High Throughput Methodology for Synthesis, Screening, and Optimization of Solid State Lithium Ion Electrolytes

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ABSTRACT: A study of the lithium ion conductor Li₃₋ₓLaₓ/₃TiO₃ solid solution and the surrounding composition space was carried out using a high throughput physical vapor deposition system. An optimum total ionic conductivity value of 5.45 × 10⁻⁴ S cm⁻¹ was obtained for the composition Li₀.₁₇La₀.₂₉Ti₀.₅₄ (Li₃₋ₓLaₓ/₃−ₓTiO₃ x = 0.11). This optimum value was calculated using an artificial neural network model based on the empirical data. Due to the large scale of the data set produced and the complexity of synthesis, informatics tools were required to analyze the data. Partition analysis was carried out to determine the synthetic parameters of importance and their threshold values. Multivariate curve resolution and principal component analysis were applied to the diffraction data set. This analysis enabled the construction of phase distribution diagrams, illustrating both the phases obtained and the compositional zones in which they occur. The synthetic technique presented has significant advantages over other thin film and bulk methodologies, in terms of both the compositional range covered and the nature of the materials produced.

KEYWORDS: solid state electrolyte, thin film, neural network

INTRODUCTION

The advancement of solid state battery technology is dependent on the development of highly conductive, stable electrolytes. A rapid means to explore candidate electrolyte materials is therefore of great interest. We present here a high throughput methodology for the synthesis, characterization, and optimization of thin film, solid state lithium ion electrolyte materials. The perovskite Li₀.₃₄La₀.₅₁TiO₂.₉₄ (Li₃₋ₓLaₓ/₃−ₓTiO₃ x = 0.11) has previously been reported to have a bulk conductivity of 10⁻³ S cm⁻¹ and a total conductivity of 7 × 10⁻⁵ S cm⁻¹.¹ Further work demonstrated that the bulk lithium ion conductivity varies along the Li₀.₃₆La₀.₂₉−ₓTiO₃ (≈0.15 > x > ~0.04) solid solution line, with an optimum value at x = 0.1.² Kawai and Kuwano also reported that at the upper limit of lithium content (x > ~0.15) Li₀.₃₆Ti₁.₅₇O₄ and Li₃La₂Ti₃O₁₀ crystalline phases were observed in addition to the solid solution. Materials produced at the lower limit of lithium content (x ~ 0.04) were observed to give rise to a mixture of La₂Ti₂O₇ and the perovskite phase. Generally this system is produced by traditional sintering methods, as in the previous examples; however, thin films have been produced by a number of routes including: sol–gel,³ laser ablation,⁴–⁶ and e-beam evaporation.⁷ As a result of the extensive work published in the literature and the high lithium ion conductivities previously measured, this system is an ideal benchmark for a high throughput screen.

A successful solid state electrolyte material must demonstrate a high ionic conductivity, although this may be compromised by utilizing a thin film (<1 μm). In addition to being a selective ion conductor (to prevent material breakdown), the material should have a very low electrical conductivity (<10⁻¹² S cm⁻¹) to ensure a long operating lifetime.⁸

The high throughput physical vapor deposition system (HT-PVD), described previously,⁹,¹⁰ provides a means to produce thin film sample libraries, containing hundreds of compositionally unique fields. This synthetic method has been previously used by the authors for studies of metallic alloys,¹¹ Au nanoparticles on substoichiometric oxides,¹² hydrides,¹³ and complex oxides.¹⁴

A complete comparison of this synthetic method with other high throughput thin film techniques is beyond the scope of this report; however, it is possible to set this method in the context of other thin film methods. There are broadly two groups of thin film synthesis: “fast sequential” and parallel. The former is characterized by the use of user defined masks or moving shutters to build up layers of different elements resulting in a net variation in composition.¹⁵–¹⁹ Typically this is followed by heating, to achieve efficient mixing of the different layers;¹⁹ however,
efficient mixing has been achieved by depositing sequential subatomic layers of various elements. The latter parallel approach takes advantage of the natural profile of off-axis sources which, under the right conditions, give deposition rates which vary across the sample. By controlling the relative rates of the elements this method has been shown to yield control over compositional ranges.

