Clean coating of lithium with parylene-N.

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Abstract

This writeup summarizes the installation and operation of a specialty parylene coater connected to a helium-filled glove box. The coater uses the glove box's antechamber as the parylene deposition vessel, so that sheets made from lithium or lithium-based materials do not have to come in contact with the outside atmosphere before they are covered with parylene.

To make lithium x-ray filters with the minimum possible contamination, lithium sheets are rolled to the desired thickness in the glove box's inert atmosphere. They are then transferred to the coating chamber, from where they are transferred back to the glove box after coating. For convenient use elsewhere the foils can be packed individually in humidity-resistant, heat-sealed plastic bags, which are further protected by the dry helium atmosphere inside a steel can that is convenient for shipping. However, if possible they should be installed in the fixture wherein they will be used, at least when the fixture is designed such that it protects the filters from exposure to the atmosphere until just before exposure to x-rays.

I. BACKGROUND.

A principal problem with lithium for use with soft x-rays is lithium's rapid corrosion. Like iron, lithium corrodes in humid air. Of course lithium does not corrode in an atmosphere of a noble gas, but it does not corrode either when the air is dry enough: acceptable is a relative humidity (at room temperature) below 2%, and the lower the better. Hence the existence of dry rooms, which makes handling lithium much more convenient than the second option, handling lithium in an noble gas atmosphere in a glove box. For cost reasons glove boxes use nitrogen rather than a noble gas whenever possible. Nitrogen is inert with all alkali metals except lithium, so that for lithium the most common glove box gas is argon. In its glove box Ecopulse prefers helium over argon, because helium allows lithium's x-ray transmission to be measured with conveniently available x-rays whose energy exceeds argon's K-edge at 3.2 keV: atmospheric-pressure argon attenuates x-rays above 3.2 keV just as much as solid lithium.

In an experiment a lithium x-ray filter has the same corrosion problems as during the filter's preparation, so that lithium in the experimental setup must handled in a dry or inert atmosphere. It is also possible to protect lithium, for some time, with a thin surface layer that is chemically inert and transmits x-rays sufficiently well not to increase the filter's attenuation excessively. This is passivation.

The following summarizes techniques that can deal with lithium's corrosion problems during an experiment.

- Provide a locally dry environment. This is easy to implement: simply stream dry nitrogen (or, preferably dry argon or helium) over both sides of the lithium filter. Ecopulse used this method with its earliest lithium filters. In reasonably dry air, at Double Eagle in the Bay Area in the winter months, this worked reasonably well.

- Keep lithium in a hermetic enclosure that is opened just before exposure to x-rays. This approach is better than a stream of dry nitrogen, but comes at a cost of more complicated engineering and sometimes bulky fixtures that, for best performance, must be adapted to a specific purpose. Ktech has available various enclosures with different in geometries and ways to let the x-rays in through passive or active opening.

- Passivation with parylene-N. Parylene-N is a pure hydrocarbon polymer with overall chemical composition C_8H_8. It is applied by polymerizing the precursor, unsaturated para-xylene or para-xylylene, out of the vapor phase against a surface. Figure 1 shows the parts of the process. When the mean free path of the molecules is small enough, or the pressure is high enough, the molecules go everywhere and the deposition gives a conformal, pinhole-free layer of uniform thickness. Useful thicknesses range from 0.3 μm to 2 μm (and higher if desired, for other purposes than x-ray transmission). Coating lithium with parylene was implemented by Ecopulse under a DTRA SBIR program. Most commercial parylene coating uses a chlorine-containing variant of parylene-N, parylene-C, which deposits faster and resists humidity better. However, chlorine can not be used in filters intended for an argon radiation source, because chlorine's K-edge at 2.83 keV is just below the strong K-line of helium-like argon at 3.1 keV. Of the various parylene choices, including a two-chlorine variant, parylene-D, and a fluorine-containing variant, parylene-F, only parylene-N is acceptable for x-ray filters. Hence, parylene in what follows parylene implies parylene-N.

