Final Technical Report

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Submitted by:	Name: Anoop Agrawal Title: CTO Phone: 5202302140 Email: anoop@polyceed.com
DOE Project Team:	DOE Project Officer: Mohammed Khan DOE Technology Manager: Marc LaFrance Project Monitor: Will Luppino
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Project Goal

The project goals were to (a) develop low-cost electrochromic (EC) devices with organic dye containing layer and (b) fabricate devices with this layer to pass ASTM E2141. The targeted performance of the integrated glass unit (IGU) containing the EC devices from the program will demonstrate a range of Solar Heat Gain Coefficient (SHGC) of about 0.5 to 0.1. The low-cost was also attributed to the processing of these devices where capital equipment costs and process complexity was significantly reduced as discussed below.

Background

The project goal was to be achieved by using UV stable organic EC dye-based layers that would confer significant cost advantages. As would be discussed in the report, several accomplishments were made even though the Covid pandemic struck soon after the program started. In addition, the test equipment at NREL was down for a few times lasting six months at a time.

The devices demonstrated at the finish of the program could be largely fabricated by using standard flat glass processing methods which saves on capex costs which were estimated to be about 80% lower as compared to the current thin-film technology devices. Second, an attractive attribute of this technology was that the dye composition in the electrochromic layer could be changed to control the color in the darkened state without having to change the manufacturing method. The separation of the two electrodes using a thick electrolyte layer ensured that the yield of such devices would be high, as the chances of developing shorts through the device substantially decrease. Further, since UV durability was of very high importance in this application, it was essential to demonstrate that devices with organic EC dyes would be able to withstand exposure to ASTM E2141 conditions. A complex step in production of EC devices is to intercalate one of the electrodes with ions (e.g., lithium ions) and then incorporate that in the device. This step is called pre-reduction, which is difficult to carry out on large planar substrates and also since the pre-reduced coatings are sensitive to oxygen, their handling becomes difficult during processiong. The proposed devices avoid pre-reduction which significantly reduces manufacturing complexity.

Initially, the project called for fabricating an organic EC layer where the dye was tethered within a polymeric matrix, and to form the device it was combined with a tungsten oxide containing EC layer by lamination using a polymeric electrolyte. Although as demonstrated below Polyceed met the program milestones in the first year, but it was also becoming evident that the EC device structure could be further simplified by incorporating EC dyes in the electrolyte which would have a major impact on achieving a lower-cost device and speed up the meeting of the durability goal. The report summarizes briefly the achievements in the first year as we met the go/no-go criteria. Thereafter, the transition to a simplified device was undertaken.

Achievements in the first year

A significant task in the first year was the development of dye containing electrode layer (Active layer). The monomers selected for the polymeric layer comprised of both urethane and acrylic chemistry. This allowed us to incorporate dyes with both hydroxyl and acrylate termination. The matrix polymers were deposited in clear coating with thicknesses varying from 5 to 30 microns. The acrylate curing was carried outby UV radiation.

Regarding the selection of the EC dyes two parallel approaches were taken. From our previous work we had seen that the coupled dyes with accepter-donor architecture had demonstrated a high level of UV stability, and we decided to work with a few known compounds by attaching reactive tails to them so that they could be polymerized into the matrix. The use of urethane/acrylate chemistry allowed us to incorporate a wide variety of reactive tails including hydroxyl groups, acrylates and methacrylates depending on the reaction complexity. In addition, significant effort was spent on modelling of dyes at NREL using time-dependent density functional theory (TDDFT) methods. However, these methods suffered from spin contamination in the predicted electronic states and failed to reproduce experimental observations using model dye systems. Higher level methods that are designed to produce the correct spin states, such as symmetry adapted cluster configuration interaction (SAC-CI), gave results with the correct spin properties, but the predicted spectra only matched experimental observations in some cases only when the dyes were in their ground states. This effort could not generate insights into new molecules. Thus, in the end, only intuitive approach from our past experience was used for new dye synthesis and some dyes were synthesized at third-party facilities and NREL assisted with their chemical expertise to help develop synthetic procedures.

