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# Scale-Up of SLIP Process: Producing Nanoengineered Coatings at High Volumes to Meet Multi-Directorate Needs

K. C. O'Brien, D. M. Sanders, K. C. Moffitt, R.  
Marquez, C. Spadaccini

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# Final Tech Base Report

Scale-Up of SLIP Process:

Producing Nanoengineered Coatings  
at High Volumes to Meet Multi-  
Directorate Program Needs

Kevin C. O'Brien  
Dave Sanders  
Chris Spadaccini  
Kevin C. Moffitt  
Rizalde Marquez

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# 1 Background

There are a variety of applications that require the use of nanoengineered surfaces for separation applications. Surfaces are commonly functionalized in order to facilitate the purification of gases and liquids. Functionalization often requires the application of a polymer to the surface. The most common means is to dissolve the polymer in a solvent and then either cast or spray it onto the surface.

This traditional approach causes two severe limitations: (1) the polymer must be soluble; (2) the solvent must be removed from the final coating. The first limitation often eliminates many potential candidate polymers. The second limitation is influential on the transport and separation properties of the coating. Low levels of residual solvents can significantly degrade the ability of the coating to perform the separation process. These two issues can be overcome through the use of *Solvent-Less vapor deposition followed by In-situ Polymerization (SLIP)*.

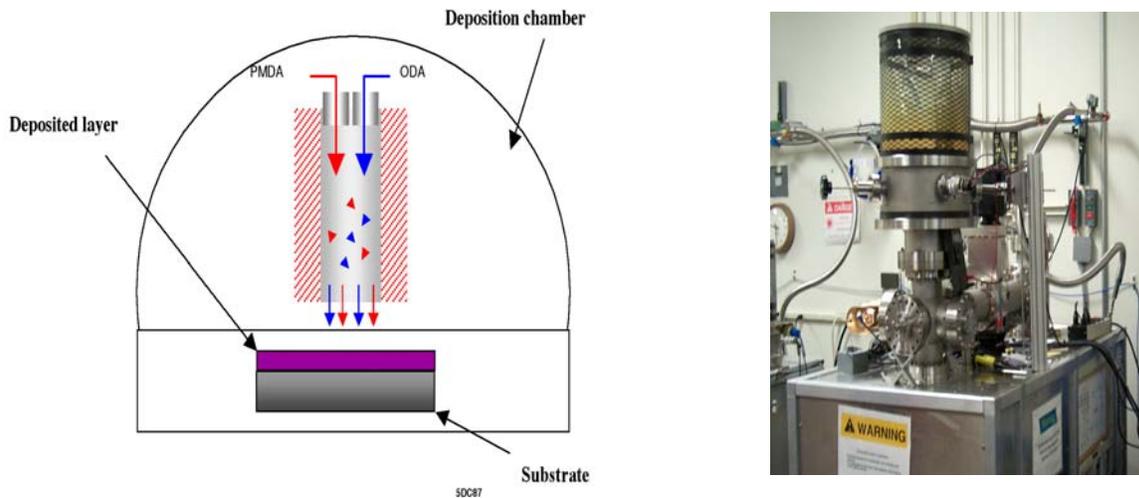
The SLIP process was originally developed for the fabrication of Inertial Confinement Fusion (ICF) targets. This application required the deposition of films of 100 to 200 microns in thickness onto a spherical substrate. The process consists of two evaporation chambers each containing a quantity of monomer. The precursors, monomers, are vaporized and flow through a mixing nozzle and eventually are deposited on a substrate surface. They react at the surface and form a nanoengineered polymer film.

The SLIP process has been utilized to develop composite membranes for gas and liquid separation applications. Polyimide films that range in thickness from 50 to 400 nm were deposited onto a range of substrates. The SLIP process has been shown to be robust and current plans are in place to scale-up the process. This scale-up would enable the coating of flat sheets and fibers. This paper will outline the roadmap to constructing a pilot scale SLIP system in order to meet multiple programmatic needs.