The parallel HT-PVD method is simple, since shadow masks are only needed if discrete samples are required. Additionally, deposits can typically be accomplished in one layer, because the elements are deposited simultaneously; therefore, the process can be accomplished quickly and without the need for thermal treatment. Combining this synthetic method with fast sequential screening of electrical properties, structural and elemental compositions, it is possible to rapidly accelerate the rate of materials development. These experimental techniques yield large data sets, which are not readily analyzed by hand. Therefore chemometric techniques such as principal component analysis (PCA); multivariate curve resolution-alternating least-squares (MCR), and artificial neural networks (ANN) have enabled the elucidation of optimum material and synthetic parameters within this system. These show good agreement with the existing literature. In addition, data mining techniques have been applied to determine the synthetic parameters which contribute to producing properties, such as a capacitive response or higher purity perovskite materials.

**Experimental Procedures**

**Synthetic Methodology.** The HT-PVD system comprises a physical vapor deposition (PVD) chamber with a plurality of interchangeable off-axis electron beam evaporator or Knudsen cell sources, for co-evaporation of elemental Li, La, and Ti onto a substrate in the presence of atomic oxygen, produced from a plasma source. Each source is independently controlled in terms of both the thickness gradient (“wedge”) across the substrate and the rate of deposition. The wedge is obtained by placing a shutter in a predetermined position prior to commencing the deposition process. This creates a shadow on the substrate. Compositional gradients can thereby be controlled utilizing both the source temperatures and the wedge positions, a distinct advantage compared to other natural profile deposition techniques. The synthetic system is described in detail elsewhere.

**Experimental Section.** Depositions were carried out on a range of substrates including: MgO; multilayer substrates; Si/ 

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Figure 1. Distribution of data set across composition space. The Li₃La₂/₃TiO₃ solid solution line is shown in red for observed perovskite materials.

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the sample libraries. These measurements were automated using a probe station. X-ray diffraction measurements were carried out on the sample libraries as close as possible to the electrode arrays. Diffraction data is generally reported for the range 20.8 ≤ 2θ ≤ 36.78° to avoid the dominant Pt (100) reflection at 39.76° 2θ from the underlying substrate. Throughout, measurements were made on every field within the sample libraries providing a consistent data set.

**Description of Samples and Analysis Methods.** Thirty-five sample libraries were synthesized, on five different substrates. The focus of the synthetic work was the Li₃La₂/₃TiO₃ solid solution line, encompassing the region surrounding this line. This line and the distribution of the compositional data around the line are shown in Figure 1. The thickness of the fields within these libraries varied between 76 and 972 nm.

All sample libraries synthesized at 25 °C were amorphous prior to ex situ thermal treatment. Crystalline materials were observed when samples were deposited at elevated temperature and following annealing. Diffraction data from representative samples of the composition Li₃La₂/₃TiO₃ were deposited on SSTOP, are shown in Figure 2. The field deposited at 25 °C was observed to be amorphous. Diffraction peaks were observed in the fields annealed to 700 °C and deposited at 700 °C. Following thermal treatment, the samples exhibited defects such as pinholes or cracking. Macro scale decrpetiation was also observed in certain regions of sample libraries.

Within the frequency limitations of the impedance instrument used throughout this investigation, it was not possible to observe the characteristic “blocking spike”, typical of bulk oxide lithium ion conductors at room temperature. It was also not possible to distinguish bulk and grain boundary components of the impedance response. This observation has been previously reported.

Since we are unable to distinguish bulk from grain boundary conductivities, all conductivity values reported here refer to total ionic conductivity.

In addition to capacitive behavior, we also observed mixed and electrically conductive materials. This was attributed to the multiphase nature of the thin films, which may include electrically conductive phases such as TiO₂. Traditional analysis, suitable for bulk samples, concentrates on the complex plane (Cole–Cole plot) which emphasizes the most resistive elements in the
measured sample. To highlight the components with the smallest capacitance it is necessary to determine the maxima in the Modulus plot (M" vs f).

