

Neutron Powder Diffraction in Metal Halide Solid-State Electrolytes

Subjects: Materials Science, Characterization & Testing

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Metal halide solid-state electrolytes (SSEs) (Li-M-X system, typically Li_3MX_6 and Li_2MX_4 ; M is metal or rare-earth element, X is halogen) exhibit significant potential in all solid-state batteries (ASSB) due to wide stability windows (0.36–6.71 V vs. Li/Li^+), excellent compatibility with cathodes, and a water-mediated facile synthesis route for large-scale fabrication. Understanding the dynamics of Li^+ transportation and the influence of the host lattice is the prerequisite for developing advanced Metal halide SSEs. Neutron powder diffraction (NPD), as the most cutting-edge technology, could essentially reflect the nuclear density map to determine the whole crystal structure. Through NPD, the Li^+ distribution and occupation are clearly revealed for transport pathway analysis, and the influence of the host ion lattice on Li^+ migration could be discussed.

Keywords: solid-state electrolytes (SSEs) ; metal halides ; neutron powder diffraction (NPD)

1. Introduction

Rechargeable batteries have been widely applied in electric mobiles and vehicles in modern industrial society. However, conventional lithium-ion batteries (LIBs) still present safety risks originating from exploiting flammable liquid electrolytes and the lower energy density of graphite anodes than Li metal anodes ^[1]. It is therefore proposed that all solid-state batteries (ASSBs) which are assembled with a solid-state electrolyte (SSE) and a Li metal anode (or anode-less design ^[2]) could be an alternative solution to the above issues ^[3]. However, realizing the above vision relies on two key factors: that is, a promising high- Li^+ ionic conductivity, and a wide enough electrochemical stability window. To fulfill these requirements, a wide range of SSEs have been developed ^{[4][5][6][7][8]}. One of the most famous SSEs are thiophosphates (sulfides) which often possess high ionic conductivities of $>10 \text{ mS cm}^{-1}$ along with their ductile nature ^{[9][10]}. However, their low compatibility with typical 4 V cathode active materials (CAMs, typically LiCoO_2 and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$) is problematic ^[11], since they would be oxidized at a low potential (2.5 V vs. Li^+/Li) ^{[12][13]}. A coating of CAM is expected to address this problem, but searching for suitable materials with proper coating-processing to achieve a homogeneous ^[14] functional coating ^[15] is not that simple. Therefore, developing new SSEs with high- Li^+ ionic conductivity, high stability/compatibility, and ductility is still a hot topic.

Recently developed metal halides exhibit great potential as promising SSEs ^[14]. Metal halides are capable of achieving wider stability windows since their anions are more electronegative than oxygen or sulfur ^{[16][17]}. In fact, metal halide SSEs were investigated decades ago, but early halides (Li_2MgCl_4 , LiAlCl_4 , etc.) ^{[17][18][19][20]} failed to attract wide interest due to relatively low- Li^+ ionic conductivity. Only until recently in 2018, when Asano et al. developed a poorly crystalline Li_3YCl_6 solid electrolyte ^[21] that has a relatively high ionic conductivity of 0.51 mS cm^{-1} and stable cycling in ASSBs with uncoated LiCoO_2 , did halide electrolytes spur renewed interest in this system. Today, several halides have been successfully found to simultaneously possess room-temperature high- Li^+ ionic conductivity ($>10^{-3} \text{ S cm}^{-1}$), ideal oxidative stability ($>4 \text{ V}$) and compatibility with CAMs. These include typical Li_3MX_6 -typed halides Li_3InCl_6 ^{[22][23]}, $\text{Li}_{3-x}\text{M}_{1-x}\text{Zr}_x\text{Cl}_6$ (M = Y, Er, Yb) ^{[24][25]}, $\text{Li}_x\text{ScCl}_{3+x}$ ^[26], $\text{Li}_{2.25}\text{Zr}_{0.75}\text{Fe}_{0.25}\text{Cl}_6$ ^[27], $\text{Li}_{2.60}\text{Yb}_{0.60}\text{Hf}_{0.40}\text{Cl}_6$ ^[28], Li_3YBr_6 ^[24] and spinel-typed $\text{Li}_2\text{Sc}_{2/3}\text{Cl}_4$ ^[29]. Others, like Li_3YCl_6 ^[21], Li_2ZrCl_6 ^[27], also exhibit good oxidative and chemical stability but a little lower (10^{-4} – 10^{-3}) ionic conductivity. $\text{Li}_3\text{Y}_{1-x}\text{In}_x\text{Cl}_6$ ^[30] also has a conductivity surpassing $10^{-3} \text{ S cm}^{-1}$ along with a high humidity tolerance. Up to now, most of these promising halides have been chlorides and bromides. Although fluorides possess the widest electrochemical window, their room-temperature ionic conductivity is considerably lower ^[31]. Generally, with obvious advantages of high ionic conductivity, good stability, humidity tolerance and facile synthesis routes, metal halide electrolytes have become increasingly attractive.

