SAND2014-17463R

SAND20XX-XXXXR
LDRD PROJECT NUMBER: 166148
LDRD PROJECT TITLE: Lithium Thiophosphate Compounds as Stable, High Rate Li-Ion Separators: Moving Solid Electrolytes into High Rate Applications
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ABSTRACT:

Battery separators based upon lithium thiophosphate ($LiPS_4$) have previously been demonstrated at UC Boulder, but the thickness of the separators was too high to be of practical use in a lithium ion battery. The separators are solid phase, which makes them intrinsically less prone to thermal runaway and thereby improves safety. Results of attempting to develop sputtered thin film layers of this material by starting with targets of pure Li, Li_2S, and P_2S_5 are reported. Sputtering rates and film quality and composition are discussed, along with efforts to use Raman spectroscopy to determine quantitative film composition. The latter is a rate limiting step in the investigation of these films, as they are typically thin and require long times to get to sufficient thickness to be analyzed using traditional methods, whereas Raman is particularly well suited to this analysis, if it can be made quantitative. The final results of the film deposition methods are reported, and a path towards new films is discussed. Finally, it should be noted that this program originally began with one graduate student working on the program, but this student ultimately chose to not continue with a PhD. A second student took over in the middle of the effort, and a new program has been proposed with a significantly altered chemistry to take the program in a new direction.

INTRODUCTION:

Lithium ion batteries are a mainstay of modern technology, but efforts to scale these chemistries into transportation needs have met with a significant challenge in the form of safety of these systems for vehicle conversion. In particular, the electrolyte of the battery is made of flammable liquids that can easily ignite with heat and air, such as during a crash environment. Additionally, overvoltage tests on these batteries cause them to oxidize this electrolyte, leading to gas generation and pressurization of the battery casing, which can lead to rupture and a fire danger as above.

Recent work at the University of Colorado at Boulder (UC Boulder) has demonstrated a powder form of a solid electrolyte that has significantly enhanced ionic conduction over more traditional solid electrolytes. Unfortunately, this separator material was only available in the bulk form as a powder, and so making thin films of this material was impossible. However, it is precisely this thin film form that would be the most useful for batteries, as the thickness of the separator is inversely proportional to how high a current the battery can maintain.

This LDRD was developed to investigate the possibility of depositing these materials in thin film form via a sputtered thin film method, starting with the same precursors as are used in the bulk synthesis; Lithium (Li), Lithium sulfide (Li_2S), and Thiophosphate (P_2S_5). However, this work had to be abandoned, due to the difficult nature of trying to sputter both the sulfur containing species as the phosphorus containing species. The sulfur, in particular, lead to rapid degradation of the lithium target, and very low overall powers, as the sulfur stayed in the gas phase for long periods of time after deposition and reacted with the other two targets.
Instead, a compromise system of Li-Si-O was selected, in that the chemistry is close to the Li-P-S system, and the same coordination centers and tetrahedrally bound structures in both systems will give rise to similar behaviors in Lithium transport.

EXPERIMENT/METHOD:

A Lesker sputtering system is used to create thin films through physical vapor deposition in this work. The sputtering system has two RF guns used to sputter off of a lithia and/or a silica target. There is also one Dc gun that is currently set up to be used on a Lithium target. The process gas is ultra high purity Argon. Typical process gas pressure is 5.5 mTorr. Lesker software is used to create and run “recipes” specifying RF power, deposition time, process gas pressure, etc. The sputtering system creates thin films of up to 30,000 angstroms on 1cm x 1cm Si substrates. KCl substrates of the same dimension are cleaved along crystalline planes to be used as substrates as well.

In order to characterize the thin films created by the sputtering system, several measurement systems will be utilized. Thickness measurements are made in the Colorado Nanofabrication Laboratory (CNL) using a profilometer. Composition will be determined using

ICP/AES at the Laboratory for Environmental and Geological Studies (LEGS). Raman spectroscopy and X-Ray Diffraction will be used in the Stoldt lab to further identify compositions of thin films. Impedance measurements will also be made in the Stoldt lab using a rig provided by Sandia National Laboratories.