- Passivation with a thin layer of LiF. Like any metal, the reaction of lithium with

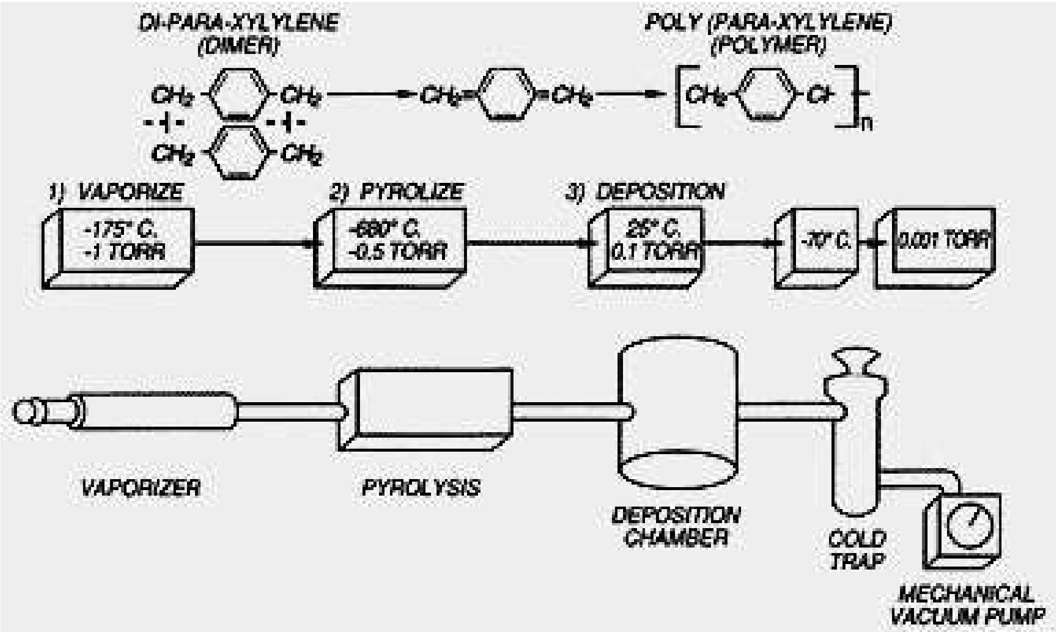

FIG. 1: Schematics of the parylene deposition process. The dimer di-para-xylylene vaporizes at 150°C, pyrolyzes or cracks at 650°C, and deposits at room temperature. (the temperatures in the figure are for parylene-C).

> oxygen in the air produces an oxide, Li_2O. For aluminum and stainless steel, and also for lithium in a dry atmosphere, the oxide layer is stable and protects against further oxidation. However, lithium's oxide is mildly hygroscopic and dissolves if it can attract water from the atmosphere. Hence, the oxide can not protect lithium when the environment is too humid. LiF is chemically more stable and less hygroscopic than Li_2O, so that in principle a covering by LiF should protect lithium against higher humidity. Protecting lithium with LiF was tried by Ktech, again under an SBIR from DTRA. Unfortunately, unavoidable cracks in LiF self-heal in a fluorine atmosphere but not in air, so that lithium still corrodes when the humidity is too high.

Of course, there is no reason that these various approaches can not be mixed and matched as the circumstances demand. For example, parylene protects lithium only for a limited time, nominally 15 minutes. When installation of the x-ray filter is planned properly, 15 minutes should be more than long enough to re-establish an inert environment around the lithium once it is in place. In this spirit, Ecopulse envisions parylene coating as an important but not the sole component of a lithium protection system: the local environment should also be kept dry or inert, whichever is the most appropriate.

Ecopulse's parylene coating station was initially located in a dry room at the Army Research Laboratory (ARL). Figure 2 shows the equipment. The blue box below the table contains the control unit, for the vacuum (also below the table), the vaporizer (the green pipe on the left), and the cracker (the blue box on top of the table). The coating vessel is to the right.