## 2 SLIP Bench Top System

The system shown in Figure 1a consists of two evaporation chambers each containing a quantity of monomer. The monomers vaporize and flow through a mixing nozzle and eventually are deposited on the substrate surface and react to form a polyamic acid coating. The sample is then removed from the coating apparatus and is subsequently imidized in a dry nitrogen oven to form the final polyimide film. Figure 1b depicts the bench top system.

The SLIP process offers the capability to deposit and polymerize films of high temperature polymers that are prepared using a condensation mechanism (as compared to a free radical type of polymerization). This includes high temperature and high performance polymers such as polyimides, nylons, polybenzimidazoles, polybenzoxazoles, etc. Films of these polymers are commonly deposited using solvents. Traditional methods are unable to deposit layers of materials at nano-levels. SLIP combines the advantage of being solvent-less and offers the promise to be able to deposit at thicknesses less than those achievable via conventional means.



**Figure 1. (a) Schematic of SLIP process (b) photograph of bench top SLIP deposition system**

The SLIP process has been used to deposit nanometer films onto a variety of substrates. These substrates include polymers such as polycarbonate, Teflon AF, nylon, and silicone as well as inorganics such as silicon wafers and glass. Excellent adhesion was observed in all cases. SLIP films have been deposited on fiber and flat sheet.

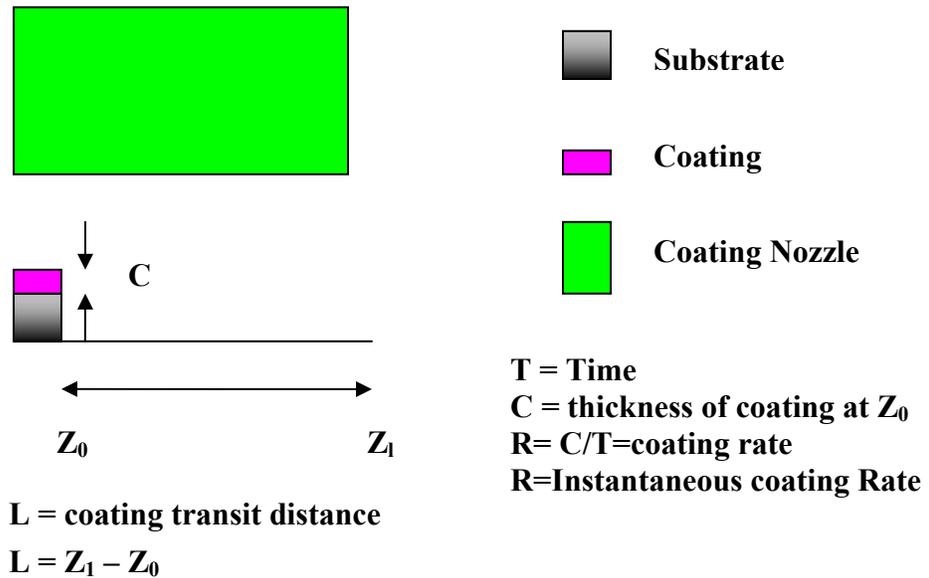
### 3 Evaluating the Economic Viability of the SLIP process

The SLIP process offers many technical advantages, but it is critical that this process be economically attractive to commercial entities. The scaled up system also needs to be able to apply coatings to both films and fibers. One of the advantages of the SLIP fabrication process is that it employs standard chemical vapor deposition (CVD) equipment with minor modifications. A company familiar with the scale up of CVD systems (Nano Scale Surface Systems Inc.) was utilized to assist in evaluating pathways to the scaling up the SLIP process. One of the first steps in the evaluation was to determine whether the scaled up process was economically attractive.

The economics of the scaled up process were evaluated using a spreadsheet-based model. The goal is to evaluate the value of the amount of coated material produced in a 16 hour day at a given instantaneous rate of deposition. The model assumes that SLIP films are deposited onto flat sheets of materials (webs). The results from this model can be adjusted to take into account changes in the form factor of the substrate (i.e. changing from deposition onto a web to deposition onto a fiber).