The Li-Si-O ternary space will be characterized and the Li ion mobility in the LGPS-like lithium silicate materials will be investigated. Deposition rate analysis is being competed on each individual target as well as for both targets at once. The maximum power each target can be sputtered at will be found by slowly increasing the power of the RF gun on each target until the target shows sign of distress such as sparking or melting. Once the deposition rate and maximum power of each target are known, the power settings and deposition time can be manipulated to create lithium silicate thin films of varying composition. Thin films will be deposited onto KCl substrates, taken to LEGS, dissolved in a solution of HF, HCl and nitric acid, and analyzed using ICP/AES. Once a range of compositions have been determined using ICP/AES, these data points will be entered into the currently incomplete raman quantitative characterization Igor code started by Trevor Dimartino so that composition can be determined through raman spectroscopy. The thin films of varying composition will then be placed in the EIS rig to take impedance measurements and determine the conductivity of the thin film material.\

In addition, a method for converting Raman spectra to concentration of the materials in the sputtered films was developed using the following methods. By collecting a large number (N > 20, the larger the better) of Raman spectra, it is possible to run Principle Factor Analysis (described briefly below) and determine the number of components that contribute to the observed spectra. This is based on an assumption of most spectroscopic methods that a composite spectrum is a linear superposition (sum) of spectra from the constitutive species, and that the contribution of each component's spectra is indicative of its concentration in the whole.

Factor Analysis (FA) can be used on a collection of spectra to determine the number of Raman active components, the concentration of each component in each film, and the individual spectrum of each component *without* previously knowing any of those qualities of the film. The challenge lies in being able to prepare the data properly before FA is applied, and then transforming the "abstract" factors determined by FA into the "true" factors that describe the system in real-world quantities.

How this is done in the case of Raman spectra of lithium silicate samples is outlined below:

1. Subtract fluorescence background from the spectra taken
2. Build a Raman data matrix

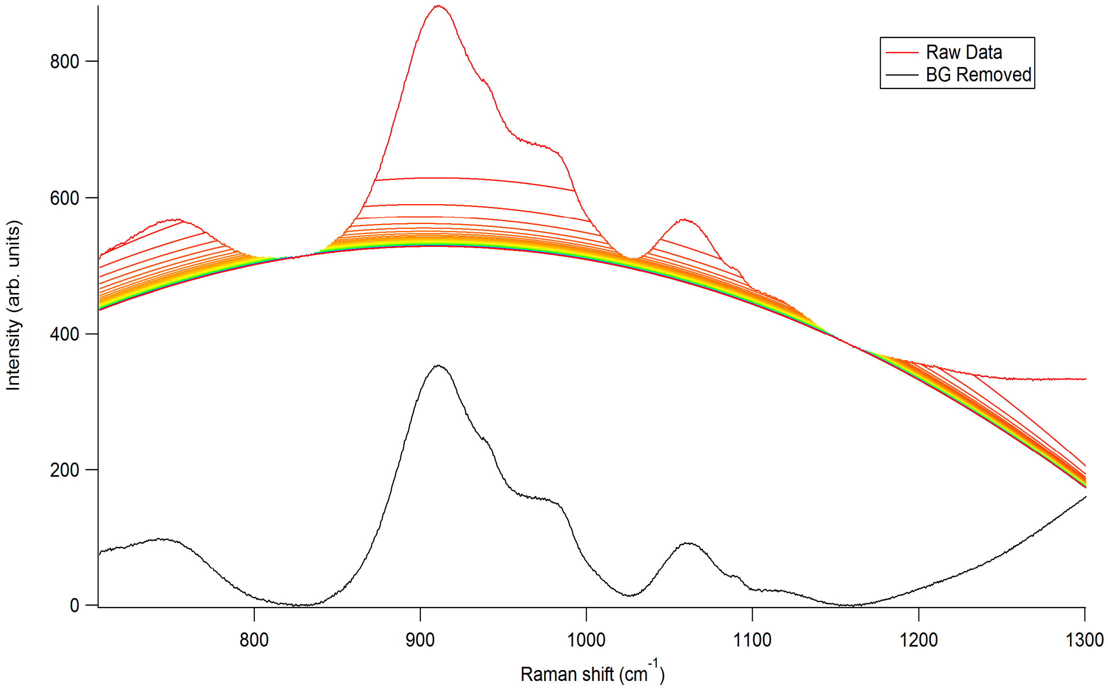

Figure 1 An illustration of the iterative background removal process. The red trace indicates the raw data, the rainbow demonstrates the iterations, and the black trace is the background-removed trace which resulted.

