The atomic level journey from aqueous polyoxometalate to metal oxide


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1. Introduction

Aqueous precursor chemistries for functional metal oxide coatings are generating considerable excitement with the goal of sustainable, simple, low energy production of advanced materials. Yet the simple practice of using aqueous precursors is complicated by the multitude of interactions that occur between ions and water during dehydration. Here we use lithium polyoxoniobate salts to investigate the fundamental interactions in the transition from precursor cluster to oxide film. Small-angle X-ray scattering of solutions, total X-ray scattering of intermediate gels, and morphological and structural characterization of the lithium niobate thin films reveal the atomic level transitions between these states. The studies show that (1) lithium-[\(\text{H}_2\text{Nb}_6\text{O}_{19}\)]\(^{8-}\) has drastically different solution behaviour than lithium-[\(\text{Nb}_6\text{O}_{19}\)]\(^{8-}\), linked to the precursor salt structure (2) in both compositions, the intermediate gel preserves the polyoxoniobate clusters and show similar local order and (3) the morphology and phases of deposited films reflect the ions behaviour throughout the journey from cluster solution to metal oxide.

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Aqueous precursors tailored for the deposition of thin film materials are desirable for sustainable, simple, low energy production of advanced materials. Yet the simple practice of using aqueous precursors is complicated by the multitude of interactions that occur between ions and water during dehydration. Here we use lithium polyoxoniobate salts to investigate the fundamental interactions in the transition from precursor cluster to oxide film. Small-angle X-ray scattering of solutions, total X-ray scattering of intermediate gels, and morphological and structural characterization of the lithium niobate thin films reveal the atomic level transitions between these states. The studies show that (1) lithium-[\(\text{H}_2\text{Nb}_6\text{O}_{19}\)]\(^{8-}\) has drastically different solution behaviour than lithium-[\(\text{Nb}_6\text{O}_{19}\)]\(^{8-}\), linked to the precursor salt structure (2) in both compositions, the intermediate gel preserves the polyoxoniobate clusters and show similar local order and (3) the morphology and phases of deposited films reflect the ions behaviour throughout the journey from cluster solution to metal oxide.

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characterization methods included small angle X-ray scattering (SAXS) of aqueous precursor solutions; and total X-ray scattering of the intermediate gels from the room temperature amorphous state up to the crystalline state. On a rudimentary level, composition was expected to be the most important controlling factor of the transition from precursor to thin film coating. However we have learned through this study that acid–base and ion-association chemistries of the aqueous and gel systems also significantly affect the key processes in this atom-level journey.

2. Experimental

2.1. Preparation of lithium hexaniobate

Li$_4$[Nb$_6$O$_{19}$]·15.5H$_2$O (Li$_8$): Lithium hexaniobate, Li$_4$[Nb$_6$O$_{19}$]·15.5H$_2$O (FW 1169.61), was synthesized by a method similar to that which we reported prior, which is essentially an ion-exchange of K$^+$ for Li$^+$ [21]. Briefly, 5 g of K$_4$[Nb$_6$O$_{19}$]·xH$_2$O (synthesis reported prior) [22], which is highly soluble, is dissolved in a minimal amount of water. One liter of 1 M LiOH solution is prepared in a large beaker. While stirring the highly concentrated K$_4$[Nb$_6$O$_{19}$]·xH$_2$O solution is added rapidly to the LiOH solution via pipette. Upon halting the stirring; within a minute, the solution begins to cloud as microcrystals of less soluble lithium hexaniobate grow. The beaker is left for two days to allow full crystallization and settling. The crystals are collected by decanting the clear solution, centrifugation of the collected crystals and some mother liquor, and washing with methanol to rid of excess lithium and potassium hydroxide. Energy Dispersive Spectroscopy coupled with Scanning Electron Microscopy was used to confirm there was no K$^+$ present in the prepared salt. If potassium is detected, the clusters are recrystallized from 1 M LiOH solution again, and usually a second crystallization will rid of all K$^+$. Compositional analysis (wt%): theoretical (experimental) Nb: 46.6(48.1), Li: 4.69(4.68) A typical solution prepared with Li$_8$ had a pH of 12.0. Li$_8$ crystallizes as glassy, 5 g of K$_4$[Nb$_6$O$_{19}$]·14H$_2$O (Li$_6$): Lithium hexaniobate, Li$_6$[H$_2$Nb$_6$O$_{19}$]·14H$_2$O in 40 ml H$_2$O was acidified from pH 11.8 to 11.0 by 0.1 M HCl. Then, 120 ml isopropanol was added into that solution to form a cloudy solution which was centrifuged for 1 h. The obtained solid was collected, washed by isopropanol for three times and air dried at room temperature. Yield: 0.16 g. Compositional analysis (wt%): theoretical (experimental) Nb: 48.3(47.7), Li: 3.58(3.75) A typical solution prepared with Li$_6$ had a pH of 10.9. Li$_6$ never produces crystals sufficient for single-crystal analysis; rather they were characterized by powder diffraction, see Supporting information. This is pertinent to later discussion on film morphology.

