Simultaneous multilayer coating of structured particulate films

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Advanced functional materials for energy and other applications are increasingly reliant on structured films which may be heterogeneous and/or multilayered, often requiring distinct stratification, intimate interlayer contacts, controlled and graded morphologies, and thin individual layers. For both new technology development and deployment, it is critical to be able to rapidly prototype and cost-effectively manufacture such films at-scale. However, traditional prototyping and manufacturing methods are cumbersome, requiring casting and careful handling of many thin individual constituent layers before laminating them all together. Saint-Gobain is applying the simultaneous multilayer slot and slide coating techniques that were originally developed and matured in the photographic film industry to films cast from ceramic slurries with focus on application to solid oxide fuel cells. These techniques promise to reduce the manufacturing complexity and cost.

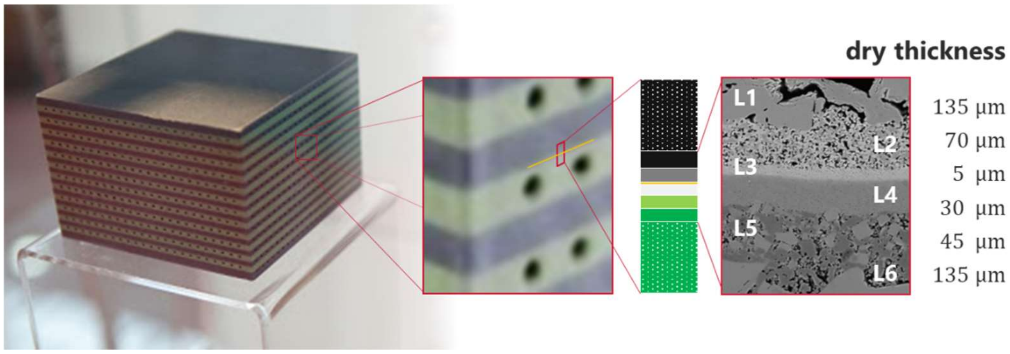

Figure 1. All-ceramic SOFC stack structure illustrating the 6-layer electrolyte component. The architecture has an engineered microstructure with various thicknesses and porosity levels

Simultaneous multilayer processes are often suggested as being potential ‘next-generation’ options. One particularly well-suited application was our internally developed all-ceramic solid oxide fuel cell (SOFC) stack. As illustrated in Figure 1, the Saint-Gobain SOFC architecture comprises a component with 6 functional ceramic layers. The individual layers range in thickness from $< 5\mu\text{m}$ to $> 100\mu\text{m}$ and are traditionally produced through a series of independent tape casting steps followed by punching and lamination. This case is particularly well suited for multilayer coating as the architecture has many layers, the casting formulations are all water-based, and the casting and handling of the thin tapes can be very challenging. Figure 2 below illustrates the process simplification that could be realized in the conversion to simultaneous multilayer coating.

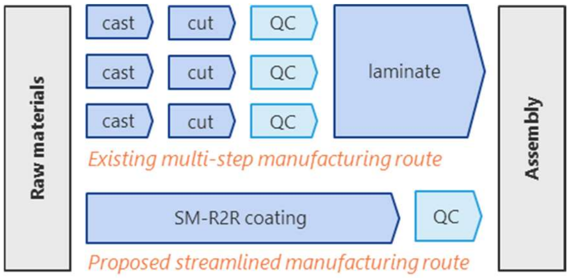

Figure 2. Simultaneous multilayer coating can consolidate and streamline existing multi-step manufacturing routes, thereby enabling rapid development and continuous, at-scale manufacturing of multilayer devices.

We partnered with the Department of Energy Advanced Manufacturing Office starting in 2017 to explore this process technology for industrialization not only of SOFC components, but potentially of other multilayered structures of interest to the DOE. With the project now nearing completion, we seek to share with the community some of our new insights and solicit from the community collective best practices and shared technical challenges. Wne will discuss in some detail our approach to open innovation, de-risking the process development, and addressing some of the challenges inherent to multilayer coating of highly loaded aqueous slurries.

Public funding de-risks process development and enables open innovation

Outside collaboration was a core part of our proposal to the DOE, and proved to be a major benefit of having undertaken the project. To address the questions of cost and energy savings, we partnered with Oak Ridge National Lab to engage in a techno-economic analysis of the benefits of replacing multiple single layer coating steps with various levels of consolidation into SM coating steps (ultimately a single SM coating step). The value of having economic analysis executed externally was two-fold: to validate our own internal cost models as a business tool, but also to lend credibility to these cost estimates. We also benefited from Oak Ridge's cost modeling expertise to develop a reusable tool that could be applied to help justify the deployment of multilayer coatings beyond this test case.