3. Use Principle Factor Analysis to determine the number of components, and
4. Determine partial Raman spectra and concentrations of each component in the system.

5. To subtract the background from the Raman spectra taken, I followed the method laid out by Lieber and Mahadevan-Jansen. It is basically an iterative method wherein the spectrum is fit to a polynomial of a certain order depending on the material system, the points of the spectrum that lie above the fit are clipped to the fit line, and the fit routine is run again. After some number of iterations, or when convergence is detected, the iterations are halted and the final fit is subtracted from the spectrum. This is illustrated below in Figure 1, where the original spectrum is seen in red and each iteration is plotted in the next progressive color down the rainbow. The spectrum in Figure 1 underwent 96 iterations to refine the background fit.

A note on the background fitting and subtraction: the choice of the degree of the polynomial to fit is important, but not extremely so as long as all the data is prepared in the same manner. It may be that the quadratic fit chosen for this preliminary study does not perfectly describe the background across this portion of a Raman spectrum for this material, but because the later steps of data analysis are looking at statistical differences, it is primarily important that all data be analyzed by a similar baseline, be that a second- or fourth-degree polynomial. The choice of a quadratic was made by the suggestion of Malfait, and can easily be changed in the Igor function created to automatically do this subtraction.

RESULTS:

The maximum power the lithia target can be sputtered at was found to be 40 W. Increasing the height of the targets in the process chamber increased the deposition rate of both targets by orders of magnitude. Figure 2 shows the thickness of the lithia think films created at each power setting for different deposition lengths of time. The deposition rate increases more quickly with increased power between 30 and 40 watts for the lithia target. Figure 3 shows the thickness of the silica films created at each power setting for different lengths of time. The silica films are significantly thinner than the lithia films. Continued experiments will focus on finding a new maximum for the Silica target and making a new matrix at his higher power in order to match the deposition rate of the lithia target more closely.

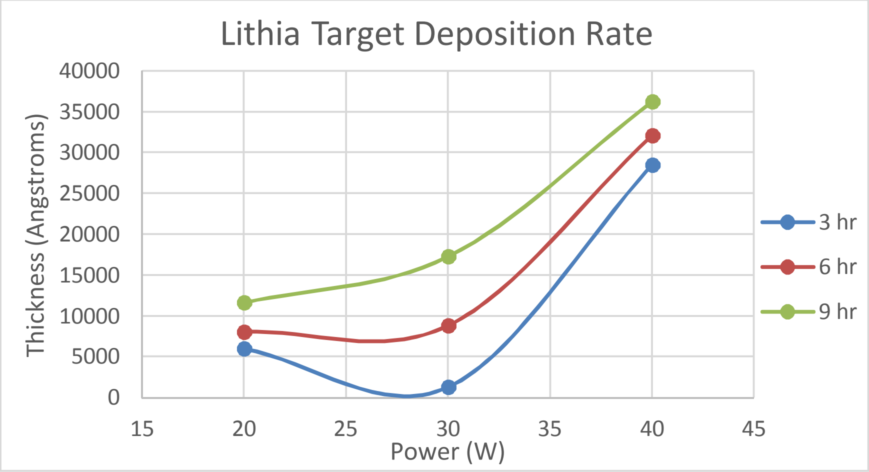

Figure 2: Lithia film thickness across different powers for varying deposition times

