. This is observed in the FTIR spectra (Fig. 3), which shows a significant absorption in the region of 3600 cm^{-1} , belonging to the OH stretch. [28,29] The existence of OH impurities may result from uncontrolled aspects of the synthesis, or possibly a thermodynamic limitation.

Fig. 3 IR spectra of Li_3OCl synthesized from Li metal without or with OH phase.

This synthesis can be further improved by using Li metal as a hydrogen getter. Essentially, we place Li metal beside the crucible containing starting materials, and this further drives the release of H_2 gas. Although the additional piece of Li metal does directly participate in the reaction in equation (2), it helps to pull generated H_2 away from the bulk synthesis, and forms LiH (equation 7 as below).

This ultimately led to the use of LiH as a reducing agent in the general reaction to synthesize the pure phase product Li_3OX .

3.1.2. *LiH as a reducer*

With LiH as a reducer to get Li_3OX ($\text{X} = \text{Cl}, \text{Br}$), the global reaction is expressed as:

The advantage of using LiH is that firstly the H^- in LiH is negatively charged, therefore it can break the O-H bond effectively; secondly, LiH is fine powder, so all the starting materials

could be mixed uniformly and hence react thoroughly. For this reaction, the LiH, LiOH and LiX ($X=\text{Cl}, \text{Br}$) were mixed with 1:1:1 molar ratio and heated at 480 °C for 1 hour. The product contains Li_3OX and small amounts of Li_2O and LiX leftover. It was also required to repeat the grinding and heating process to get the pure phases of Li_3OX . The lattice parameters of synthesized Li_3OCl and Li_3OBr (Fig. 1b, 1c) are 3.92 Å and 4.05 Å, respectively.

Analogous to the reaction using Li metal, this reaction can be separated into two steps. The first step is the reaction between LiOH and LiX to get $\text{Li}_2(\text{OH})\text{X}$, and the second step is the reaction of the obtained $\text{Li}_2(\text{OH})\text{X}$ with LiH, as shown in equations (9) and (10). There are several merits of this routine. Firstly, in each step the two reagents can be mixed uniformly, ensuring good physical contact. Secondly, it is straightforward to make $\text{Li}_2(\text{OH})\text{X}$; heating the LiOH and LiX mixture at 400 °C for 3 hours is sufficient to make the pure product. Thirdly, the $\text{Li}_2(\text{OH})\text{X}$ products are themselves anti-perovskites, [30] and the final step is just a removal of hydrogen from the lattice. The XRD patterns of Li_3OX via this two-step reaction are shown in Fig. 4. The insets of magnified reflections around $2\theta = 32^\circ$ show the difference of $\text{Li}_2(\text{OH})\text{X}$ and Li_3OX . Orthorhombic $\text{Li}_2(\text{OH})\text{Cl}$ transforms to cubic Li_3OCl upon significant hydrogen release; cubic $\text{Li}_2(\text{OH})\text{Br}$ changes to cubic Li_3OBr with lattice expansion.

Fig. 4 XRD patterns of $\text{Li}_2(\text{OH})\text{X}$ and Li_3OX synthesized via $\text{LiOH} + \text{LiX} \rightarrow \text{Li}_2(\text{OH})\text{X}$ and $\text{Li}_2(\text{OH})\text{X} + \text{LiH} \rightarrow \text{Li}_3\text{OX} + \text{H}_2 \uparrow$, $X = \text{Cl}$ (left), Br (right). Insets are magnified reflections around $2\theta = 32^\circ$. Peaks noted with green square are contributed by parafilm, red arrows by Li_2O , blue star by LiCl and yellow triangle by LiBr.

3.2. Improved synthesis of Li_3OX from lithium oxide and lithium halides

Li_3OX can be formed from Li_2O and LiX ($X = \text{Cl}, \text{Br}$) directly, via reaction (11). Although the advantage of this approach is the absence of H_2O and OH , the yield is insufficiently low.

Fig. 2 (d) gives the TG-DSC curves of Li_2O and LiCl mixture. The main peaks around 570 °C represent the melting and crystallizing of LiCl , and the small peak around 320 °C corresponds to the melting and crystallizing of Li_3OCl . Here the melting temperature is lowered due to the existence of the other phases. The low yield can be explained by the theoretical calculation, as shown in Fig. 5, the energy difference between Li_3OCl and the starting material (Li_2O and LiCl) is quite small, and the formation energy of Li_3OCl is 5.01 kJ/mol higher than that of the starting materials ($\text{Li}_2\text{O} + \text{LiCl}$), indicating that Li_3OCl is not thermodynamically stable and easily decomposes to Li_2O and LiCl . However, Li_3OCl can be kinetically obtained as indicated by thermal analysis.

The next step is to enhance the yield through kinetic control. Looking into the details of the reaction, Li_3OX is formed at the contact interface between Li_2O and LiX particles. The melting temperature of Li_3OX (320 °C) is much lower than those of Li_2O (1438 °C), LiCl (605-614 °C) and LiBr (552 °C). Therefore, at the synthesis temperature (*ca.* 500 °C), the as formed Li_3OX is melting and coating on the surface of starting material particles. Ultimately, a diffusion-limited condition is met as the Li_3OX product prevents further reaction between Li_2O and LiX grains, resulting in low yield. Grinding the Li_3OX - Li_2O - LiX agglomerate helps expose Li_2O surfaces, thus allowing further reaction. Repeatedly grinding and heating allows one to drive the reaction to completion.