The model, depicted in Figure 2, assumes that a web of a specified width is rolled through a coating zone. The coating zone, or coating transit distance, has a defined length **L**. The thickness of the film (**C**) deposited per unit time (**T**) is defined as the instantaneous rate (**R**). Assume that the coating can be uniformly applied along a web of a pre-specified width (**W**). Target thickness of coating is **C'**. The area of web that can be coated in a specified time frame is calculated as:

$$\text{Area of web coated per unit time} = \mathbf{RLW/C'}$$



**Figure 2. Model for economic evaluation of coating process**

This area per unit time can then be calculated as area of coated web per 16 hour day. Using a standard commercial value for coated web (\$/area), the total value of product produced in a 16 hour day can then be calculated.

Instantaneous Coating Rate (nm/min)	200	200	200	400
Coating Transit Distance (cm)	15.3	30.5	15.3	15.3
Sheet Width (cm)	30.5	30.5	30.5	61.0
Coated Area (cm <sup>2</sup> )	467	930	467	933
Coating Thickness Required (nm)	200	200	100	200
Area coated per Time at Required thickness (cm <sup>2</sup> / min)	467	930	933	1867
Area coated per 16 hr day (m <sup>2</sup> / 16 hr)	44.8	89.3	89.6	179
Coated sheet value (\$/m <sup>2</sup> )	53.8	53.8	53.8	53.8
Product value / 16 hr day	\$2410	\$4804	\$4820	\$9640

**Table 1. Effect of design parameters on economics of process**

Table 1 summarizes the calculations discussed above and demonstrates the effect of altering design parameters (i.e. transit distance, width of web, required thickness). Doubling the length of the coating transit distance doubles the throughput of the coating system and the associated value of generated product. A similar benefit can be achieved by reducing the required thickness. In all cases, the total value of product produced in a 16 hr. time frame is well over \$1000. This suggests that the process is economically viable at the given instantaneous rates.