We also established from the outset an advisory board including representatives from national labs, universities, and industry. The purpose of the board was primarily to identify potential new applications for simultaneous multilayer coating processes that could be of interest to DOE and they provided suggestions and contacts to explore the process applicability to, for example, multilayer capacitors, solid state batteries, and other fuel cell architectures. Beyond this role, some members of the board provided invaluable technical input in support of the project deliverables.

These partnerships together with the connections to the AMO community in general have also led to fruitful new connections that we continue to leverage.

Stepwise approach to de-risk development

The external connections were one axis of a broader de-risking strategy used for the transition from single layer tape casting to multilayer slot and slide coating. There were many challenges captured in the risk matrix submitted as part of the original proposal. Some key questions we planned to address were:

1) Can the tape-cast microstructure of each layer be reproduced via slot coating?
2) Will the multiple layers intermix or heavy particles settle during coating or drying?
3) Will any layer components inter-diffuse during coating or drying? Is that bad or good?
4) Will it be possible to dry the layers without colloidal or stress cracking?
5) If the multilayer coating fails, how will we know where the problem originated?

We took a stepwise approach to address these and a myriad of other concerns associated with adapting the tape casting process to multilayer slide. Broadly, the project was divided into two phases, the first phase focused on slot die coating and the second phase on slide die coating.

In the first phase, each sub-layer layer was coated by a benchtop single layer slot coater to identify fluid handling, jamming, and microstructure concerns. Next, each adjacent layer pair was coated simultaneously in a 2-layer slot die on our roll to roll pilot coater in order to identify problems in wet-on-wet interlayer compatibilities. This dual-layer pairing step would also elucidate if simultaneously coated bilayers would impart any adverse effects to the fuel cell electrochemical performance in a button cell.

After demonstrating by dual layer slot coating that each layer pair was fundamentally compatible for simultaneous coating, the second project phase was aimed at using slide coating to progressively increase the number of simultaneously coated layers. Critically, the formulations and conditions for the slide coating process were largely informed by knowledge gained in the first phase. Many of the first phase trials provided invaluable insights and opportunities to solve technical problems that would have been more challenging to overcome in the more complex and expensive multilayer slide configuration.

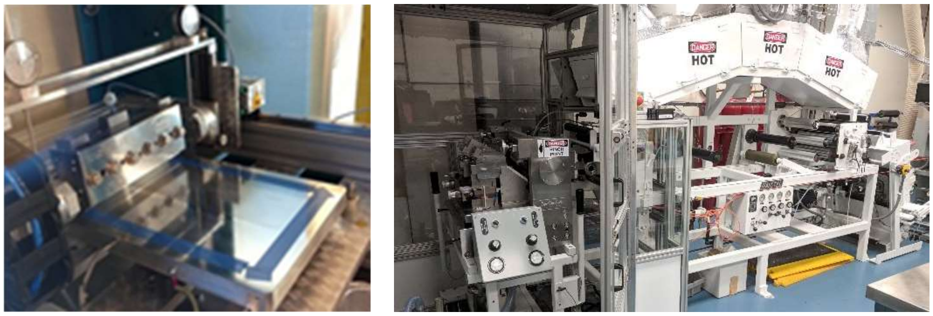

Figure 3. (left) Batch coater used for initial formulation adjustments and (right) small pilot coater used for 2-layer slot and multi-layer slide trials.

We now highlight our strategies to addressing some specific challenges encountered during the project. We will discuss our approached to die design, mitigating pseudoplastic rheological behavior, eliminating wet-on-wet inter-layer dewetting, and also present an open question around a coating defect dubbed "tectonic cracking".

Successes of open collaboration and stepwise development strategy

Die design

Specifying multilayer die design can be a challenging task. The patent literature abounds with design options and nuances such as slide/attack angles, lip configurations, edge guides, corner chamfering, etc. The academic literature highlights the effects of nuanced die design considerations for avoiding flow recirculation and coaxing well behaved laminar flows. Speaking with former Kodak and Polaroid researchers revealed the existence of vast “libraries” of dies with sophisticated lip designs explored in pursuit of optimal designs. Discussions with our die manufacturer on adjustability of various design aspects for R&D purposes ran into practical limits.

Despite the wealth of know-how contained in the community of multilayer coating practitioners and die designers, we found that consultation with these same experts all led to the same conclusion: take the “consensus” values for aspects like angles and keep everything else simple and easy to design and machine.