As is clear from the description above, putting a parylene coater in a dry room is convenient, but unless lithium's oxide layer is somehow cleaned off, the parylene goes right over the oxide layer. Even though the layer is thin (although it increases slowly in thickness as the lithium remains exposed to oxygen-containing air), it does absorb x-rays more than the lithium itself (but less than the same mass per unit area of LiF). On our samples the oxide layer's thickness has not been measured, but the x-ray transmission of the foil including its two oxide layers differs little from the calculated value assuming no oxide layers, so that the oxide layers seem to add little to the x-ray attenuation. Depositing a parylene coat over the oxide is then not so bad, although it is clearly best to coat virgin lithium metal, without the oxide.

When the demand for ARL's dry room increased, the coater took too much place and we lost the coating capability. This offered the opportunity to implement a system for coating lithium without any exposure to oxygen at all. Avoiding all exposure to the atmosphere is even more necessary for a mechanically stronger version of lithium, lithium-lithium hydride: Li-LiH corrodes faster than lithium, and even reacts with nitrogen.

The next section describes the improved the parylene coating capability.

II. IMPROVED PARYLENE COATING CAPABILITY.

Coating with parylene takes place in a deposition vessel downstream of the hot region that creates the parylene monomer from the dimer, see Figure 1. Deposition is uniform on all the surfaces, also on the walls of the deposition chamber and everything else that's in it. When coating only a few samples of lithium, most of the parylene is then lost to the walls. Standard parylene coating vessels are therefore not much bigger than they have to be. In principle it is possible to couple a standard parylene coater with a glove box,