## **4 Other Factors that Effect Process Economics: Deposition Pressure and Blocking**

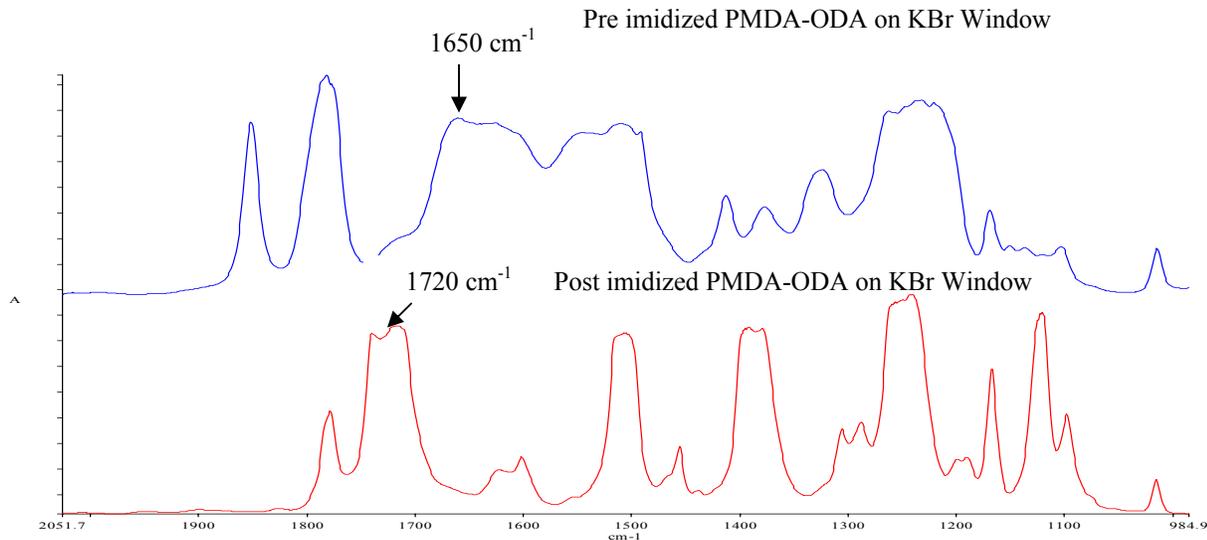
### **4.1 Deposition Pressure**

Another key factor that would influence the economics of the scale up process was the deposition pressure. Depositions using the system depicted in Figure 1 were typically done with a mechanical and a diffusion pump ( $10^{-6}$  Torr). The use of a diffusion pump would significantly increase the capital cost of the scaled up system. Preliminary tests on the bench top system were performed to determine whether the coating process could be accomplished with a simple mechanical pump ( $10^{-3}$  Torr) or at atmospheric conditions.

The coating used for these tests was a polyimide (PMDA-ODA) based on the reaction of pyromellitic dianhydride (PMDA) and oxydianiline (ODA). This polyimide has a structure similar to Kapton® and has been successfully applied previously to a variety of substrates using a diffusion pump. Infrared spectroscopy was used to evaluate the stoichiometry of the applied film (amount of PMDA and amount of ODA applied), degree of reaction of the PMDA and ODA to form a polyamic acid, and the amount of imidization that occurred after heating.

Figure 3 depicts the infrared spectra of a film of PMDA-ODA deposited onto a KBr window under conditions using only a mechanical pump ( $10^{-3}$  Torr). The as deposited film exhibits bands commonly observed for a polyamic acid. For example, the very large and broad  $1650\text{ cm}^{-1}$  band is indicative of the carbonyl stretch of the carboxylic acid group of the polyamic acid. This denotes that polyamic acid was formed on the substrate. The sample was then heated to  $220^{\circ}\text{C}$  in order to imidize the polyamic acid. Note that the  $1650\text{ cm}^{-1}$  band is no longer present in the imidized sample. The imidized sample exhibits a large band at  $1720\text{ cm}^{-1}$  that can be attributed to the carbonyl stretch of the imide. This data demonstrates that a film can be deposited using only a mechanical pump. The subsequent polyamic acid film appears to be readily imidized using standard conditions.

The infrared spectroscopy of films deposited at atmospheric conditions on KBr windows did not exhibit the polyamic acid bands that are evident in Figure 3. This result suggests that it may not be feasible to perform the SLIP process under atmospheric conditions.



**Figure 3. Infrared Spectra of PMDA-ODA deposited on KBr Window using only mechanical pump.**

## 4.2 Blocking

Blocking refers to the ease of handling of the coated web. Coated film will be wound on a take-up roller after coating. Coated layers will be in contact with one another and will be under a significant amount of pressure. If the coated layers adhere to one another (i.e. block), it may be very difficult (if not impossible) to later unwind the roll and remove the coated material. This condition can be overcome by using interleaving material between the rolls of coated material. This added step would add material cost and most importantly add to the capital cost of the equipment.