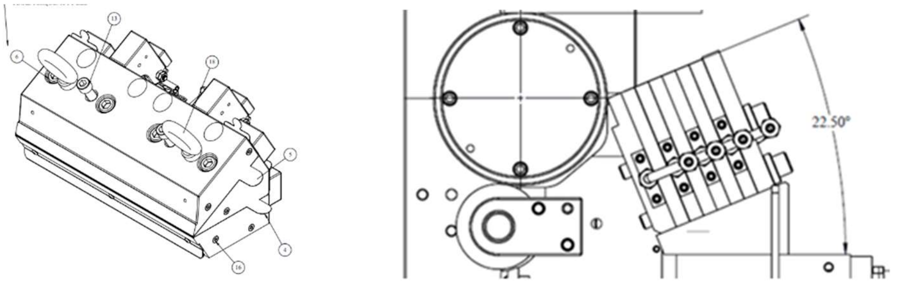

Figure 4. Drawing of (left) dual layer slot die and (right) 7-layer slide die.

The real value of our consultations and partnerships was to glean those details that were found from experience to be important for process development, and to receive focused advice based on knowledge of our specific material system. For example, maintain the bottom lip corner of a slide die as sharp as possible to pin the upstream static contact line, and if possible put an acute angle on it—practical advice that is not so visible in the literature.

After these consultations, we designed our multilayer slide die starting with the simplest design possible: all 90° angle blocks with the minimum thickness for stiffness and to accommodate internals. We addressed adjustability by opting for attachments, such as swappable edge guides and bottom lip extensions, rather than the costlier approach of alternate components. So far, we have not encountered any situations or issues that could have been alleviated by a more sophisticated die design.

Rheology and slurry jamming in die internals

Another benefit of the stepwise strategy starting at the bench-scale single layer slot die coating was to identify and solve a problem with slurry jamming and settling in the slot die internals. One of the layer formulations, which we found early in the slurry characterization stage to be shear thickening, exhibited some jamming in the slot die internals (Figure 5). The slurry did not suffer any coating difficulties in the tape casting process (for which it was originally formulated).

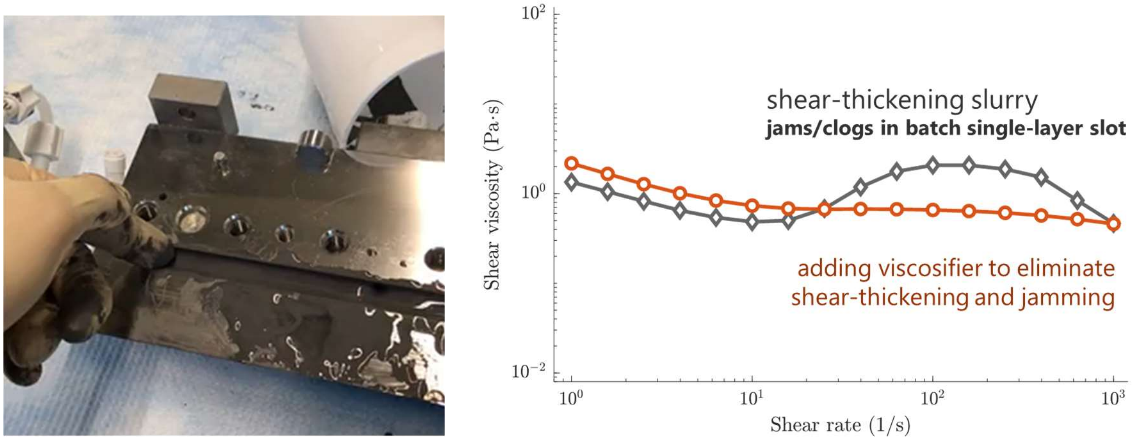

Figure 5. Jamming of die internals associated with shear-thickening slurry (left). Shear viscosities of the original shear-thickening and reformulated non-shear-thickening slurries (right).

Assuming the simplistic explanation that shear-thickening is generally is associated with particle jamming in flow, we “addressed” the issue by changing the rheology modifier package to increase the low shear viscosity and eliminate the shear thickening feature. This modification eliminated the jamming as far as we could observe, suggesting that simplistic correlation between “shear thickening” and “jamming” may be a sufficient paradigm for rheology tuning, as long as there are no other difficulties with coatability or coating defects.