2.2. Aqueous cluster solution studies

Small-angle X-ray scattering data were collected on an Anton Paar SAXSess instrument with Cu-K$_\alpha$ radiation and slit collimation in the q-range of ~0.1–7 nm$^{-1}$. Solutions of Li$_8$ and Li$_6$ were prepared by dissolution of the pure crystalline (Li$_8$) and microcrystalline (Li$_6$) powders isolated as described in prior Section 2.1 for a variety of concentrations ranging from 2.4 to 60 mM in H$_2$O solution and contained in a reusable 1.5 mm diameter quartz capillary tube for SAXS measurements. To ensure consistency between solutions, the most concentrated solution was prepared first, and less concentrated solutions were obtained by dilution of these solutions. Scattering was measured for 30 min or 1 h. After background subtraction and desmearing, the data were analyzed to determine size, size distribution, structure factors and PDF (pair distance distribution function) using the IRENA macros [31] within IGOR Pro.

2.3. Intermediate gel state studies

2.3.1. Preparation of glassy Li$_6$ and glassy Li$_8$

Saturated aqueous solutions (~70 mM) of Li$_6$ and Li$_8$ were separately prepared by dissolving in water and syringe-filtering (0.2 µm pores). The filtered solution was placed in a 40 ml beaker, and set in a fumehood for rapid evaporation. The resulting powders were a glassy form, confirmed amorphous by X-ray diffraction. These samples, along with microcrystalline Li$_6$, were used for total X-ray scattering studies. Thermal analysis was performed with a TA Instruments Q600 for thermogravimetric under nitrogen flow with a heating rate of 10 °C/min.

2.3.2. Total X-ray scattering studies

Total X-ray scattering data on glassy Li$_6$, glassy Li$_8$ and crystalline Li$_6$ were collected at the Advanced Photon Source, beamline 11-ID-B. Samples were prepared by grinding and packing powders into a kapton capillary and then encasing in a quartz capillary to ensure rigidity upon heating. These prepared samples were then mounted in a custom resistive element furnace and nitrogen gas was flowed over the sample during heating. Data was collected at one minute increments with a ramp rate of 10 °C/min and a wavelength of $\lambda=0.2114$ Å.

Phase purity of the lithium niobate was confirmed using Topas Academic [32] to fit a simulated diffraction pattern to the crystallized Li$_6$. To analyse the total scattering data, the collected CCD data was processed using a custom script utilizing Fit2d [33] and pdfgetx3 [34]. Fit2d was calibrated against cerium dioxide and used to subtract the background, perform instrument and sample corrections, and obtain the structure function, S(Q). The S(Q) was converted to the PDF through a fourier transform according to $G(r)=2\pi \int [Q S(Q) - 1] \sin(Qr) hQ dQ$ with a $Q_{max}$ value of 28 Å$^{-1}$.