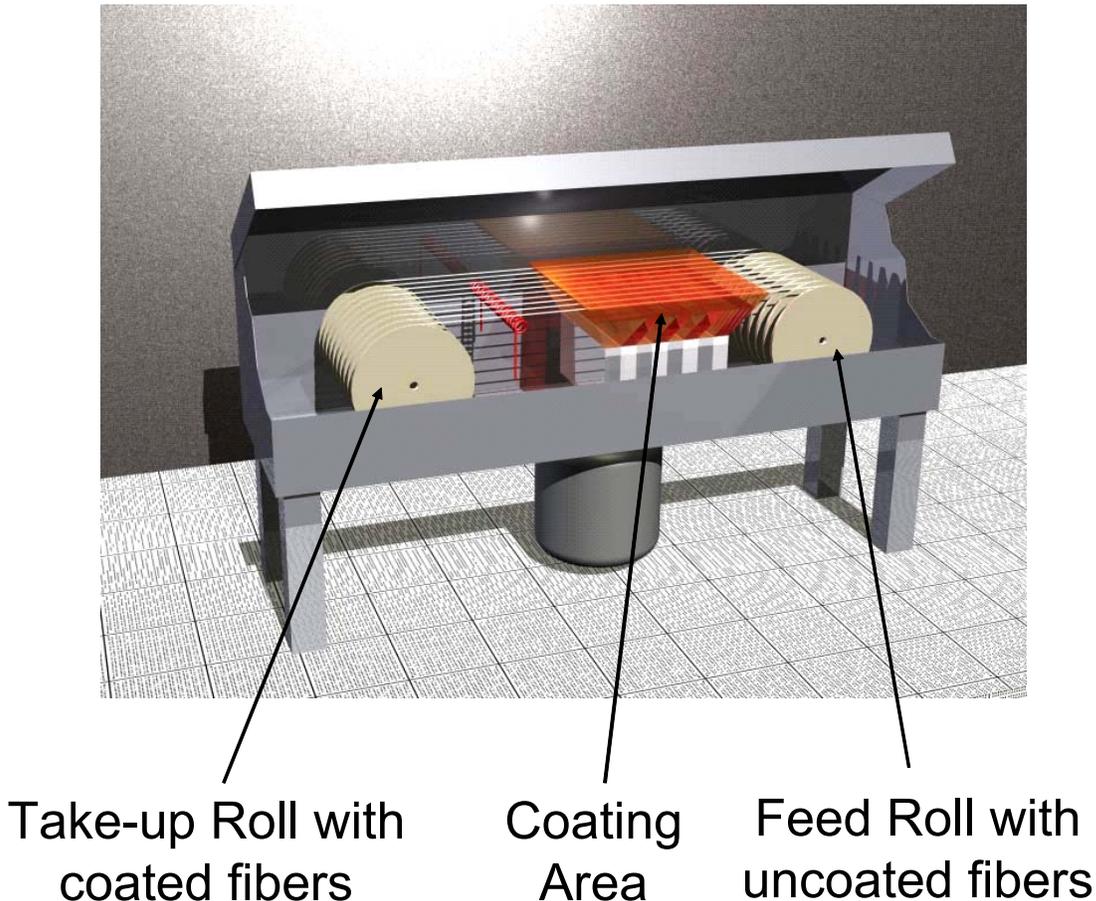
Preliminary tests suggest that blocking may not be a problem with SLIP coated materials. Future work will focus on more detailed studies to verify these preliminary results.

## 5 Preliminary Design for Scaled Up SLIP Coater

Based on the results discussed previously as well as consultation with Nano Scale Surface Systems Inc., a preliminary design for a scaled up SLIP coater was produced. Figure 4 shows the pilot production equipment with the top cover raised. The system is shown coating fiber, but would also be able to coat flat sheet as well. Deposition would occur under vacuum and a mechanical pump would be used to produce the required vacuum. The overall dimensions of the unit shown in Figure 3 are 8 feet long, by 2 feet

wide and 4 feet in height. The pump would be contained in the cylindrical unit underneath the housing of the unit in Figure 4. Both the feed and take-up rollers would be under vacuum.

## *Pilot Production*



**Figure 4. Preliminary design of scaled up SLIP coater**

Fiber moves from right to left. Uncoated material is unwound from the feed rollers, goes through the coating area, and is heated and imidized. The coated fiber is then wound onto the take-up rollers. Ten strands are coated simultaneously.