To process the raw electrochemical impedance data into a useful figure of merit for our investigation, it was initially necessary to classify the data into one of four responses. The classification of materials as “straight short”, “resistive short”, “mixed conductor”, and “capacitive” was determined by the different types of response observed within a given frequency range (1 – 10⁶ Hz). Data which did not fall into one of the four categories above was classified as “insulating”. For typical samples, these criteria can be evaluated as thresholds, detailed in the Supporting Information with examples of data.

Once classified, the total ionic conductivity of the material was calculated. The method used was specific to the behavior observed. The conductivity of materials exhibiting straight shorts was calculated by determining the material resistance using the Z" value at the minimum Z". The case of resistive shorts, the conductivity was calculated by finding the maximum value in the M" versus log(f) plot. Assuming a single resistor and capacitor in parallel, the conductivity of the material was then determined using eq 1. In the case of both mixed conductors and capacitive behavior the resistance of the material is determined using the modulus method. Gaussian curves were fitted to the M" versus log(f) to determine both the maximum modulus value and the frequency at which it occurs. The resistance of the material was then determined using eq 1. Materials exhibiting behavior which could not be classified by any of the criteria detailed above, or gave rise to Gaussian curve with poor fits, were classified as resistive. Analysis of the whole data set, including raw measurements make up the data matrix, the resultant analysis presents the scores and loadings of i components. In all MCR models reported here, closure constraints and non-negative constraints were applied.

\[
\text{Data Matrix} \times \text{Model scores} \times \text{Model loadings} + \text{Error} = 0
\]

The scores were interpreted as a series of fractional concentrations for each of the i identified components. The loading data was interpreted as diffraction patterns for each of the i identified components. A complete explanation of this methodology is given by Long et al. Since this analysis does not take into account the structure factor for each of the different phases, the percentage values shown here can only be taken as a first approximation of the true values.

The number of components required to describe the diffraction data sufficiently, was determined by comparing the variance captured using a Principal Component Analysis (PCA) model and that captured by the MCR model. Thirteen components were selected to model the SSTOP data set.

Once calculated, the component patterns of the model were compared to literature diffraction patterns (ICDD database, PDF 4+, 2009). The thirteen components were attributed to six unique materials. Multiple components were attributed to La₆Ti₉O₂₄, La₃Ti₂O₇, and TiO₂₋ₓ (x = 0.25, 0.33). It is thought that multiple components were required to describe these single phases, because of different degrees of preferential orientation across multiple sample libraries. The resultant changes in peak intensities, because of orientation, lead to the identification of multiple components for a single phase. In the case of TiO₂₋ₓ distinct patterns were expected as a result of differing oxygen stoichiometries.

**RESULTS AND DISCUSSION**

To establish an overview of the large data set (6276 fields) it was beneficial to use a summary plot, such as that generated using recursive partitioning. In this case, a decision tree was produced showing the number of fields exhibiting a given impedance behavior. The splitting of the data within the analysis was carried out by searching all possible divisions and selecting the division which maximized the significance of each split. Analyzing the data using such a recursive partition method, we observed that 19.0% of the samples deposited on SSTOP, Silica/Pt, and SSTOP/SRO (Group A) exhibited capacitive behavior. Within the second group of substrates SSTOP, Si/SRO and MgO/Pt (Group B) 1.4% of the samples exhibited such behavior. In this instance, analysis was limited to the synthetic parameters (substrate, thermal processing temperatures) and elemental composition (see Supporting Information). Note that the distribution of compositions within Group A and B were similar (see Supporting Information) assuring us that the difference observed because of the substrates is not confounded with the composition.

**Phase Behavior of Samples Deposited on SSTOP.** In an effort to further understand the crystallization behavior of this system, 18 sample libraries, all deposited on SSTOP were selected for further analysis. In this case, the diffraction data, in addition to the electrical response, was analyzed. The diffraction data was factorized into components using multivariate curve resolution-alternating least-squares (MCR). The concept of this process is shown in eq 2: m samples with n intensity measurements make up the data matrix, the resultant analysis presents the scores and loadings of i components. In all MCR models reported here, closure constraints and non-negative constraints were applied.

\[
\text{Data Matrix} \times \text{Model scores} \times \text{Model loadings} + \text{Error} = 0
\]

The scores were interpreted as a series of fractional concentrations for each of the i identified components. The loading data was interpreted as diffraction patterns for each of the i identified components. A complete explanation of this methodology is given by Long et al. Since this analysis does not take into account the structure factor for each of the different phases, the percentage values shown here can only be taken as a first approximation of the true values.