Experimental PDF data of the crystallized LiNbO$_3$ was fit using PDFgui [35] and a good match between the two was achieved, demonstrating that the cluster transitioned completely to lithium niobate in its standard ferroelectric arrangement.

2.4. Thin film preparation and characterization

Prior to deposition, all substrates (sapphire 001 and silicon-001) were rinsed with H$_2$O, acetone and isopropanol, followed by a 10 min ash in an O$_2$ plasma. For standard characterization,
a 50 mM Li6 precursor solution was created by dissolving the clusters in DI water. Films were deposited on substrates by spin coating at 3000 rpm for 30 s, followed by an immediate hot plate cure at 80 °C for 3 min. The deposited films were then annealed in air at selected temperatures in the range 600–900 °C for 1 min. Films on Si substrates were used for scanning electron microscopy (SEM), X-ray reflectivity (XRR), and atomic force microscopy (AFM) measurements. SEM images were obtained by an FEI NOVA 230 high resolution SEM using immersion mode. XRR data were collected with Cu Kα radiation (40 kV, 40 mA) on Rigaku Ultima-IV. The beam was conditioned by using a 0.2 mm divergence slit, a 0.5 mm scattering slit, and a 0.2 mm receiving slit. Low-angle reflections from 0° to 5° (2θ) were collected in 0.01° steps at speed of 0.1°/min. Analyses were conducted with XPert Reflectivity V1.0 software using sample thickness, surface roughness, and density as fitting parameters. Surface roughness was also evaluated by using a Veeco Di Innova atomic force microscope operated in tapping mode with a Silicon TAP150 Al-G-10 probe at a scan rate of 1 Hz. A third-order plane fit was applied to all samples to limit distortion from the cantilever and sample tilt.

3. Results and discussion

3.1. The precursor salts

Lithium hexaniobate, Li8[Nb6O19]·15.5H2O, (Li8) was synthesized for this study and characterized by single-crystal X-ray diffraction (see Supplementary information). However, in its native form it has the incorrect ratio of Li:Nb to evolve any pure phase lithium niobate, LiNbO3, upon heating. Thus we converted Li8 to Li6[H2Nb6O19]·14H2O (Li6) via acidification in solution and re-isolation in the solid-state by precipitation with ethanol, which resulted in a phase with the correct ratio for the evolution of pure-phase LiNbO3. These two phases served as precursors for this study. The hexaniobate cluster, [Nb6O19]8−, has been described many times prior [22]. Briefly it is a superoctahedron of six mutually edge-sharing, distorted NbO6 octahedra (also presented later in Table 2 and Fig. 5). The central oxygen is μ6-bonded to all six Nb with long Nb–O bonds, ~2.35 Å. Trans to this for all six Nb atoms is a Nb=O double bond, ~1.78 Å. The Nb–O bond lengths of the twelve μ2-ONb2 are ~2.0 Å. In Li6, the cluster is diprotonated, [H2Nb6O19]15−, and we assume, based on many prior structures [22], that the protons reside on the μ2-ONb2 bridging oxos, which lengths the Nb–O=H bond distance to 2.2 Å. In the structure of Li8 and previously reported structures of lithium hexaniobate [21,27], the lithium forms its own adamantine cluster with water, see Fig. 2a. Moreover, the lithium–water lattice forms an interconnected network of the adamantine clusters, edge-sharing octahedral, and an 8-member ring of alternating lithium and water (Fig. 2b). The prevalence of this Li–water cluster in lithium hexaniobate crystalline lattices indicates this is a stable arrangement for Li+–water at the high pH (>12) conditions of self-assembly and crystallization. Li6, on the other hand, exhibits poorer crystallinity (powder diffraction pattern shown in Fig. S1), as we were unable to grow a good-quality single crystals for structure determination. The Li:Nb of both Li6 and Li8 is confirmed by wet-chemical analysis. We also identify the hexaniobate cluster in Li6 by the pair-distribution function (PDF) analysis of this precursor, which is discussed later.