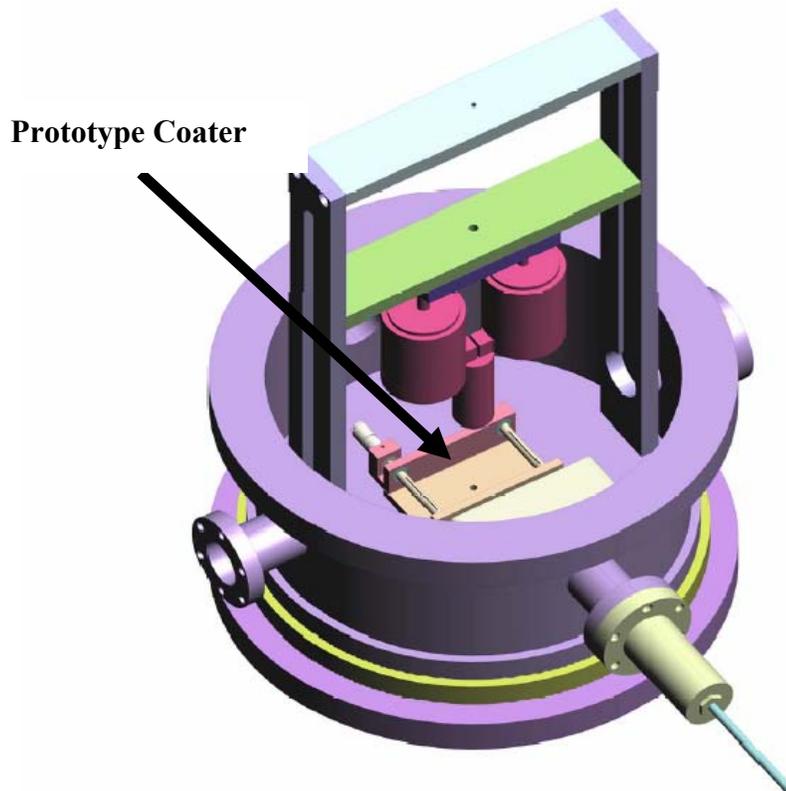
The units are designed for a distributed manufacturing environment. This means that capacity increase can be achieved by simply adding more units. The units are designed to be relatively inexpensive (\$100,000 to \$200,000) and easy to maintain. Components are those commonly used in CVD systems. This reduces risk, keeps capital costs low, and avoids catastrophic shut downs of production lines. Estimated time to construct a pilot scale system would be approximately 4 to 6 months. The unit is

estimated to be able to coat 200 km of fiber per day. This would easily meet projected demand for many of the high volume applications, e.g. membrane applications.

## 6 Prototyping the Scaled Up System

Risks can be reduced significantly by producing a prototype system that simulates the pilot scale system shown in Figure 4. The prototype system could then be used to apply SLIP coatings to small scale samples of fibers and films. It provides for a means to test the proposed design and identify potential issues.

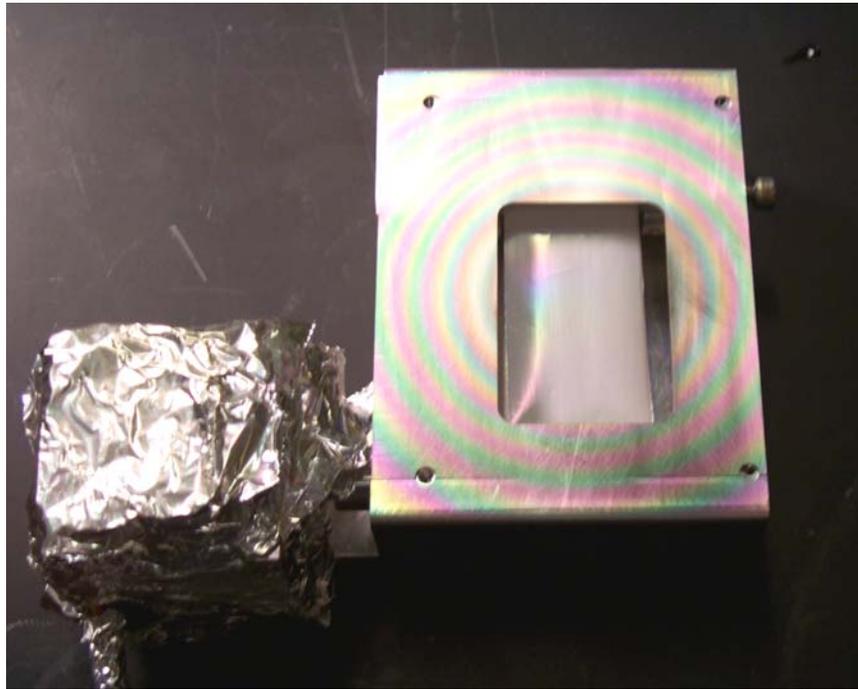
The prototype system that was designed is shown in Figure 5. It simulates the pilot scale system, but is small enough that it can be simply placed in the bench top system shown in Figure 1.