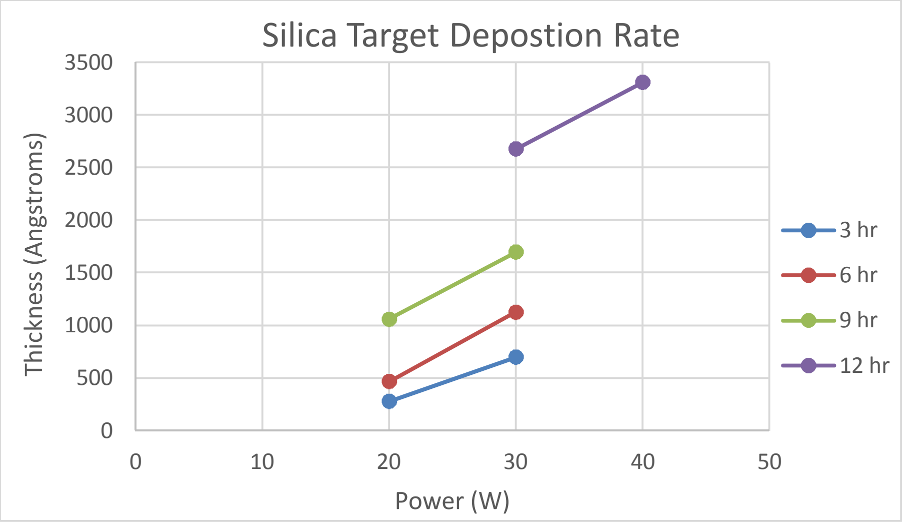

Figure 3: Silica film thickness across different powers for varying deposition times

The Raman data matrix is built in two fashions, one through a set of multi-peak fits, and one through trimming background-removed Raman spectra and combining each spectra as a column in the data matrix. I'll describe both below briefly.

Multi-peak fitting is a method used to "deconvolute" a spectra into a collection of Gaussian curves, which can then be assigned to different vibrations and used for qualitative descriptions of the data. It can be useful to see how one particular sub-peak moves, changes in intensity, or changes in width across a range of spectra to help describe what is changing in the local order of the material in question. Figure 4 is an illustration of a spectra which has been fitted with a collection of ten Gaussian curves (shown in rainbow colors).

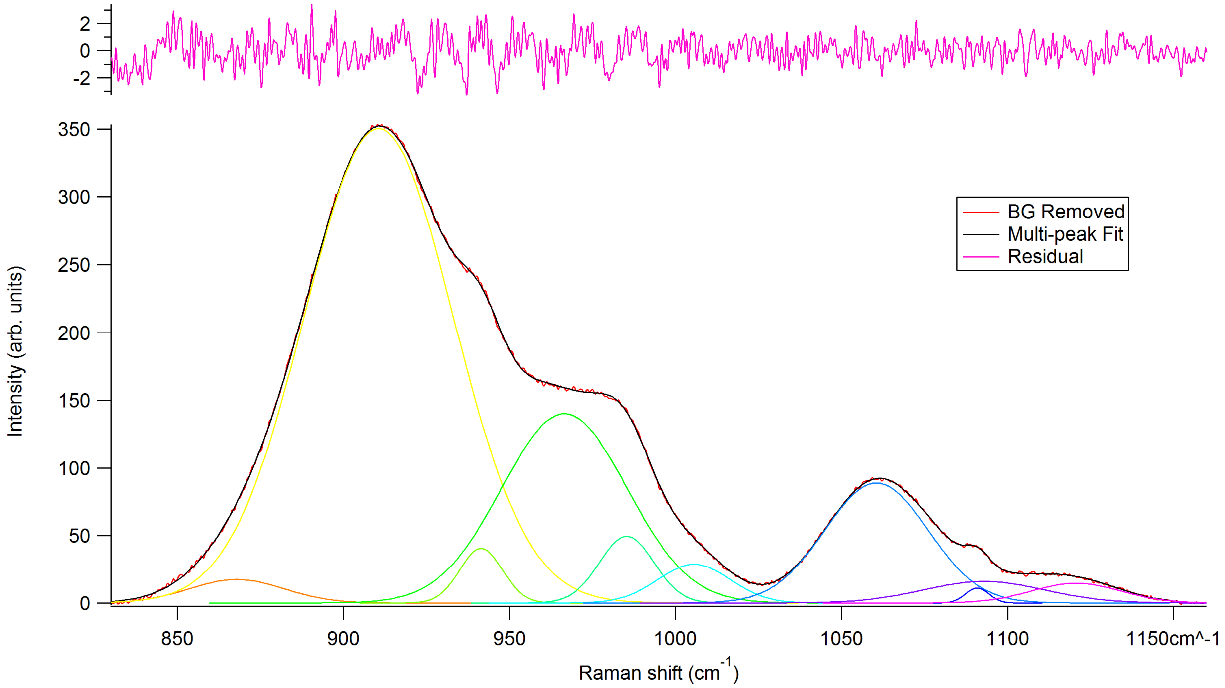

Figure 4: The background-removed spectra from Figure 1 with ten Gaussian curves (shown in rainbow colors) fitted to describe the range of interest. The residual from the fit is plotted above the fitted spectra.