Highly uniform polymeric coatings with dyes attached to them and containing conductive carbon nano-tubes were deposited using wire wound Mayor rod technique using a semi-automated equipment (Figure 1).

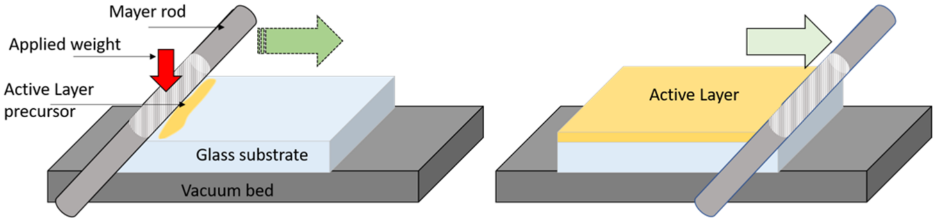

Figure 1: Active layer coating method using a Mayer Rod technique

In the above experiments the coated surface area size was 10 cm x 10 cm. The quality of the coatings was excellent, and an image of the coated substrate is shown in Figure 2. We then optimized the adhesion of the coatings to the substrate and measured the impact of these changes in the performance of electrochromic cells.

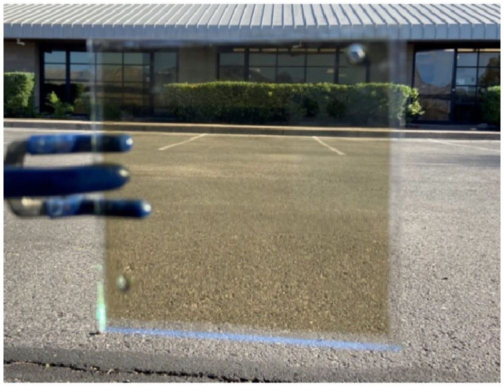

Figure 2: Image of cured active layer coating

These coatings were integrated into an EC device using a polymeric electrolyte and a second electrode which was a wet-chemically deposited tungsten oxide. Devices were produced that showed an optical density of 1 and showed less than 10% change after 504-hour exposure to the ASTM E2141 testing protocol. Figure 3 shows a schematic of such a device and Figure 4 shows a kinetic trace at 550nm before and after this exposure. Figure 5 shows the device pictures before and after cycling both in the colored and in the bleached states.

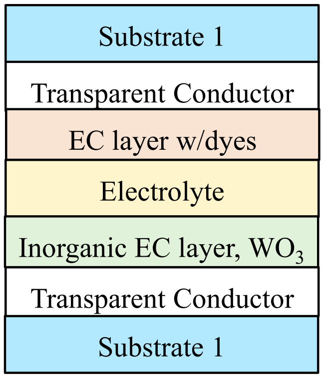

Figure 3: Device schematics

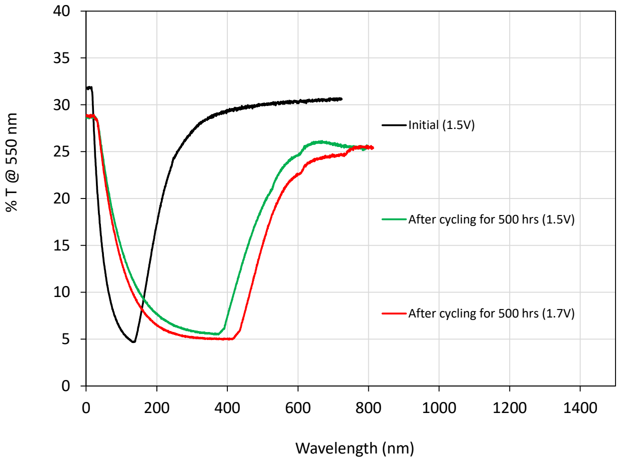

Figure 4: Kinetic traces of devices before and after testing at NREL for 504 hours

Figure 5: Photos of the devices before and after cycling at NREL

Simultaneously, device fabrication methods were developed where extruded polyurethane films were used to laminate substrates while placing edge butyl sealants. An edge sealed laminate using glass substrates in a size of 30 x 30 cm is shown in Figure 6, which was found to hold well under environmental testing by varying temperature (-40 to 85C) and humidity (0 to 100% at 45C).