3.2. The precursor solutions

We utilized SAXS (small-angle X-ray scattering) to evaluate the size, shape, and interspecies-interactions of Li6 and Li8 dissolved in water. Before any analyses were performed, we noted qualitatively poorer solubility of the Li8 salt. We analyzed three concentrations of Li6 and Li8 in water; the minimum concentration was limited by the signal to noise ratio of the scattering curve, and the maximum concentration represented the concentrations used for film deposition. The log(intensity)-log(q) (nm−1) plots for all six measurements are shown in Fig. 3; and pertinent calculated form and structure factors from curve fitting analyses are compiled in Table 1. The pair distance distribution functions (PDDF) of 2.4 mM solutions of both Li6 and Li8 show symmetric Gaussian curves (see Fig. S2) that indicate no polydispersity or ion-association. Additionally, Rg values determined from two different methods (Guinier approximation and PDDF) [31] suggest a monodisperse solution of [H2Nb6O19]8− (Table 1). These experimental Rg values agree reasonably well with the Rg calculated from the radius of the Lindqvist ion (from structural data, 4.2 Å), assuming an approximately spherical scatterer (3.25 Å, radius=Rg√3/5).

On the other hand, the higher concentration solutions from which the films are deposited reveal altogether different behaviors. The Li6 24 and 60 mmol concentration solutions have a structure factor (the small ‘bump’ around log q = 2, see Fig. 3), indicating the clusters are interacting with each other with a center-to-center distance of ~26 Å. Moreover, the PDDF curves (radial probability p (r) as a function of radius, Å, from the edge of the particle) show a second smaller peak which indicates dimer formation (Fig. 4). This is also seen in the slightly large Rg determined from the PDDF fit compared to that obtained from the Guinier approximation.

Since we are not able to grow diffraction quality single-crystals of Li6, we turn to the many solid-state structures we have available for A6[Li6Nb6O19]·xH2O (A=alkali) salts [22] for a structural model of the dimerization observed in the SAXS data. In K+, Rb+, and Cs+ salts of [H2Nb6O19], the protons reside on adjacent μ2-O ligands. This diprotonated edge is mutually H-bonded to the same face of a second cluster in the solid-state lattice (see Fig. 4 inset). This dimer has also been observed for the related decavanadate cluster in both the solid-state [36] and in solution [37]. Thus solid-state and solution evidence together suggest dimerization of diprotonated clusters as shown in Fig. 4 is not uncommon. The long axis of this dimer specie is ~15 Å, which is in agreement with linear extent of the second peak of the P(r) curve. Using SolX [38,39] and the solid-state structure of [H2Nb6O19]6− dimer [22], we calculated theoretical scattering curves for the specie shown in the inset of Fig. 4, and generated PDDF plots of both the dimer and the monomer forms. Linear combinations of these curves (Fig. S3) suggest the 24 and 60 mM Li6 solutions consist of 80–90% unassociated [H2Nb6O19]6− and 10–20% dimerized [H2Nb6O19]15−.