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The positions of the pure phases observed are shown in blue. Solid black lines indicate the boundaries between mixed phases, as determined from mean distribution of components. The dashed black lines indicate the extent on the data set. The gray line indicates the predicted extension of the $\text{TiO}_2$ line + La$_2$Ti$_6$O$_{18}$ + ($\text{LiLa}_{1.5}$)$\text{Ti}_5\text{O}_{15}$ region. The asterisk above the Li$_2$La$_2$(Ti$_3$O$_{10}$) phase indicates that this is the parent compound; the phase identified within the MCR model is thought to be a modified form of this material.

![Figure 3](https://dx.doi.org/10.1021/co100075f) Crystalline phase distribution map for samples deposited on SSTOP at 25 °C and annealed at 700 °C in O$_2$. The bold solid red line indicates the position of the known Li$_3$La$_{2/3}$Ti$_{10}$O$_{30}$ solid solution line. The positions of the pure phases observed are shown in blue. Solid black lines indicate the boundaries between mixed phases, as determined from mean distribution of components. The dashed black lines indicate the extent on the data set. The gray line indicates the predicted extension of the TiO$_2$ line + La$_2$Ti$_6$O$_{18}$ + ($\text{LiLa}_{1.5}$)$\text{Ti}_5\text{O}_{15}$ region. The asterisk above the Li$_2$La$_2$(Ti$_3$O$_{10}$) phase indicates that this is the parent compound; the phase identified within the MCR model is thought to be a modified form of this material.

![Figure 4](https://dx.doi.org/10.1021/co100075f) Baseline corrected diffraction pattern of Li$_{0.30}$La$_{0.22}$Ti$_{0.48}$ deposited on SSTOP at 25 °C and annealed in O$_2$ for 3 h at 700 °C (black). This material was calculated to have a Li$_2$La$_2$(Ti$_3$O$_{10}$) (01-087-1169) component score (concentration) of 0.83). The region of the diffractionogram analyzed using MCR is highlighted in gray (20.8° ≤ 2θ ≤ 36.78°). The peak positions of Li$_2$La$_2$(Ti$_3$O$_{10}$), with a reduced $c$-axis, are indicated by the + signs. The peak marked * is attributed to the Pt(100) reflection.

From this analysis it was possible to illustrate the distribution of phases across compositional space, Figure 3. Although the phase distributions encompass the position of the pure phases (with the exception of Li$_2$La$_2$(Ti$_3$O$_{10}$)) the distributions do not exactly match those expected at thermodynamic equilibrium. This diagram should not be considered as an equilibrium phase diagram, but instead as a crystalline phase distribution map observed within these thin films, as a function of composition.

![Figure 5](https://dx.doi.org/10.1021/co100075f) Crystalline phase distribution map for samples deposited on MgO at 700 °C. The bold solid red line indicates the position of the known Li$_3$La$_2/3$-xTiO$_3$ solid solution line. The positions of the pure phases observed are shown in blue. Solid black lines indicate the boundaries between mixed phases, as determined from mean distribution of components. The dashed black lines indicate the extent on the data set.

In the case of Li$_2$La$_2$(Ti$_3$O$_{10}$) the crystalline phase distribution map indicated a region away from the pure phase composition of this phase (Figure 3). Examination of the MCR component reveals that this component can be attributed to the Li$_3$La$_{2/3}$$(\text{TiO}_3)$ material, with a reduced $c$-axis (26.4383 Å cf. 26.56 Å, 0.45% reduction). This reduction is concomitant with the increased lithium concentration within the material. A material with a high component score (0.83) for this phase is shown in Figure 4. The calculated pattern for the Li$_3$La$_{2/3}$$(\text{TiO}_3)$ with a reduced unit cell is also shown. Previous work by Kawai and Kuwano has shown that a small amount of Li$_2$La$_2$(Ti$_3$O$_{10}$) is obtained in bulk samples when excess lithium is used to prepare the Li$_3$La$_2/3$-xTiO$_3$ solid solution.