Figure 6

Achievements after the first year

Extruded electrolyte films were obtained from our development partner. These films had good adhesion to the transparent conductor and exceeded 40 pounds/linear-inch as established by a 90-degree peel test. An ionic conductivity of 3.6×10^{-6}S/cm was achieved. However, these films had poor adhesion to the active layer (dye containing layer) and to the tungsten oxide and the adhesion dropped to below 5 pounds/linear inch. Faced with this situation, we developed lamination using liquid monomeric formulations which are in-situ polymerized into a solid after placing the liquid formulation between the two electrodes.

We demonstrated devices having dye containing coatings (active layers) with tungsten oxide as the other electrode with 65% visible transmission and an optical density change of 1 at 550nm, we also started exploring durable devices where the organic EC dyes could be directly added to the electrolytes so that the electrolytes only came in contact with the transparent conductors. The prospects of developing devices on this idea gained momentum as these would result in the lowest cost devices since no coatings had to be deposited, thus no processes were required to remove the coatings from the perimeter area in order to seal them, and no electrode matching was needed. The electrolyte films only contacted the transparent substrates and most of the standard flat glass processing equipment could be used which would yield additional reductions in capex. Further, the dye compositions could be changed in the future to obtain any desired color and/or absorption in the NIR without a change in device structure or its manufacturing process. It certainly would require more work after the program termination to come up with the appropriate dye packages with color control and NIR absorption, but the important point was to see if such devices with organic EC dyes would have the required durability. The front substrate of these devices had a PVB lamination or a polymeric film which attenuated the UV and also provided protection against impact.

Given very significant advantages of these devices in terms of cost, the focus changed towards development and optimization of devices with organic dyes in the electrolyte which could pass the ASTM E2141 exposure testing. Two types of devices were evaluated simultaneously, one which only had an electrolyte with organic dyes in contact with the two transparent electrodes, and the other where a wet-chemically deposited tungsten oxide layer was used along with an organic dye in the electrolyte.

Devices with the second type of construction, i.e., tungsten oxide and a dye in the electrolyte layer successfully passed 2,000 hours of exposure under the ASTM testing. However, it became difficult to develop and test these along with the devices employing organic dyes only due to the large number of variables and test-chamber availability constraints. We decided to focus only on the dye devices as they had the best economics due to simplicity of construction and requiring no coatings to be deposited, etched or treated other than purchasing glass with already coated transparent conductors.