In searching for new metal halides as SSEs, neutron powder diffraction (NPD) ^[32] is a powerful technique since it determines the whole crystal structure, especially the Li^+ sublattice, and analyzes the Li^+ migration pathway. It offers an

essential understanding of the interplay between the structure and underlying Li^+ migration mechanism. NPD data is usually collected on a diffractometer in the national neutron beam center. It has played an increasingly indispensable role in the in-depth study of SSEs. Similar to X-ray diffraction (XRD), NPD also follows the Bragg diffraction law and diffraction geometry, and its structure-determination also follows a similar mathematical procedure: that is, firstly determining the phases of the structure factors, and secondly conducting an inversed Fourier transform to yield a 3D atomic distribution map of the rough crystal structure, followed by Rietveld refinements with least-square method to yield a final structure.

One unique advantage of NPD is that a neutron can pass through an electron cloud to directly interact with a nucleus, which is in a clear contrast to XRD, that only resonates with electron clouds. Using this capability, neutron diffraction can detect nuclei-density distribution rather than electron-cloud distribution in the crystal structure, which indicates a precise determination of true atomic positions in the structure model. Another advantage of NPD resides in its superior sensitivity to light elements H(D), Li, C, N, O, etc., while XRD is much weaker in detecting them. This is because NPD has a totally different elemental scattering length/intensity compared to XRD. In XRD, scattering intensity is proportional to the atomic number. The more electrons surround it, the stronger scattering intensity the atom contributes. Therefore, XRD is excellent in detecting heavy atoms (like metals or halogens) but very insensitive to light elements. However, NPD does not follow this rule, and its elemental scattering intensity depends on the interaction between neutron and nucleus. Since the intensity/interaction of light atoms is not much weaker than heavy atoms, the light atoms can be well-distinguished from heavy atoms, especially lithium, due to its negative neutron scattering length [32]. Last but not least, unlike XRD, neutron scattering intensity does not undergo obvious decay as the diffraction angle increases. This feature guarantees its high-angular (low d -spacing) signal to be of sufficient quality for further analysis of the local Li coordination environment and disorder. Besides all of the above, one may argue that Raman spectra also involves scattering. However, a Raman incident beam cannot trigger diffraction since its wavelength is too high (NPD and XRD wavelength is usually 0.1–3 Å corresponding to interplanar spacing), which means there is no diffraction peak at a certain angle, representing certain hkl indices. Raman spectra come from inelastic scattering, while NPD or XRD peaks come from elastic scattering, which means that Raman spectra undergo adsorption/excitation to identify components, type of bonding and functional groups via a shift in wave number. However, it is unable to locate atomic positions in a 3D crystal structure model as NPD or XRD does. In general, NPD is the only technique capable of precisely determining Li^+ nuclei locations in the lattice, along with their surrounding chemical environments and sublattice.

2. Fundamentals in Metal Halides and Neutron Powder Diffraction (NPD)

2.1. Crystallography

For a metal halide, its stacking structure is dependent on the arrangement of ions with a different radius and polarity. In halides, anions have larger ionic radii (Shannon radius [33], F^- 122 pm, Cl^- 167 pm, Br^- 182 pm, I^- 202 pm) than metal cations (88–118 pm) and Li^+ ions (Li^+ is 73 pm in tetrahedra, and 90 pm in octahedra). Therefore, the structural framework generally depends on an anion stacking sublattice and is modulated by the polarity and radius/volume of the cation species. According to the law of ionic packing, only when the cations and anions are in close contact (tightly stacking) can the structure be stable. Here, the radius ratio of cation to anion (r^+/r^-) is represented by δ . From a solid geometry deduction, when δ ranges from 0.732 to 1, the cation will adopt a MX_8 cubic polyhedron similar to that in CsCl structure. When δ is between 0.414 and 0.732, the smaller cation will coordinate with six anions to form an MX_6 octahedron. When the cation is even smaller, it will adopt an MX_4 tetrahedral structure with δ from 0.255 to 0.414, or an MX_3 triangle structure with δ from 0.155 to 0.255.