**Figure 5. Prototype coater shown in deposition chamber. Top has been removed from chamber.**

The take up roller is motor driven and the motor is designed to withstand high vacuum conditions. An external controller (not shown) is used to controller the motor speed.

The prototype coater from Figure 5 was placed in the deposition chamber shown in Figure 1 and a SLIP coating was applied to a substrate. The substrate used was a microporous polypropylene substrate (Celgard®) supplied by Celanese. A PMDA-ODA SLIP coating was deposited onto to the substrate.



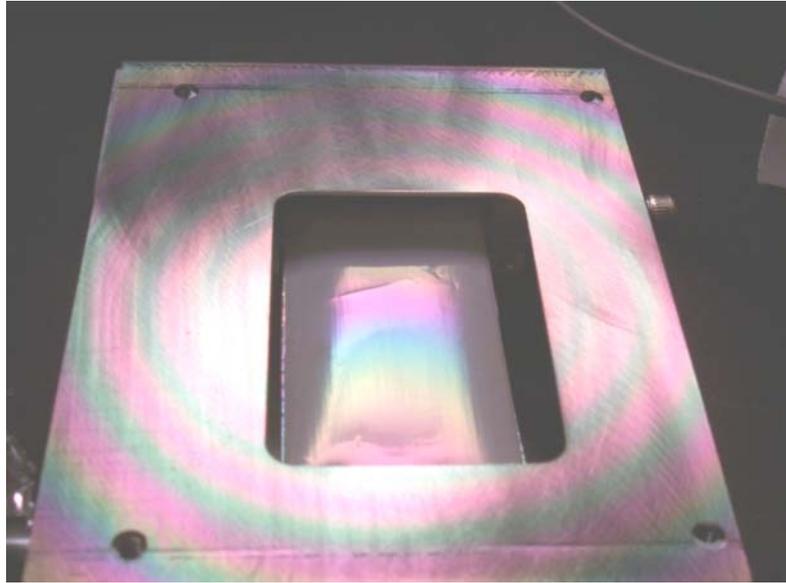
**Figure 6. Prototype coater after deposition of PMDA-ODA.**

Figure 6 is a photograph of the coater after deposition of the PMDA-ODA. The white sheet is the Celgard substrate. The motor is covered and is on the left. A metal shutter covers the roller mechanism. Note the interference fringes (green and red colored rings) on the metal shutter. These are indicative of the deposition of PMDA-ODA.

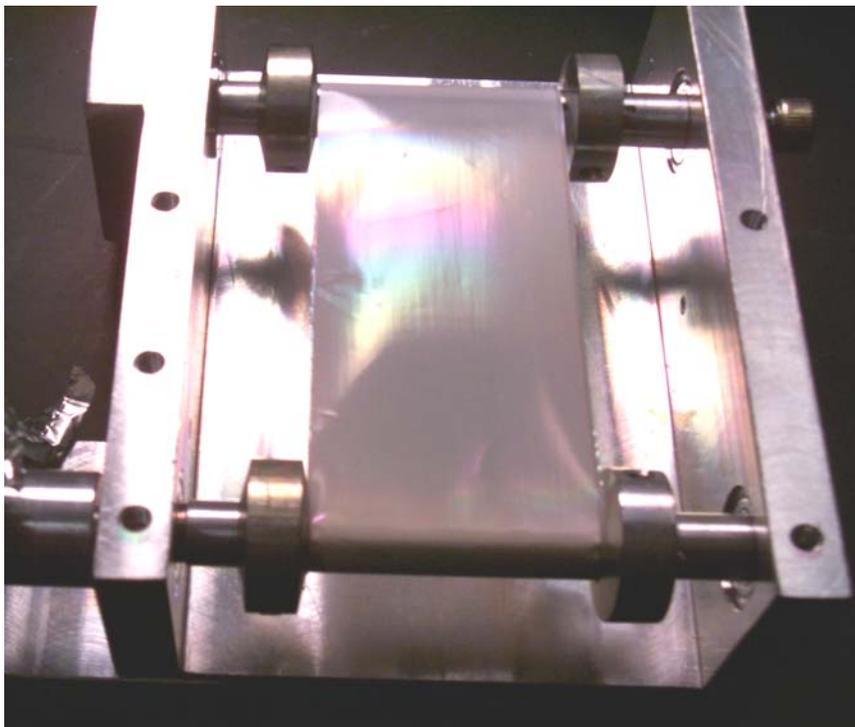
Figure 7 is a close-up of the coated Celgard materials. Note again the presence of interference fringes on the substrate. This demonstrates that coating has occurred. Figure 8 is a similar view, except that the metal shutter has been removed in order to illustrate how the film was mounted in the coater. The deposition was conducted with only the mechanical pump running.