The structure of these devices is shown in Figure 7

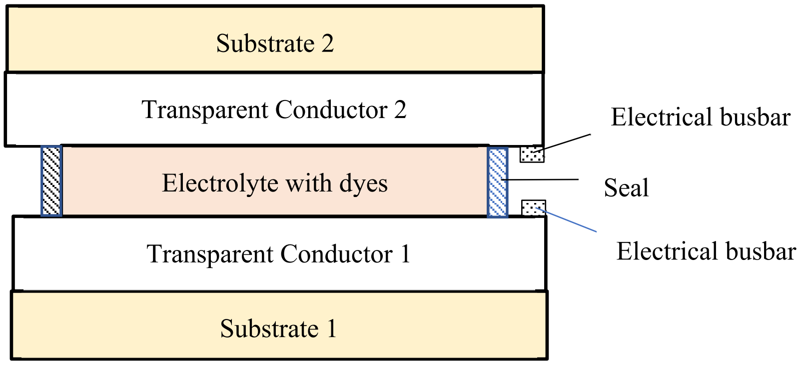

Figure 7: Polyceed's Device structure

There was a change in test equipment at NREL from the XR260 chamber, after the devices had been successfully tested in excess of 4,000 hours of exposure (but fell short of the required duration of 5,000 hours). The new chamber was Ci5000. Some parametric differences in these chambers were overlooked that caused several samples to fail suddenly in the last phase of testing. A few did survive and passed the 5,000 hours of exposure, as shown below. Data on these samples before and after testing along with their kinetic traces and change in the colored and bleached states is shown below in Figures 8 and 9 respectively. The exposure time under ASTM E2141 was 5005 hours and they were cycled for 150,150 times. These were not IGUs and the sample size was about 9cm x 13 cm. Figures 10 and 11 show photos of these devices in the bleached and the colored states before the start of testing and after 5,005 hours of testing.