Use of proxy materials for initial multilayer trials

We used lower cost proxy materials during early trials for in both the dual layer slot and multilayer slide stages. Rather than completely reformulate less costly slurries from scratch, we chose a variant of the functional slurry with the lowest cost materials and mixed in colored dies to be able to visually distinguish layers. The proxy system enabled us to sort out the details of the process and work out the major operational kinks prior to using more expensive formulations, namely to optimize our (1) slurry preparations before the coating trial, and (2) fluid handling during the trial.

Surfactant speed is important for wet-on-wet aqueous inter-layer stability

With some minor reformulations completed, the next step was to attempt 2-layer slot coating to identify specific layer incompatibilities. By casting each layer pair serially and integrating them into small scale devices, we could be sure that each interface had the proper structure and that each pair was fundamentally amenable to simultaneous casting and drying.

It is known in the literature that wet-on-wet interlayer interfacial tensions should be matched to avoid unwanted capillary phenomena (Kistler & Schweizer, 1992). It is also known that a good rule of thumb is to measure the surface tension of each layer formulation with the air, and grade those surface tensions through the multiple layers: high to low surface tension going from the web up to the film surface (Cohen & Gutoff, 1992).

Although all our slurries are aqueous, they had been formulated with varying types and amounts of surfactants as wetting, dispersing, and/or foam control aids. Because they had not been formulated specifically for wet-on-wet application by simultaneous coating, their surface tensions in air were not properly graded according to the known rule-of-thumb.

However, even after reformulation to properly grade surface tension, we encountered a significant non-wetting defect as shown in Figure 6b (comparison of a different layer pair appropriate graded in Figure 6a). We ultimately realized that it is not sufficient to grade the equilibrium surface tensions, but rather to account for surfactant speed measured by dynamic surface tension, such as by a bubble tensiometer.

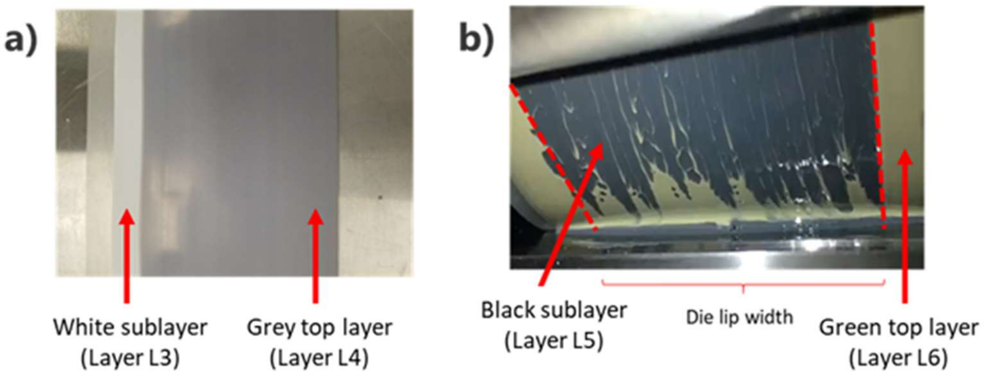

Figure 6. Examples of dual layer slot coated bilayers with (a) and without (b) proper dynamic surface tension grading. Without proper dynamic surface tension grading (b), the wet interlayer is prone to instability, which could not be corrected by coating process knobs alone.

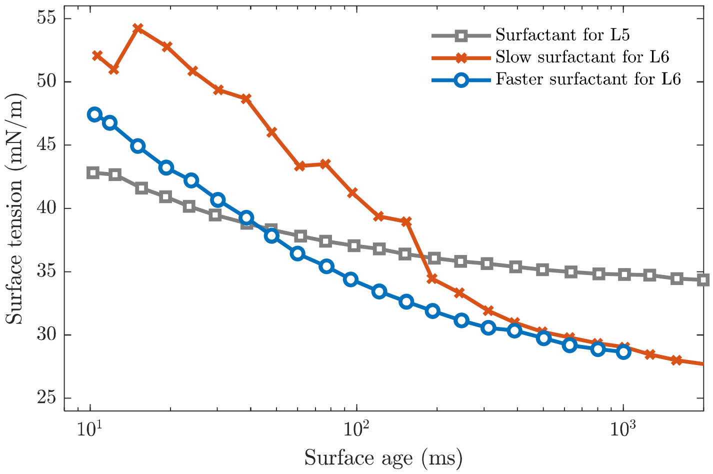

Figure 7. Dynamic surface tensions measured by bubble tensiometer of 0.1 % solutions of surfactant in water.

