Layer-by-Layer Deposition for Stretchable Gas Barriers

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Motivation

Layer-by-Layer (LbL) deposition processes are used to synthesize thin films by applying layers of materials to a substrate via dip-, spin-, or spray-coating layers of alternating materials with a rinsing step in between. LbL deposition has proven to be an inexpensive method of synthesis, and certain LbL-constructed thin films have been shown to possess low oxygen permeability even after undergoing cyclic stress.

Figure 1. LbL deposition-synthesized thin film undergoing tensile stress. Source: *Cho, et al. [1]*

In this experiment, the dip-assisted LbL synthesis of a polyethylene oxide (PEO)/polyacrylic acid-stabilized carbon nanotubes (CNT-PAA)/graphene oxide (GO) trilayer thin film is performed for future implementation in flexible Li-ion pouch cells. Special emphasis is placed on optimizing experimental procedures to produce a consistent film.

Objectives

Qian, et al. report the tensile strain objectives for various consumer electronic applications. [2]

- Most stretchable electronics (phones, watches, televisions) prototypes are projected to require ~5% strain achievable
- Battery packaging should aim for small OTR and WTR approaching aluminum plastic laminates
- Stretchable film packaging should maintain structural integrity and a low OTR during and after undergoing cyclic stress
- SEM characterizations are required to view surface morphologies and trilayer quality

Methods

- Polyethylene terephthalate (PET) and polyurethane (PU) substrates were cleaned using methanol and DI water, followed by Corona treatment to apply a surface charge.
- Aqueous solutions were prepared with DI water and pH of all solutions was set to 3 using HCl.

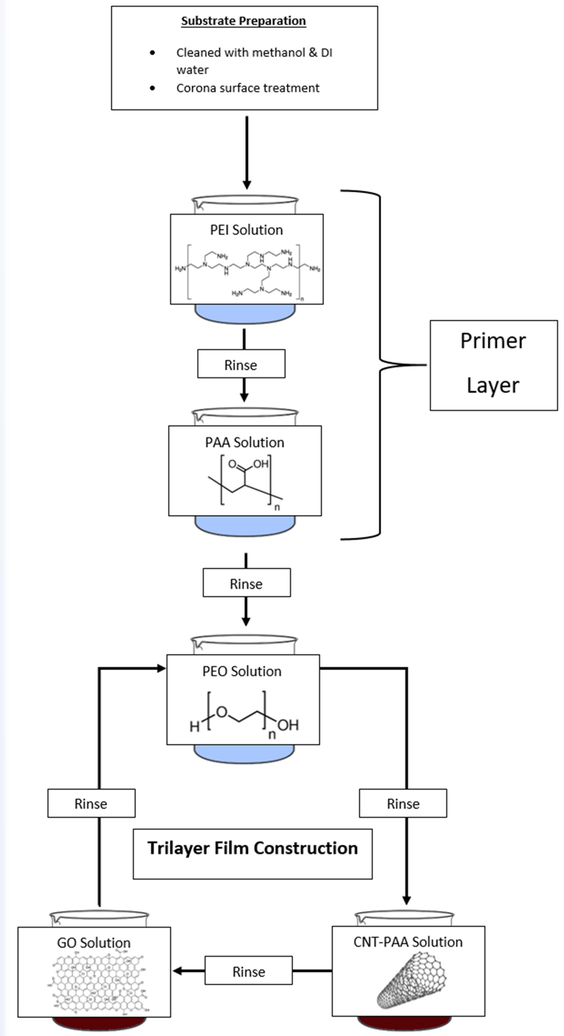

Figure 2. Step-by-step substrate dipping procedure.

- A "primer" layer was deposited by submerging the substrate in PEI and PAA solutions for 5 minutes each, with a rinsing and drying step in between layers.

Trilayer Construction

- After preparation, the substrate was dipped in PEO solution for 5 minutes, followed by a rinsing and drying step.
- The remaining CNT-PAA and GO layers were deposited using the same procedure.
- The PEO/CNT-PAA/GO trilayers were deposited 40 times.

Results

Figure 3. On left: trilayer film on PU substrate. Right: trilayer film on PET substrate.

- SEM, tensile and OTR testing not possible due to unforeseen circumstances
- Visible material buildup near bottom of film suggests rinsing/drying step may cause excessive material loss
- Fan-assisted air drying more effective than heat-assisted drying

Discussion & Comparisons

- Rinsing and drying steps may need modification to ensure consistent film quality
- Drying configuration may need to be changed to reduce contributions from gravity towards uneven consistency
- Skipping drying step altogether may result in higher quality results

- Seo, et al. report dip-assisted synthesis of PEO/PAA films without drying step, longer dipping & rinsing times [3]
- DeLongchamp, et al. report another PEO-based LbL film with the final rinsing step skipped [4]
- Alternatively, spin-assisted deposition should be considered with regards to consistent surface morphology

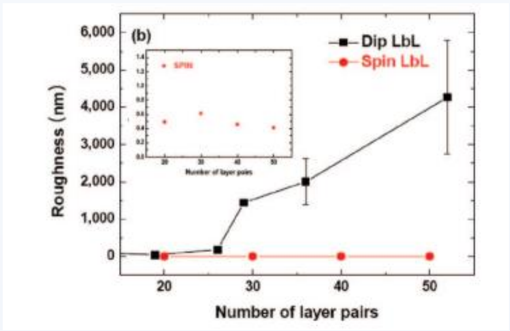

Figure 4. Comparison of dip- and spin-assisted LbL film roughness. Source: *Seo, et al. [3]*

- Layer materials may also be changed for a potential performance increase
- Qin, et al. report OTR values of 2.54 (cc/cm^3 day atm) at 10% strain using a PEI/montmorillonite (MMT) LbL bilayer on PET substrate [5]

References

- [1] Cho, C. et al. "Stretchable Electrically Conductive and High Gas Barrier Nanocomposites." Journal of Materials Chemistry C, 2018.
- [2] Qian, G., et al. "Designing Flexible Lithium-Ion Batteries by Structural Engineering." ACS Energy Letters, 2019.
- [3] Seo, J., et al. "Effect of the Layer-by-Layer (LbL) Deposition Method on the Surface Morphology and Wetting Behavior of Hydrophobically Modified PEO and PAA LbL Films." Langmuir, 2008.
- [4] DeLongchamp, D., Hammond, P. "Highly Ion Conductive Poly(ethylene oxide)-Based Solid Polymer Electrolytes from Hydrogen Bonding Layer-by-Layer Assembly." Langmuir, 2004.
- [5] Qin, S., et al. "Combined High Stretchability and Gas Barrier in Hydrogen-Bonded Multilayer Nanobrick Wall Thin Films." ACS Appl. Mater. Interfaces, 2017.