The prominent feature of the Li8 log(I)−log(q) plots for 25 and 50 mM solutions (Fig. 3) is a distinct upward slope in the low-q region. This is indicative of polydisperse solutions, and these curves were fit with two populations of scatterers: the population of smaller scatterers is consistent with [Nb6O19]8− monomer while the population of larger scatterers is likely an aggregate of multiple Lindqvist ions (Table 1). The PDDF curves (Fig. S2) could only be fit for the high-q region of the curve which is dominated by the population of smaller scatterers. Both the Rg and the symmetric P(r) curve shape indicate unassociated monomers; and these make up the majority of the solution. However, the low-q range is fitted to a second minor population of larger scatterers; 46 Å in radius (0.14% of total volume of scatterers) for the 25 mM solution and 22 Å in radius (1.6% of total volume of scatterers) for the 50 mM solution. We have interpreted this as incipient crystallization of the Li8 salt, and the large aggregates are still-soluble nuclei. The smaller, more abundant nuclei in the higher concentration solution are indeed consistent with crystallization/precipitation behavior; smaller and more abundant crystals are grown from a solution of higher concentration, and larger and fewer crystals grow from a lower concentration solution.
Finally, we return to the solid-state structure of \( \text{Li}_8 \) to discuss why these large aggregates form in the solution, whereas as dimerization is the more prevalent association mechanism for \( \text{Li}_6 \). In \( \text{Li}_8 \) solutions, we may expect cationic lithium–water clusters that are evident in solid-state structures to persist. Polynuclear anions plus polynuclear cations (\([\text{Nb}_6\text{O}_{19}]^{8-}\) and lithium–water clusters, respectively) result in poor solubility, presumably due to high negative enthalpy of crystallization, as has been observed for aluminum polycation Keggin ions with tungstate polyanion Keggin ions [40]. This likely explains why we observe nucleation in these solutions via SAXS, as well as qualitatively poorer solubility of \( \text{Li}_8 \) compared to \( \text{Li}_6 \). On the other hand, the lower pH (\( \sim 10 \)) of the \( \text{Li}_6 \) solutions appears to both disrupt the assembly of the \( \text{Li}^+ \)–water clusters and favor dimerization via

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**Fig. 2.** Views of \( \text{Li}_8 \). (a) (left) shows two \([\text{Nb}_6\text{O}_{19}]^{8-}\) Lindqvist ions plus the \( \text{Li}^- \)–water adamantoid cluster. (b) (right) shows the arrangement of \( \text{Li}^+ \) and water only on the lattice. Blue octahedra are \( \text{NbO}_6 \), green spheres are \( \text{Li} \), red spheres are \( \text{O} \), black spheres are \( \text{H} \). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 3.** \( \log(\text{intensity}) – \log(\text{q}) \) SAXS scattering curves for \( \text{Li}_8 \) (left) and \( \text{Li}_6 \) (right) solutions of variable concentration with the concentration decreasing from top to bottom. The dotted black lines are curve fits that include structural parameters (\( \text{Li}_6 \)) or simultaneous fit of two phases (\( \text{Li}_8 \)).

**Table 1**
Calculated parameters from SAXS data of precursor solutions.

<table>
<thead>
<tr>
<th>Form factors: ( R_g ) (Å)</th>
<th>Guinier approximation</th>
<th>PDDF</th>
<th>Modeling II*</th>
<th>Ratio of two phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_6 )</td>
<td>2.4 mM</td>
<td>3.5 (1)</td>
<td>3.1 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5 mM</td>
<td>3.4 (1)</td>
<td>3.3 (4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24 mM</td>
<td>3.6 (3)</td>
<td>4.4 (2)</td>
<td>3.6 (2)</td>
</tr>
<tr>
<td></td>
<td>25 mM</td>
<td>3.9 (3)</td>
<td>3.4 (3)</td>
<td>3.4/46.0</td>
</tr>
<tr>
<td></td>
<td>60 mM</td>
<td>3.4 (3)</td>
<td>4.4 (3)</td>
<td>3.6 (2)</td>
</tr>
<tr>
<td></td>
<td>50 mM</td>
<td>4.8 (3)</td>
<td>4.0 (1)</td>
<td>3.5/22.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure factors</th>
<th>Number of scatters in nearest neighbor sphere (phi)</th>
<th>Center-to-center distance of scatters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_6 )</td>
<td>24 mM</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>60 mM</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>25</td>
</tr>
</tbody>
</table>

* Modeling II in Irena used to simultaneously fits \( R_g \) and relative concentration of two phases.
cluster protonation and hydrogen bonding. This is self-evident by the inability to crystallize Li6, as well as the observed different solutions behavior.

3.3. The intermediate gel state

The intermediate gel state is deposited on a substrate via spin coating of the precursor solution, see Fig. 1. With rotation of the substrate, the solution spreads and evaporates very rapidly. Obtaining a gel is one of the most crucial steps, and usually the least well-understood step in the transition from precursor to final thin film product. An optimal gel is continuous and smooth, and usually an amorphous network. To characterize the intermediate gel-state and its conversion to metal oxide, we produced glassy samples (i.e. not crystalline) of Li6 and Li8 in a bulk form. These glassy Li6 and Li8 samples lack long-range order, and thus are suitable for characterization via total X-ray scattering to determine the local structure in addition to the long-range structure that evolves with in-situ heating.