**Phase Behavior of Samples Deposited on MgO/Pt.** In the same manner as described previously, four samples deposited on MgO, were analyzed using the PCA and MCR method. In this case six components were noted to describe the data adequately. The six components were compared to a database of diffraction patterns and were assigned to five phases: La$_4$Ti$_6$O$_{24}$, Li$_{20}$La$_{24}$Ti$_5$O$_{56}$, La$_2$Ti$_2$O$_7$, TiO$_2$-$x$ ($x = 0.14$) and Li$_{13}$La$_{2/3}$-xTiO$_3$ ($x = 0.11$). Two components were attributed to the La$_2$Ti$_2$O$_7$ phase. It was noted that the modified Li$_2$La$_2$(Ti$_3$O$_{10}$) phase observed previously was not observed in this system, instead the same compositional region is occupied by a mixture of La$_4$Ti$_6$O$_{24}$ and TiO$_2$-$x$. Figure 5. Because of the low diffraction cross section of Li, crystalline materials dominated by this element may be missed in thin film materials.

**Synthesis of Crystalline Li$_3$La$_2/3$-xTiO$_3$.** Performing recursive partitioning analysis on the calculated percentage of crystalline Li$_3$La$_2/3$-xTiO$_3$ within the 3903 fields deposited on SSTOP allowed us to determine the important factors in achieving high concentrations of crystalline Li$_3$La$_2/3$-xTiO$_3$. Figure 6 illustrates that the primary difference in the data was determined to be caused by the concentration of lithium within the thin film.
The second most important factor in achieving high concentrations is the annealing temperature.

To make best use of the large number of data points collected, over a wide range of parameter space (composition, thickness, deposition temperature, annealing temperature) an artificial neural network was constructed utilizing 11 selected samples from the data set of 35. Sample libraries were selected from sets deposited on SSTOP and SSTP based on compositional range covered, range of thermal parameters, and the number of fields exhibiting capacitive behavior. To ensure a reliable set of conductivity measurements, the results from the automated analysis were verified by hand.

Description of Neural Network Modeling. A radial basis neural network was utilized throughout; modeling was carried out using MATLAB (2010a, The Mathworks) including the Neural Network Toolbox (7.0, The Mathworks). This type of model was used as it is quicker to train and is more appropriate for use with smaller data sets than other network types.\(^2\)

The model was constructed using a Model Data Matrix (MDM), which consisted of the eight parameters that were thought to influence the ionic conductivity behavior of the material being studied. These parameters were selected based on scientific knowledge and the partition analysis performed previously. The content of the MDM was preprocessed to account for missing values, and to remove any outlying data points. Only samples which exhibited a capacitive response were considered.

It was found that the process of random data division gave rise to differing neural network responses, all with reasonable fitting parameters. Therefore, 20 iterations of the model were evaluated, each with the same parameters. The data was redivided randomly at the start of each iteration. Over the 20 iterations calculated, the mean correlation was found to be 0.95, 0.92, 0.92 for the training, validation, and testing data sets, respectively. The correlation was not noted to be significantly reduced for 1000 iterations.

The elemental composition and phase concentration of Li\(_{3-x}\)La\(_{2/3}\)TiO\(_3\) was then used in conjunction with the neural network model to predict the total conductivity of the Li—La—Ti—O system. The mean predicted total conductivity (20 iterations) of the Li—La—Ti—O system is shown in Figure 7.