The coefficients from the fitting process are then concatenated together to form one column of the Raman data matrix which will be used in Factor Analysis. This is similar to using one spectra as a column for Factor Analysis, which is the other way in which I built a Raman data matrix. These data matrices were then run through the PCA (“Principle Component Analysis”; same as Principle Factor Analysis) function in Igor.

The primary purpose of Principle Factor Analysis (PFA) is to reduce the dimensionality of the data from c dimensions (used to describe the entire factor space, including experimental error) to n dimensions that properly represent the data without experimental error. The PFA step also decomposes the data matrix into two matrices, **R** and **C**, which can be used (if transformed properly) to determine both the spectra of each Principle Factor, but also the concentrations of those Principle Factors.

Table 1, below, shows the first 10 factors as determined by PFA. As can be seen in the cumulative variance column, the majority of the variance can be described by the first four or five factors, which fits well with the model used to describe glasses. Any number of the Q^n species (Q^0, Q^1, Q^2, Q^3, and Q^4) could be contributing to the variance of the Raman spectra. Zakaznova-Herzog, in [2], finds there to be three principle factors in the range from 17 to 38 mol% K_2O (in the K_2O–SiO_2 system), and attributes those to the Q^2, Q^3, and Q^4 species. Since we are potentially looking at a wider range of compositions, potentially as wide as 15 to 85 mol% Li_2O (in Li_2O–SiO_2), it would make sense that we would see more species involved in the variance. It is also possible that the Silicon wafer upon which the films were deposited is contributing another factor to the problem at hand.

Table 1: Summary of the first 10 factors found in Principal Factor Analysis.

Factor	Eigenvalue	Variance	Cumulative Var.
1	109.064	0.990542	99.0542
2	8.65972	0.00624474	99.6787
3	5.05705	0.00212961	99.8916
4	3.14506	0.000823692	99.974
5	1.56785	0.000204699	99.9945
6	0.379973	1.20E-05	99.9957
7	0.286147	6.82E-06	99.9964
8	0.24127	4.85E-06	99.9968
9	0.209625	3.66E-06	99.9972
10	0.188428	2.96E-06	99.9975

ANTICIPATED IMPACT:

With the move away from the Li-P-S system and toward the Li-Si-O system, we expect the learning done on thin film preparations of lithium containing solids to translate directly, and the issues of high vapor pressure and reactivity of the P and S components to be largely suppressed. The increased powers accessible with the Li_2O and SiO_2 targets are showing much more promise towards a rapid, stable film growth that plagued the early thiophosphate work. In addition, the novelty of this system is that it is little studied in the literature, which should allow for significant new publications in this area to be developed. Finally, the similarity in structure between the two systems means that learning made in studying the Li-Si-O system may be more broadly applicable to the high rate systems, and can lead to further work in durability of these systems, either as separators in their own right, or as protective layers for use in other areas of the lithium ion batteries, such as engineered surface/electrolyte interphase (SEI) regions.

CONCLUSION:

The capability to sputter thin films of lithium/sulfur/phosphorus containing materials has been investigated, both from a structural standpoint as well as from a methods study to help elucidate film composition as a function of sputter conditions. The principle challenge in sputtering thin films containing sulfur or phosphorus was found to be the latent reactivity of these species in the gas phase after sputtering leading to contamination and degradation of the sputter targets over time, as well as very low energies needed to create excessive wear in the substrates. The program was converted into studies of the Li-Si-O system, which is structurally analogous to the Li-P-S system. Initial studies with this system are more promising, and good, stable film depositions have been demonstrated at a variety of conditions. In addition, film studies have been characterized using Raman spectroscopy, and principle component analysis (PCA) of a number of starting thin film structures have been used to build a basis state of film components to allow for faster analysis of the compositions of the films going forward.