Ternary chloride Li_3MCl_6 often adopts hexagonal close-packing (hcp) or cubic close-packing (ccp) for its Cl^- sublattice structures [17]. The hcp anion lattice can be further divided into a trigonal structure (space group $P-3m1$, marked as hcp-T), and orthorhombic structure (space group $Pnma$, marked as hcp-O). The difference between hcp-O and hcp-T is that, while their Cl^- adopts ABAB stacking, their Li^+ and M^{3+} in octahedral sites obey orthorhombic and tetragonal symmetric arrangements, respectively. As for ccp, its anion Cl^- sublattice adopts an ABCABC stacking, but its cations adopt a monoclinic arrangement that makes the total structure monoclinic (marked as ccp-M). In fact, for all the above structures, it is the M metal radius that decides the lattice symmetry. When the M^{3+} Shannon radius [33] is in the range of 106.3 pm (Tb^{3+})–102 pm (Tm^{3+}), the Li_3MCl_6 lattice adopts a hcp-T structure with $\delta_{\text{M/Cl}}$ among 0.611–0.637. When M^{3+} gets smaller, that is 102 pm–100 pm (i.e., Yb^{3+} and Lu^{3+}), the Li_3MCl_6 structure will transform to the hcp-O with $\delta_{\text{M/Cl}}$ among 0.599–0.611. When the M^{3+} radius further reduces, the anion sublattice will transform from hcp to ccp, as illustrated by Li_3InCl_6 ($\delta_{\text{In/Cl}} = 0.563$) and Li_3ScCl_6 ($\delta_{\text{Sc/Cl}} = 0.530$). In contrast to the chloride-based ternary halides, bromide and iodide (Li_3MBr_6 and Li_3MI_6) all adopt the same monoclinic ccp-M structure [17].

2.2. Li⁺ Migration Kinetics

The Li⁺ ions' transport behavior is strongly dependent on the crystal lattice. In a monoclinic ccp-M structure [16][21], Li⁺ ions migrate along shared-edge octahedral sites which are connected by tetrahedral interstitial sites that form a 3D isotropic diffusion network. In a structure with hcp anion arrangements (hcp-O and hcp-T) [16], Li⁺ ions transport in a similar way via octahedra and interstitial tetrahedra in the ab-plane, but only via octahedra along the c-axis, since neighboring octahedral sites are directly linked to form the diffusion paths. It worth mentioning that, in contrast to a long-range order crystal lattice, local order–disorder of the Li⁺ sublattice can exist as a unique feature in a halide lattice, which is often accompanied by local octahedra distortion and phase transition due to defects. Both the disorder and distortion significantly affect the Li⁺ migration behavior. In addition, Li⁺ transport kinetics can be modulated by polarity-induced lattice dynamics. The proximity of metal ions will also stimulate or block the Li⁺ hopping (blocking effects), which influences Li⁺ transport kinetics.