Fig. 5 shows the room temperature PDF (pair distribution function) of Li6 and Li8, in addition to the simulated PDF for a single [Nb6O19]8– cluster and a dimer of [H2Nb6O19]6– clusters associated by hydrogen-bonding. Also shown is a structural representation of the [H2Nb6O19]6– dimer, and atom–atom distance contributions to the PDF peaks are listed in Table 2. For this structural representation, we used a previously published diprotonated Lindqvist structure Cs6[H2Nb6O19].9H2O [22] to describe pair distances within the cluster, between two mutually H-bonded clusters and between clusters and water molecules. Dominating are two peaks attributed to the Nb–Nb distances (3.3 and 4.8 Å) within a single cluster, showing preservation of the [Nb6O19]8– ion in this intermediate gel state. The peak centered at 2.0 Å is the Nb–O distance of the μ2–ONb2 bonds. In both the calculated and experimental PDFs, we do not see a distinct Nb=O (1.75 Å) peak, as it is overlapping with the aforementioned 2.0 Å peak. On the other hand, we distinctly observe the 2.4 Å peak that corresponds with the Nb–O distance between the central O and the six Nb of a cluster. It is unclear why the Nb=O peak is not distinct in the simulated PDF. In the glassy Li6 and Li8 samples, the clusters are distorted via association with lattice water, Li+ and H+, which likely results in a range in Nb–O distances from 1.7 to 2.2 Å, consistent with the base width of this peak. In general, the PDFs of Li6 and Li8 are very similar. The peaks between r~6 and 8 Å are most likely related to cluster–cluster association, as peaks in this region are observed in the simulated PDF for the dimer. However, we do not expect these to match exactly between simulation and experiment, because the simulation provides only one arrangement, but these samples without long range order have many possible arrangements of the clusters. Peak 3 (2.7 Å) is a very common H-bonding distance between two water molecules or water and a cluster oxygen. We have assigned both peak 3 and peak 6 to O–O distances between clusters and water in the disordered lattice. These are not observed in the simulations which are dominated by Nb–Nb distances. Contributions from Li–O and Li–Li distances are diminutive, as the scattering intensity scales with atomic number.

The variable temperature PDFs of Li6 and Li8, from room temperature to 700 C reveal differences in their evolution to crystalline lithium niobate phases (Fig. 6). The Bragg diffraction peaks (top spectra in Fig. 6) for heated Li8 become evident around 300 C, and approximately 400 C for Li6. Simultaneous with the appearance of diffraction peaks for Li8, the short Nb=O distance at 1.75 Å becomes evident and the 2.0 Å Nb–O distance loses intensity. This may be a direct result of dehydration and therefore decreased hydrogen-bonding of water with Nb=O. Additionally, both the diffraction peaks and the PDF of heated Li8 reveal that

<table>
<thead>
<tr>
<th>Peak</th>
<th>Distance (Å) from structural model</th>
<th>Description of atom pair(s)</th>
<th>Examples of atom pair(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>μ2–O–Nb</td>
<td>Nb6–O1</td>
</tr>
<tr>
<td>2</td>
<td>2.2</td>
<td>μ2–O–Nb</td>
<td>O6–Nb</td>
</tr>
<tr>
<td>3</td>
<td>2.9</td>
<td>μ2–O–OH2</td>
<td>O1–O25</td>
</tr>
<tr>
<td>4</td>
<td>3.4</td>
<td>cis–Nb–Nb</td>
<td>Nb6–Nb1</td>
</tr>
<tr>
<td>5</td>
<td>3.8</td>
<td>Nb–OH2</td>
<td>Nb5–O25</td>
</tr>
<tr>
<td>6</td>
<td>4.1</td>
<td>μ2–O–Nb of adjacent H-bonded clusters</td>
<td>O18–Nb5</td>
</tr>
<tr>
<td>7</td>
<td>4.8</td>
<td>trans–Nb–Nb</td>
<td>Nb6–Nb3</td>
</tr>
<tr>
<td>8</td>
<td>5.1</td>
<td>Nb–Nb of adjacent H-bonded clusters</td>
<td>Nb5–Nb3</td>
</tr>
</tbody>
</table>