## **7 Roadmap for System Design and Scale Up**

These preliminary results demonstrate that the scale-up of the SLIP process looks very promising. The pathway to a building a pilot scale system is illustrated in Figure 9.



**Figure 7. Close-up of coated substrate (white) in prototype coater.**



**Figure 8. Coater from Figure 6 with metal shutter removed. Illustrates design for mounting.**

## Roadmap to Scale Up of SLIP

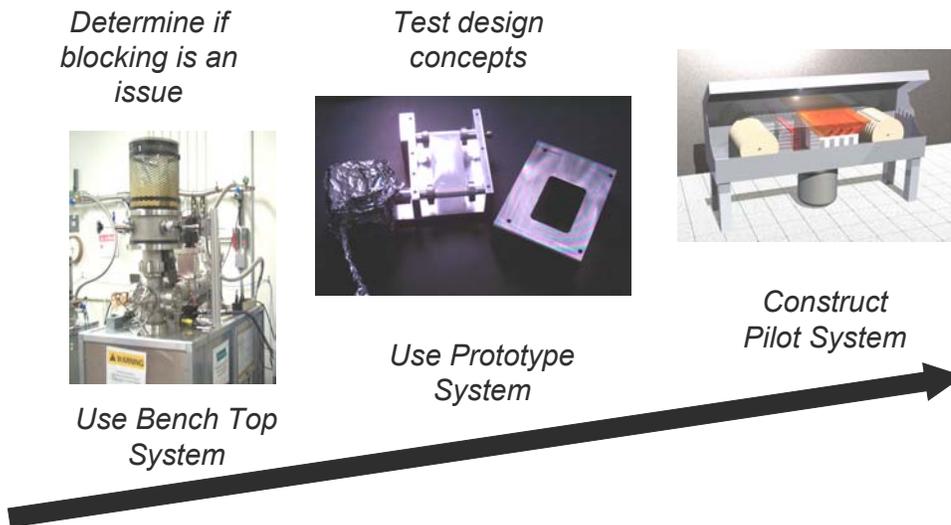


Figure 9. Roadmap for scale-up of SLIP process.

The first step is to use the existing bench top system to determine whether blocking is an issue. The prototype system that has been constructed can be placed in the bench top system and used to test design concepts. This will aid in validating the pilot system design and reduce risks. It is projected that within a 9 month time frame the pilot scale design could be validated and a system could be constructed.

## 8 Summary

A roadmap for scale-up of the SLIP process has been developed. A semi-continuous laboratory scale system was designed and inserted into the existing vacuum chamber. This system was used to apply SLIP coatings to porous polypropylene substrates. An equipment vendor was identified and assisted in the design of a pilot-scale system that would be capable of coating fiber at a rate of approximately 200 km/ day.

Funding and completion of this project provides a pathway to scale-up the SLIP process. This is critical in growing a membranes program within LLNL and would provide a pathway to additional DOE funds. The subsequent DOE funding would employ Engineers from a number of divisions including EETD, NTED, LSED, and MMED. This pilot scale system would provide vital resources to programs within Energy & Environment, Defense & Nuclear Technologies, and NAI.