PRF#: 58453 ND-4
Project Title: Field-Effect Catalysis in Continuous-Flow Synthesis
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Research Progress

1) Optimization of a belt-drive electrochemical reactor with continuous laminar flow

We have refined the operation of a belt-drive reactor that can apply an electric field across a conductive platen during continuous flow (**Figure 1**, *left*). A grounded, stainless steel belt serves both as counter-electrode and as a driver of laminar flow at fixed velocities. The tension of the steel belt is adjusted by a support post to prevent minimum sagging or deflection during operation. Anodic reactions will be performed on the Au platen (2.5 × 10 cm) mounted on an adjustable stage that can maintain belt−platen separations as small as 10 μm, using micrometers for fine adjustment (**Figure 1**, *right*). Reactant solutions were initially delivered onto the steel belt using a syringe pump and microfiber glass pad, and maintained as a continuous liquid film between the belt and Au platen by capillary force. Alternatively, we have also fashioned conductive platens out of solid carbon plates, etched with square troughs (1 × 1 mm) for turbulent mixing.

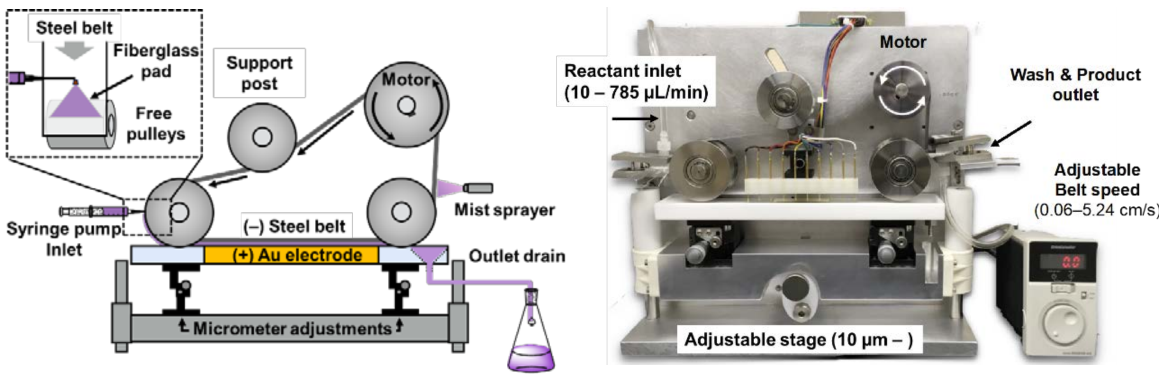

Figure 1. A schematic diagram and a photo of belt-driven electric field-effect catalysis flow reactor.

The operation of the belt-drive reactor is being optimized by using the Shono oxidation (anodic oxidation of amides to *N*-acyliminium ions followed by nucleophilic addition) as a test reaction. The anodic oxidation of *N*-formylpiperidine was easily performed in a standard electrochemical cell (IKA Electrasyn 2.0) using carbon/Pt electrodes, however two technical issues were encountered when using the belt-drive reactor. First, the reactant inlet needed further modification to introduce the reaction mixture more smoothly. Second, the reactants tended to adsorb onto the electrode surfaces. The syringe applicator is now being replaced with a slot die prototyped by 3D printing (**Figure 2**, *left*), and the anodic platen is being coated by PVD sputtering with perfluorinated silicone ($C_{10}H_4F_{17}Si(OEt)_3$) to minimize nonspecific adsorption (**Figure 2**, *right*).

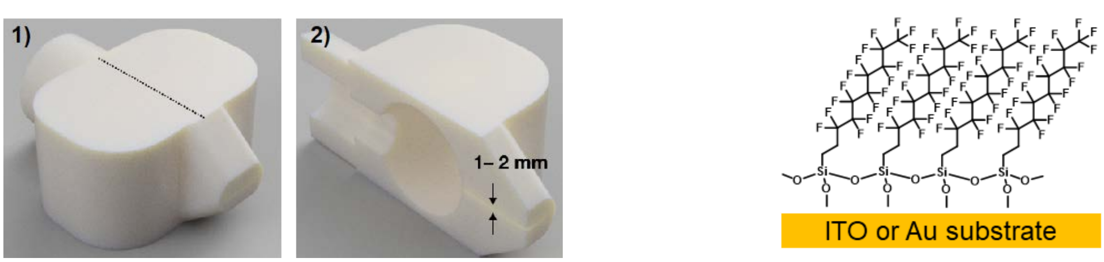

Figure 2. (Left) Prototype slot die created by 3D printing (top and interior views); (right) surface functionalization of the conductive platen electrodes by PVD sputtering.

2) Continuous manufacturing process for the photo-polymerization of thin-film electrets. In the course of the studies above, we had the opportunity to apply our belt-drive reactor toward the preparation of novel polymer films with a permanent electric dipole in the normal direction. This work is in collaboration with Shimpei Ono, Central Research Institute of Electric Power Industry (Japan). The dipoles are generated by the electric poling of "ionic liquid" (cationic and anionic) monomers, prior to their photo-polymerization (**Figure 3**). To achieve this, we designed a reaction tub with a UV-transparent (365 nm) window to enable photo-polymerization during belt-drive operation. Polymerization would be performed using commercially available ITO-coated PET substrate. So far, photo-polymerization has been tested using a mixture of ionic-liquid monomers, cross-linking reagent, and photoinitiator inserted between transparent ITO and Au-coated electrodes. A voltage was applied for 10 minutes to generate the electric dipole within the thin film followed by 10-minute irradiation using a 365-nm LED source, which successfully produced polymerized film with evidence of electret behavior. This condition is now being used with the belt-drive reactor.

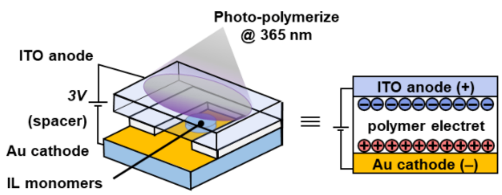

Figure 3. Photo-polymerization of electrically poled monomers into a thin-film electret.

Career Impact

This New Directions project has enabled the P.I. to explore the use of electric fields to modulate the outcome of chemical reactions, and to develop a novel tool for chemical and materials synthesis. It has also supported the efforts of a postdoctoral research associate, whose prior expertise in organic electronics and light-emitting materials has proven to be complementary to the activities and goals of this project, and two graduate students who have acquired valuable training in organic synthesis and electrochemistry.