* Two mutually H-bonded [H2Nb6O19]6– clusters in Cs6[H2Nb6O19].9H2O (Cs2) [22] was used as a model to identify pair distances in the experimental data.
two phases crystallize simultaneously: ordered Li$_3$NbO$_4$ and perovskite LiNbO$_3$ (see Fig. S8 for Pawley fit of Li$_6$ at 600 °C). Within the lattice of ordered Li$_3$NbO$_4$, there is an Nb-tetramer of edge-sharing Nb octahedra that resembles a fragment of the Lindqvist ion, see Fig. 7. This phase likely forms because of the similarity of its local structure to that of glassy Li$_8$. At ~400 °C, the 1.75 Å peak diminishes in correlation with rise in the 2.0 Å peak; and once again around 600 °C, these peaks swap intensity. These events correlate with conversion of Li$_3$NbO$_4$ to LiNbO$_3$, and formation of Nb$_2$O$_5$ as a result of lithium volatilization, respectively. On the other hand, Li$_6$ converts directly to LiNbO$_3$ at 400 °C, with no other intermediates or products detected in either the X-ray PDF or the X-ray diffraction data (see also Figs. S9 and S10 for Pawley and PDFgui fits, respectively). These results lead to the question of why does ordered Li$_3$NbO$_4$ form from Li$_6$ and not Li$_8$, when they have similar local structure featuring the Lindqvist ion? Two possible hypotheses include: (1) the protonated state of Li$_6$Lindqvist ions renders it more reactive to atomic level mobility that is necessary to rearrange and form LiNbO$_3$ with less Nb–O–Nb connectivity (Fig. 7) or (2) glassy Li$_8$, like its crystalline form, has
more short-range order in the Li–water species than Li6. To summarize, these X-ray scattering results provide compelling direct evidence that atomic-level structure in a precursor profoundly affects its evolution to a metal oxide product.

The thermogravimetric curves (Fig. 8) provide further information regarding the conversion of Li6 and Li8 (crystalline and glassy) to lithium niobate phases. The higher weight loss of the Li8 phase quantitatively corresponds with evaporation of lithium oxide. This agrees with the X-ray scattering studies discussed above, showing formation of Nb2O5 upon loss of lithium above 600 °C. Moreover, these results are also confirmed by the ex-situ heating-X-ray diffraction studies of Li6 and Li8 (see Supporting Information). This is particularly evident in the glassy sample, as there is a distinct weight-loss event above 600 °C, in correlation with the formation of more Nb-rich phases in both the in-situ and ex-situ heating studies. Crystalline Li6 and glassy Li6 have more similar dehydration behaviour than crystalline Li8 and glassy Li8. This is because Li6 is poorly crystalline, and its arrangement of ions and water molecules is likely more similar to the glassy state than the case of Li8. The less ordered phases lose water and lithium oxide in more distinct steps, compared to crystalline Li8. Initially this seems counterintuitive, but it is probably because the poorly ordered phases are more dense and therefore species are less readily volatilized.