The inter-layer instabilities observed could only be solved when we further reformulated the top layer using a different "faster" surfactant (Figure 7). Both reformulated top layers had the same equilibrium surface tension (~30 mN/m versus the bottom layer's ~35 mN/m), but the time of cross-over with the bottom layer dynamic surface tension is much later (200ms versus 50ms) for the slow surfactant than the fast one. This indicates that time-scale of surface activity, namely in the 100ms range, matters in determining the inter-layer stability during wet-on-wet simultaneous multilayer coating. Note that while the measurements shown in Figure 7 were for simple solutions rather than complete formulations, the coating results are in clear qualitative agreement with the dynamic surface tensions.

The importance of dynamic surface tension for simultaneous multilayer coating is mentioned in the academic literature (Valentini, et al., 1991) and in the patent literature [US6824828B2US6, US4233346US4, US20040022954A1US2, US7754285B2US7, EP0706081A1EP0]. However, we were not able to identify literature or patents describing the phenomenon in the context of all-aqueous systems differing only in their surfactant packages. Literature describes, for example, systems with solvents or water-alcohol combinations. Thus, surface tension grading considerations, especially dynamic surface tension grading, may be an easily overlooked in designing all-aqueous multilayer coating processes.

While dynamic surface tension grading was effective in eliminating the observed coating instabilities, we do not yet fully understand the underlying mechanism at work. It seems counterintuitive to think of "interfaces" for surfactancy to act between all aqueous and fully miscible liquid layers differing only slightly in terms of organic components and concentrations; how do the surfactants "know" to migrate to the interlayers? Indeed, the lack of liquid-liquid interfacial tension between adjacent layers was verified experimentally using the pendant drop tensiometer (Figure 8, left): no surface tension was available to support a pendant drop. Thus, when the layers in this process are simultaneously cast, there is no reason to believe that an interfacial tension should exist between the layers absent some driving force for surfactant migration.

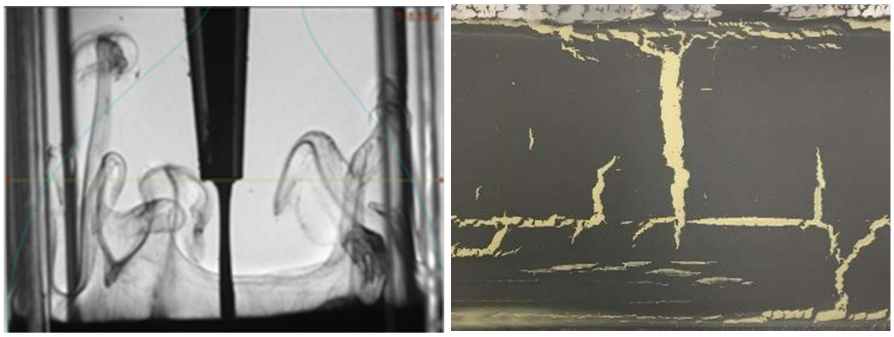

Figure 8. (left) Attempt to measure an interfacial tension between L5 (black) and L6 (transparent) liquids after removal of solids from the formulations by centrifugation. (right) Cracks developed during drying of L5 co-cast with L6 where the L5 has lower surface tension than the L6 layer. Image height is approximately 100 mm.

Open challenges in drying: the mystery of "tectonic" cracking

An additional challenge that seems to point to the existence of buried interfaces in the all-aqueous multilayer films was a defect that we dubbed "tectonic" cracking: the cracks would penetrate a single layer with very large spacings over the visibly unperturbed underlying layer (Figure 8, right), reminiscent of the earth's crust floating atop its mantle. These cracks were in some cases greater than 1 cm across, which is orders of magnitude larger than the film thicknesses.

The implication of this defect seems to be that there remains an interphase between coated layers that enables one layer to slide over another during drying and densification. The presence of interphase again appears to contradict the expected lack of an "interface" with an interfacial tension.

This "tectonic" cracking appears to be distinct from the relatively well understood colloidal cracking or mud cracking during drying/densification (Singh & Tirumkudulu, 2007; Scherer, 1987), though the phenomena may be related. While it's origin remains unclear, it can be practically mitigated, similarly to mud cracking, by re-formulation and drying process adjustments.

In closing

We have described our stepwise development approach to industrializing simultaneous multilayer slot and slide coating techniques and the strategies we used in overcoming key challenges throughout the journey. We reduced risk and cost through a systematic approach of progressively increasing process complexity and solved technical challenges through a combination of rigorous characterization and practical problem solving. As a final note, we hope that by continuing to engage with the coatings community in open collaborations on this topic, we can facilitate the broader adoption of the technology so we can jointly solve our collective challenges.

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