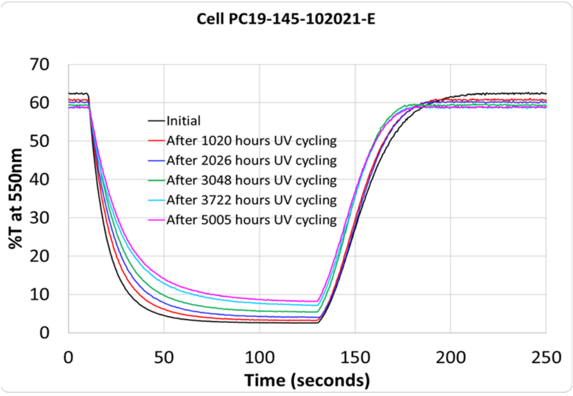

Figure 8

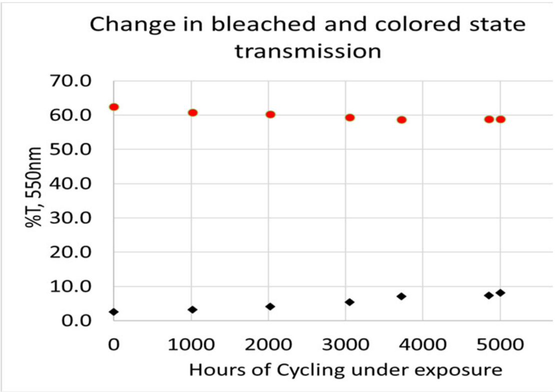

Figure 9

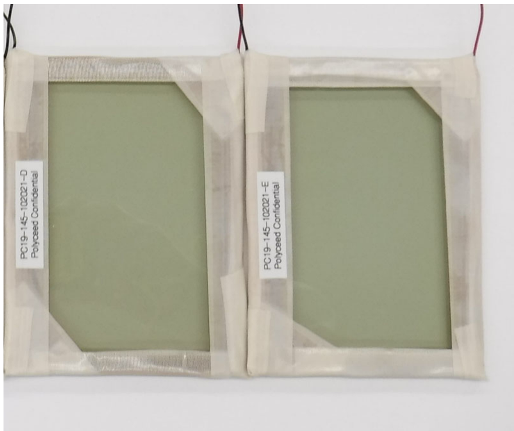

Figure 10a: Initial, bleached

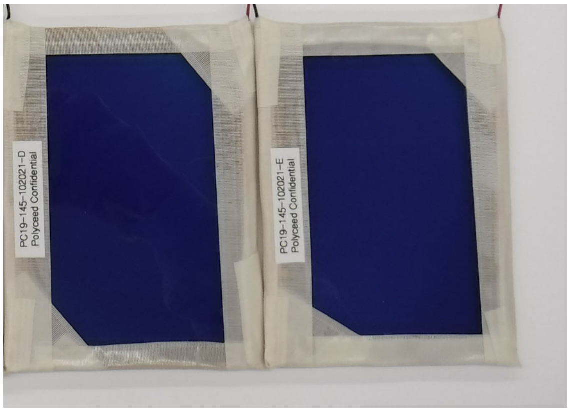

Figure 10b: Initial, Colored

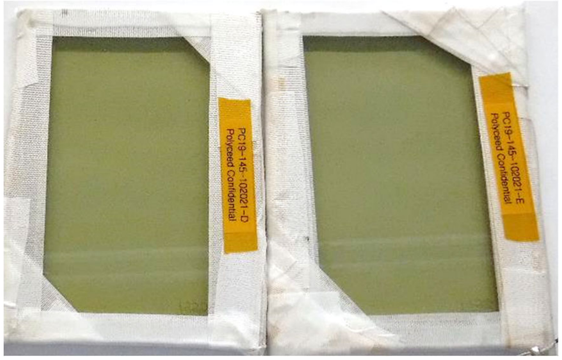

Figure 11a: After 5005 hours, bleached

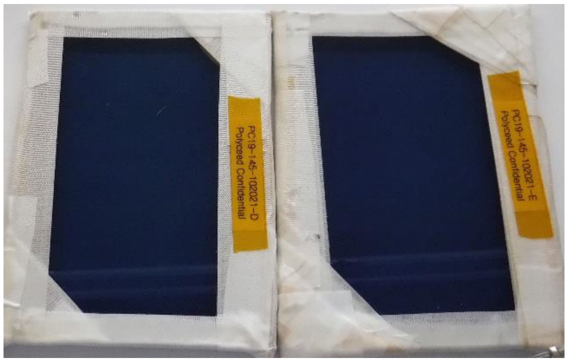

Figure 11b: After 5005 hours, colored

IGUs with EC devices passing the above tests in a size of 25 cm x 25cm have been prepared. These have been shipped to NREL for ASTM testing but the results on these will be only available after the program termination. Photographs of these are shown below in the colored and in the bleached states in Figures 9, 10, 11, 12 and 13. In making these devices, a change has been made to the busbars from spring clips to conductive tapes (with conductive adhesives) used in the solar industry as charge collection tapes. This change was required so that there is no offset between the two EC device substrates so that IGUs can be made (see Figure 7). We do not expect any material change in performance (durability) of the EC devices within these IGUs as this change is external to the device. Since there no change in substrates or electrolyte composition, and these tapes are external to the sealed area where they do not contact the electrolyte, we expect the EC devices to be durable. However, to be cautious about this change, we are submitting these devices for preliminary evaluation and changes in busbar resistance will be evaluated periodically. Testing of such busbars and alternatives with better performance and/or process advantages is being evaluated outside of this DOE program. This preparation will increase our readiness to resubmit the samples in the fourth quarter if necessary.