3.4. The metal oxide coating

Crystallization of a dissolved precursor on a substrate instead of gel-formation can be detrimental to film quality, because it does not provide a continuous coating. The disparate behaviors of Li6 and Li8 in solution as observed by SAXS and interpreted by the solid-state structures suggest they should also exhibit different film deposition character. Fig. 9a shows surface and cross-section SEM images of a typical film from Li6 dehydrated at 80 °C (a & b) and annealed at 600 °C (c & d). The surface of the film dehydrated at 80 °C is very smooth: no features are discernible in the top-view SEM. The high-resolution cross-section SEM image reveals a continuous and dense film. For the crystallized film annealed at 600 °C, grain growth and grain boundary formation become apparent in both top-view and cross-section SEM images. It is noteworthy that all films from Li6 are smooth and continuous without visible cracks and voids even after undergoing shrinkage associated with drying and crystallization. X-ray reflectivity (XRR) and ellipsometry data quantified film thickness, roughness, and density. These data for the 80 °C (3 min) and 600 °C (1 min) heated films, along with the model fits, are compiled in Supplementary information (Figs. S6 and S7). The surface roughness for the film dried at 80 °C for 3 min is 0.3 nm, and it increases to about 1.3 nm after annealing at 600 °C. The in-situ heating, X-ray scattering studies discussed prior showed crystallization initiated at 400 °C. The density increases from 3.0 to 4.3 g/cm³ [3] from the room-
temperature gel state to the 600°C annealed film. The 4.3 g/cm³ density corresponds to 92% of the theoretical density of LiNbO₃, which is similar to that reported prior for LiNbO₃ films deposited from aqueous solution [30]. To summarize briefly, Li₆ precursor produced pure-phase LiNbO₃ (Fig. 10) films with continuous coverage.

On the other hand, Li₈ produced films that are composed of both Li₃NbO₄ and LiNbO₃, and exhibit island-growth morphology (Figs. 10 and 9b). This film was likewise annealed at 600°C, and the euhedral ‘islands’ of lithium niobate phases preserve the morphology of the Li₈ crystalline salt. It is evident that Li₈ is crystallizing on the substrate upon spin coating and rapid evaporation of the water. These results relate directly to the behavior of Li₆ and Li₈ in solution as observed by SAXS: crystallization of the Li-water adamantoid cationic clusters with anionic Lindqvist ion clusters is energetically favorable. Therefore, the intermediate gel formation necessary for continuous metal oxide coating is inhibited.

4. Conclusions

This work illustrates the importance of both manipulating and interpreting the atomic level interactions of aqueous species that are precursors to materials self-assembled in water. Almost always in aqueous chemistry, there are counterions which are considered ‘innocent’; and in the case of solution deposition, these counterion species need to be removed (such as by ion-exchange, vaporization or combustion) if they are not a desired component of the targeted thin film product. In the current study, the counterions are both byproducts (H⁺ or excess Li⁺) and film components (stoichiometric Li⁺); yet all significantly influence the film properties. By simply replacing 25% of the Li⁺ counterions with H⁺, the interactions between the anionic metal-oxo clusters, alkali counterions, and water molecules change dramatically, as observed in solution behavior, dehydration and crystallization of the gel state, and the resulting thin film morphologies and phases. This evolution in solution and subsequent gel chemistry made the difference between an excellent precursor solution and a problematic precursor solution; the former producing a continuous dense coating of a single phase and the latter exhibiting island growth and formation of mixed phases. Several explanations are possible in this particular case; and it is likely that all factors contribute: (1) the lithium–water adamantoid clusters of the Li₈ precursor that impart poor solubility and high lattice crystallization energy are disrupted by the pH decrease of the Li₆ solution, (2) the more prevalent dimer association of the [H₂Nb₃O₁₉]⁶⁺ cluster competes with association of the lithium–water clusters, resulting in a more soluble precursor chemistry, or (3) the dimer association dominates in the transition from solution to a solid gel state, and serves as the ‘glue’ for continuous and smooth substrate coverage. Moreover, extensive inter-cluster H-bonding, and H-bonding between water molecules and the clusters in the amorphous gel state may weaken the intracluster bonds and ease rearrangement into the final metal oxide product. While each solution-to-gel-to-solid system for aqueous preparation of metal oxides has unique characteristics and challenges associated with its specific chemistry; the universal importance of interaction of ions with each other and with water in solutions and gels cannot be underestimated.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jssc.2014.09.039.

References