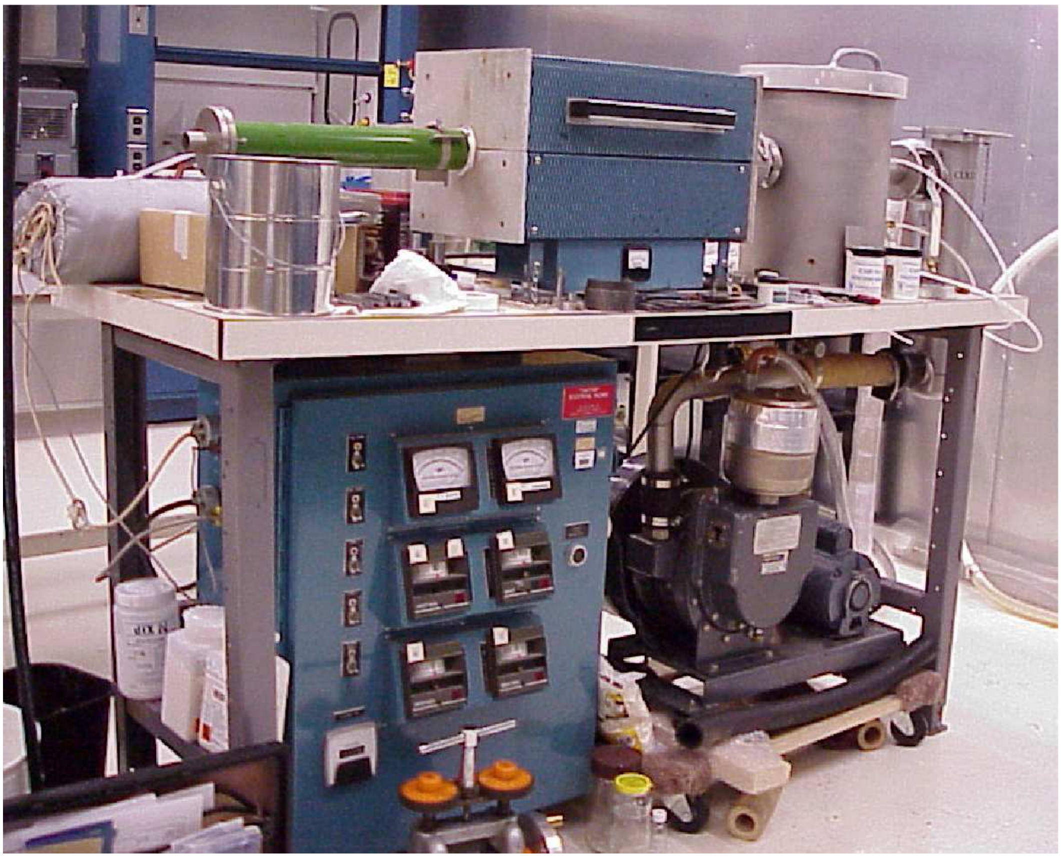

FIG. 2: Parylene coater setup in the dry room of ARL's building 207.

but implementing this on Ecopulse's glove box would have been complicated. Instead, we decided to use as the deposition vessel the glove box's antechamber, even though this is twice as large as it needs to be.

FIG. 3: Parylene coater connected to the glove box in NRL's building 256.

Figure 3 is the resulting hardware. The glove box itself is to the right. On the left, attached to the antechamber, is the parylene coater. It is a slightly smaller version of the coater in Figure 2 turned on its side. The vaporizer is inside the aluminum cylinder that supports the (blue) hot zone. Individual control units below the glove box supply heat to the vaporizer and the hot zone: the vacuum pump is behind the controls and below the glove box. In front is a rotating stage, which helps to make the deposition more uniform than it would otherwise be. It is on slides, making it loading with lithium foil inside the glove box convenient. Still lacking is the condenser that takes care of un-polymerized parylene before this gets to the vacuum pump.

While probably sub-optimal, the parylene coater works well enough, as is clear from the data in Table I. One annoyance is to put the dimer in the right place, in a 40 mm stainless steel pipe that may be only 20 mm from the floor.

sample	m (g)	$m\Delta m$ (mg)	Δd (μm)	T
1	0.6115	23.9	0.78	0.99
2	0.6197	20.3	0.66	0.99
3	0.6155	19.9	0.65	0.99
4	0.6130	20.3	0.66	0.99

TABLE I: mass, mass per unit area, parylene thickness and transmission at 3.1 keV.

The sample coating was done with 5 g dimer, on 4 rectangular pieces of aluminum foil 9.9 cm by 14.2 cm. The different pieces of foil were cut together so that they have exactly the same area, $S \simeq 140.6$ cm^2 on one side or $2S \simeq 281$ cm^2 for both sides. Still, the foils have different masses, presumably from different foil thicknesses: the first column in Table I gives the sample's mass m before coating. The mass differences between the foils actually exceed the mass Δm added by the parylene, in the second column. Parylene's thickness Δd on each side is given by parylene's density $\rho \simeq 1.1$ g/cm^3 as $\Delta d = \Delta m/2S\rho$. Despite the small differences in coating thickness on the different samples, the two coating's x-ray attenuation T at 3.1 keV in the last column is the same, $T \simeq 0.99$. Differences that appear in the third decimal are suppressed because they are meaningless in comparison to the shot to shot variation in PRS output (perhaps 0.1) or the variation in transmission through the lithium foil itself (which may be on the same order as the differences in mass between the sample aluminum foils).

We should mention that this first implementation of the parylene coater does not yet behave as well as it should. One problem is a rather large ($\simeq 50°$) overshoot in the vaporization temperature: the ideal is 150°. However, the temperature is not measured at the dimer, but on the vacuum vessel's metal pipe about 10 mm from the vaporization heater so that neither the controller nor the dimer sees exactly this temperature. Judging from the pressure during deposition, about 50 mTorr, the vaporization temperature seemed to be acceptable.

We will continue to improve the parylene coater, with better hardware and where possible by the use of better deposition parameters. For example, according to some research findings that seem to have been overlooked by commercial parylene coating companies, coating proceeds faster and leads to a better product if the coated surfaces are kept cold, perhaps -10

°. Another paper mentions that an electric field might improve coating speed and quality. How to implement these ideas is not yet clear.