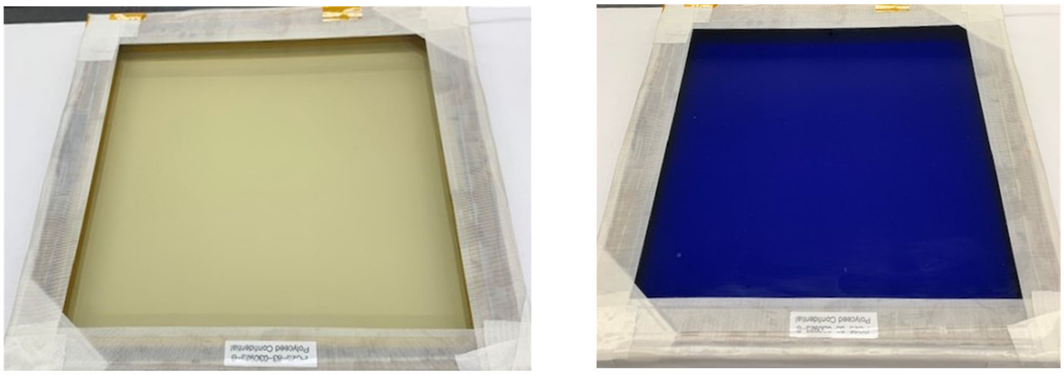

Figure 9: IGU 1

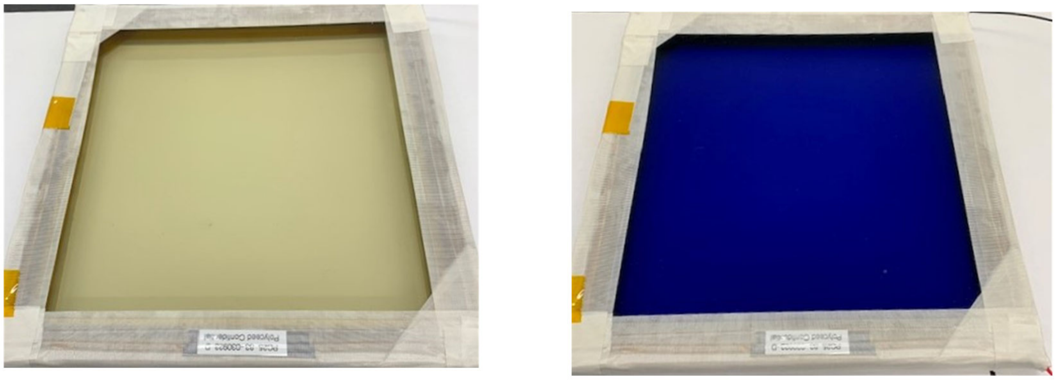

Figure 10: IGU 2

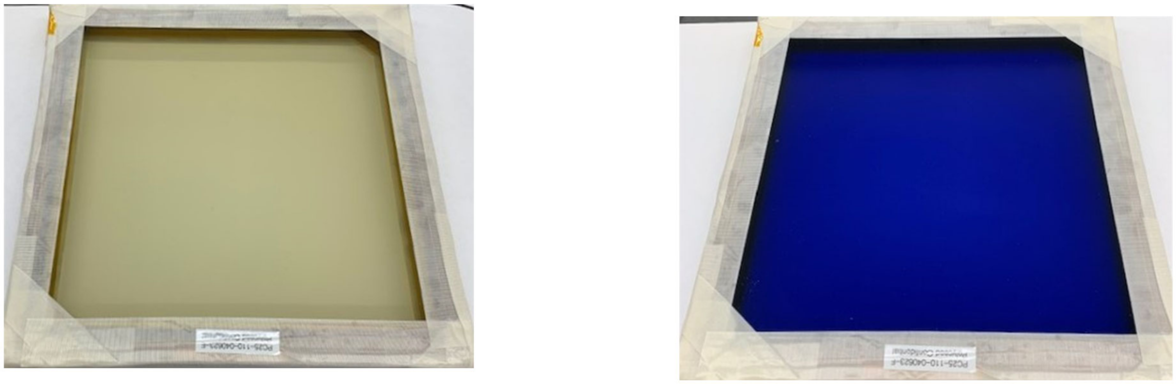

Figure 11: IGU 3

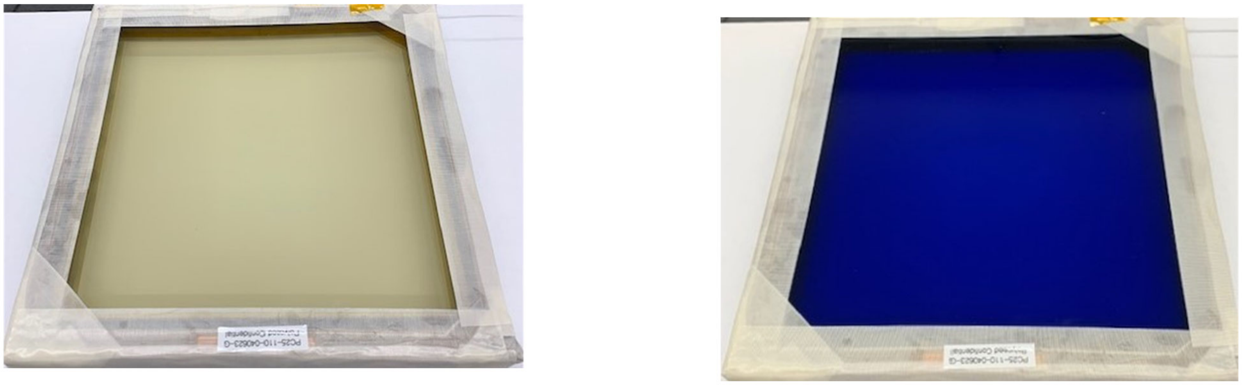

Figure 12: IGU 4

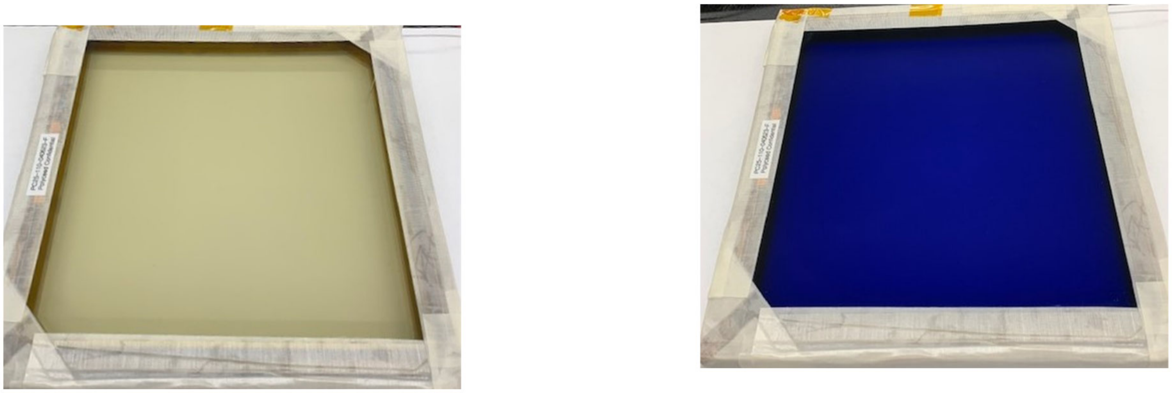

Figure 13: IGU 5

Window commercialization

While the devices are being tested at NREL, several technical developments are being carried out to ready the technology for commercialization of these in building windows. These efforts are outside the current BENEFIT program.

In addition, we have identified markets within residential window glass to initially introduce the product into. For rapidly commercializing the technology we are teaming up with key suppliers, glass and IGU manufacturers for further testing and test-installations. A very attractive aspect of this technology is its low cost due to the device simplicity.

Summary

During the program period, EC devices were successfully fabricated with organic EC materials which have simple construction, high expected manufacturing yields and attractive economics.

First, the materials of construction in this device avoid the necessity of pre-reducing any layer while assembling the device, which contributed to significant cost reduction. The devices demonstrated at the finish of the program could be largely fabricated by using standard flat glass processing methods which saves on capex costs which were estimated to be about 80% lower as compared to the current thin-film technology devices. In addition, several processing steps including EC glass coatings are not required in the processing of these devices. A highly attractive attribute of this technology is that the electrolyte composition can be changed to impact device performance such as their color and NIR performance without having to change the manufacturing method.

It has been demonstrated within this program that these devices were durable as they could be successfully cycled for 5,000 hours under ASTM E2141 exposure conditions. The EC devices used to fabricate 25cm x25cm IGUs and submitted to the NREL for preliminary testing incorporate the structure and composition of the successful devices.