Empirical data (elemental and phase composition) for samples deposited on SSTOP at 25°C and annealed at 700°C was used to simulate this data, assuming a thickness of 349 nm. Although the predicted value of the total conductivity was higher than that observed in the literature (7 × 10\(^{-5}\) S cm\(^{-1}\)),\(^1\) the optimum value was observed to coincide with the maximum observed in the literature (Li\(_{0.18}\)La\(_{0.28}\)Ti\(_{0.54}\) \(\sigma_{\text{Total}} = 7 \times 10^{-5}\) S cm\(^{-1}\), \(x = 0.11\)).\(^1\) The mean predicted total conductivity of the solid solution line, Li\(_{3-x}\)La\(_{2/3}\)TiO\(_3\), is shown in Figure 7.

CONCLUSIONS

The use of high throughput physical vapor deposition to synthesize Li\(_{3-x}\)La\(_{2/3-x}\)TiO\(_3\) has proved to be successful. Although it was not possible to produce the phase pure perovskite, it was possible to determine the ionic conductivity behavior of the system utilizing an artificial neural network model. This model, based on empirical data, enabled the determination of the highest total conductivity value within the range of compositions studied, assuming deposition was carried out at 25°C followed by annealing at 700°C.
The synthetic method described here demonstrates significant advantages over other thin film methodologies, such as pulsed laser deposition,\textsuperscript{29} RF sputtering,\textsuperscript{30} and electron beam evaporation.\textsuperscript{7} All of these techniques require bulk materials for each composition to be studied typically limiting studies to small numbers of compositions. Such studies do not generally enable the experimentalist to access thermodynamically unstable materials, which are accessible via the mixing of elements at an atomic level. Since the high temperatures (1100–1200 °C) typically required to form the perovskite materials were not required during this study, the loss of lithium during processing was reduced.\textsuperscript{31} The use of lower temperatures has also reduced the decomposition and disproportionation of the materials. The same limitations are also encountered in bulk synthesis. A true optimization of a material system is therefore not viable, unless the problem is tackled in a high throughput manner, such as that described here.

By applying data analysis techniques usually used in data mining, such as partition analysis, it has been possible to determine the important parameters to synthesize successful Li$_{1-x}$La$_{2/3-x}$TiO$_3$ thin films for analysis by electrochemical impedance spectroscopy. In this case the choice of substrate proves to be important, with SSTOP, Si/Pt, and SSTOP/SRO exhibiting greater number of capacitive measurements. Additionally, this analysis has indicated that the composition, specifically the lithium content, and the annealing temperatures are the important factors when producing a crystalline Li$_{1-x}$La$_{2/3-x}$TiO$_3$ film on SSTOP.

Empirical observations, as well as partition analysis, also indicate thickness may be of importance. In the case of thin films, two hypotheses are put forward. The thinner films exhibit pin holes or cracking, leading to short circuits after the deposition of the Pt electrodes.\textsuperscript{29} Alternatively, the thin films may be pierced during the measuring process, leading to direct contact between the probe and the Pt electrode.

Analysis of raw diffraction data by Principal Component Analysis (PCA) and Multivariate Curve Resolution-Alternative Least Squares (MCR) allowed phase distribution diagrams to be produced in the case of fields deposited on SSTOP and MgO.

**ASSOCIATED CONTENT**

* Supporting Information. Complete experimental details, including details of the instruments used are provided. Details of the threshold values used to classify each impedance response are given, along with an example set of impedance data, including behaviors at elevated temperature. Preprocessing details are provided for XRD data, further details of the neural network data set are also provided. The results of the partition analysis of the entire data set using the electrical classification as the responses are provided. Additional compositional maps of Groups A and B, determined from this analysis, are also shown. A comparison of the PCA and MCR fits is shown as a means to determine the number of components required to successfully model the diffraction data. Fractional distribution of components, used to generate the phase distribution diagrams shown in Figures 3 and 5, are provided for the readers interest. This material is available free of charge via the Internet at http://pubs.acs.org.

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**ABBREVIATIONS**

PCA  Principal Component Analysis  
MCR  Multivariate Curve Resolution  
HT-PVD  High Throughput Physical Vapor Deposition

**REFERENCES**


**NOTE ADDED AFTER ASAP PUBLICATION**

This paper was published on the Web on April 11, 2011, with an error in the affiliation and Funding Statement. The corrected version was reposted on May 23, 2011.