Fig. 5 Energy difference between the lithium-rich anti-perovskite Li_3OCl and the starting materials ($\text{Li}_2\text{O} + \text{LiCl}$) as function of cell volume. Insets are energy differences around the energy minimum.

Based on the experiments and analyses above, a protected ball milling process was used to improve the synthesis. The ball milling of Li_2O and LiX mixture results in well contacted fine powders, which greatly enhancing the surface area, thereby increasing the reaction rate. Consequently, we are able to obtain pure phase Li_3OX in a single pass, without the need to reheat and regrind. The XRD pattern in Fig. 1d shows the pure Li_3OBr product via the ball milling approach. It was indexed as the cubic $Pm-3m$ phase, with lattice parameter $a = 4.0468 \text{ \AA}$. It should be mentioned that excess LiBr was added in raw materials considering the evaporating during sintering.

The conductivities of the as prepared LiRAP samples were investigated by EIS, and an equivalent circuit was used to fit the spectra (Fig. 6). In the studied temperature range ($25 \text{ }^\circ\text{C} - 175 \text{ }^\circ\text{C}$), the conductivity of Li_3OBr (obtained from LiBr and Li_2O) follows Arrhenius behavior, with activation energy $E_a = 0.74 \text{ eV}$, and conductivity $\sigma = 1.0 \times 10^{-6} \text{ S/cm}$ at $25 \text{ }^\circ\text{C}$ (Fig. 6 a). In this work, samples synthesized via different methods give similar conductivity results. This conductivity value is lower than the previously reported value for Li_3OCl , which is $0.85 \times 10^{-3} \text{ S/cm}$ at room temperature. [20] It should be mentioned that lower conductivities of the LiRAP family were also reported by other researchers. [24] Discrepancies are likely due to differences in sample preparation. Depending on the synthesis method and how the sample is prepared prior to EIS measurements, a wide range of results may be observed due to differences in stoichiometry and/or grain boundary structure. In Fig. 6b, the typical impedance spectra of Li_3OBr at $25 \text{ }^\circ\text{C}$ consists two semicircles, the high frequency arc contributed by bulk impedance, and low frequency arc due to grain boundaries. The bulk and grain boundary conductivities from equivalent circuit fitting are $1.02 \times 10^{-5} \text{ S/cm}$ and $1.09 \times 10^{-6} \text{ S/cm}$, respectively. It is clear that the grain boundary contribution dominates the total impedance. One possibility is that our samples melted between two pieces of gold foil may have a density much lower than physically achievable, resulting in poor ionic transport. For superionic Li_3OCl [20], the samples were synthesized by heating at $360 \text{ }^\circ\text{C}$ under vacuum for several days, probably resulting in depleted lithium rich anti perovskite $\text{Li}_{3-\delta}\text{OX}_{1-\delta}$; additionally, Al^{3+} may have been incorporated into the lattice when the sample was melted between Al foils for conductivity tests. Lithium vacancies introduced by synthesis and fabrication enhance the conductivity. However, in our work, the samples were synthesized with Li excess (Li metal, or LiBr in raw materials), so that the as synthesized LiRAP has minimal Li vacancies. As indicated by theoretical calculations, in LiRAPs the nearest-neighbor Li^+ hopping is along the edge of the Li_6O octahedron via Li vacancies [22], and a perforce LiRAP with minimal lithium vacancies is not assumed to be a good Li^+ conductor [23]. Therefore, building upon the success of this solid state reaction, further efforts of creating Li vacancies in LiRAPs are under way.

Fig. 6 Arrhenius plot of the total conductivity of Li_3OBr (synthesized from LiBr and Li_2O) between 25 °C and 175 °C with Au foil as electrodes; the activation energy E_a is derived by linear fitting of $\ln(\sigma T)$ versus $1/T$. (a) The impedance spectrum of Li_3OBr at 25 °C, and equivalent circuit fitting result. (b)

4. Conclusions

In this work, lithium-rich anti-perovskites Li_3OCl and Li_3OBr were synthesized using a variety of approaches, of which the solid state reactions yield the purest product. To increase product yield and remove impurity phases, different efforts were made to improve the synthesis. On one hand, reducing agents such as Li metal or LiH were included in the starting mixture to eliminate the OH in the lattice. The LiOH and LiX form $\text{Li}_2(\text{OH})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) firstly at relatively low temperature. As temperature increases, $\text{Li}_2(\text{OH})\text{X}$ melts and reacts with reducer at around 300 °C, forming Li_3OX , exothermically liberating H_2 . LiH is more effective than Li metal as far as reaction uniformity, and the function of negatively charged H^- . On the other hand, using Li_2O and LiX as starting materials can form Li_3OX directly, with the added benefit of avoiding moisture and OH at the very beginning. Ball milling process greatly increases the surface area of the reactants and make them mixed thoroughly, enabling the reaction proceed much more efficiently. The advantages of this solid state reaction are simple and easy to scale up. Further efforts will be focused on increasing the conductivity of **LiRAP** by introducing Li^+ vacancies in the lattices.

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