2.3. NPD Data Processing

Similar to XRD, NPD also follows the Bragg diffraction law and diffraction geometry. NPD can be performed using a constant wavelength (CW) neutron beam or time-of-flight (TOF) neutron beam. The NPD data can be proceeded by Jana [34], Fullprof [35], etc. Conventionally, NPD data-processing includes the following steps: (1) Data collection. Instrument scientists will help users to load a powder sample in the sample holder on the diffractometer. A neutron beam will penetrate the sample and trigger diffraction. Multiple detectors at different angles will simultaneously collect diffraction peaks. After data correction, the original NPD data is returned to the users. (2) Indexing. If the crystal structure is already known, then this step can be skipped. However, if the structure is new (unknown, unreported), then this step is unavoidable. One needs to identify most diffraction peaks and then run an “indexing” function to find out the lattice type, lattice parameters, and space group. Note that indexing can be pre-run in the XRD pattern. The indexed lattice must be in agreement with TEM diffraction. (3) *hkl* Profile matching. This is also a refinement procedure. Before solving the atomic positions, one needs firstly to refine the peak shape, peak asymmetry (if it has any), zero shift, background and lattice parameters, with correct instrument parameters. Each peak and the background line should be well-simulated, usually with a total evaluating factor $\chi^2 < 2$. Since the program will later extract these simulated peak intensities of *hkl* indices for structure solution and structure refinements, this profile-matching step must be well-done. (4) Structure solution. If the structure model is already known, then this step is skipped. If it is new, then one must run a “solve” function. The program will try to solve the phases of structure factors and finally return a rough structure model via an inversed Fourier transform. This rough model is usually incomplete, and may have some flaws or mistakes in atom positions. (5) Rietveld refinements with structure model. By the least-square method, parameters like atom positions, occupancies and thermal displacements will be refined. As the simulated intensities (of the structure model) gradually approach the observed ones, the structure model is getting more and more close to the true crystal structure. (6) Difference Fourier calculation. This is to check the residue nuclei densities in the structure and to identify if they represent missing atoms. One needs to complement the missing atoms in the structure model and go back to step (5) to refine again, until all of the atoms are found out. (7) Completing the structure. After locating all the atoms, final rounds of refinements are needed to complete the whole structure. The structure and all parameters should be chemically reasonable, and evaluating factors should be within an acceptable range, empirically, $\chi^2 < 2$, $R_{wp} < 13\%$. (8) Bond-valence site energy (BVSE) calculation [36][37]. On the basis of this refined structure and *hkl* intensities, the BVSE will calculate the overall landscape of Li⁺ site energy and point out possible Li⁺ diffusion pathways in the structure.

For halide SSEs, NPD data can be singly used in a structure solution and subsequent Rietveld refinement to identify the Li⁺ distribution, which provides critical evidence to elucidate the mechanism of Li⁺ transport enhancement. In situ NPD as heating or charging/discharging can be used to monitor the dynamic process of continuous phase/structure evolution. Besides the above single usage, NPD and XRD/Synchrotron are often jointly refined to tackle a complicated structure or new structural phase. In this joint-refinement, NPD and XRD will be simultaneously refined. The XRD/Synchrotron data use their good advantage in detecting heavy ions (Cl⁻, Br⁻, Y³⁺, In³⁺, Zr⁴⁺, etc.) to quickly settle the whole lattice framework, while NPD data focus on locating Li⁺ ions and quantifying their chemical occupancy.

Whether singly or jointly used, the first important step is always to check the lattice type (space group) and lattice parameters, which give preliminary information on phase transition and lattice evolution. Note that lattice evolution is often associated with a distortion or tilting of Li/metal octahedra, which essentially affects Li⁺ migration behavior. The second step is to analyze the position (coordinates), occupancy, and isotropic/anisotropic thermal displacement of all ions. These three factors provide key information on the following: Li⁺ order–disorder, the existence of new Li sites, vacant interstitial sites (as intermediate states for ionic motion), blocking effects from metal ions, distortion or tilting of Li/Metal octahedra, dual-halogen mixing, etc. Particularly, Li⁺ thermal displacements are associated with migration behavior and anion lattice modulation. Last but not least is the difference Fourier procedure, which is based on the difference between simulated and

observed *hkl* intensities to calculate residual nuclei densities in one's structure model. Some of these residual densities may represent missing atoms. Difference Fourier procedure is significantly advantageous in discovering unexpected new Li⁺ sites which may reside in Li⁺ migration pathways and promote the migration.

The comprehensive structure model determined by neutron powder diffraction refinements enable the probable Li⁺ migration pathways to be revealed via a bond-valence site energy (BVSE) calculation [36][37]. Li⁺ site energies, $E_{\text{BVSE}}(\text{Li})$, will be calculated and presented in the form of a dense grid of points throughout the whole structure with the user-defined resolution (for instance 0.1 Å) using the Morse-type SoftBV interaction potential. An overall 3D isosurface landscape of $E_{\text{BVSE}}(\text{Li})$ will be depicted, superimposed upon the crystal structure. Regions of low BVSE can be identified as probable Li⁺ diffusion pathways. Metastable interstitial Li⁺ sites as a possible transition state for motion in the pathway can even be found. Moreover, an energy profile along certain migration pathways can be extracted from the above overall landscape to further analyze the migration barrier. The above information provides an intuitive explanation as to how structural modulation exactly affects migration behavior.

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