



공학박사학위논문

Analysis and applications of the blade coating process

고기능성 박막 생산을 위한 블레이드 코팅 공정 분석 및 응용

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Abstract

Analysis and applications of the blade coating process

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The blade coating process is one of the coating processes that apply a liquid thin film of uniform thickness to a substrate. It is a representative post-metered coating method, widely used in various fields from laboratory scale to industrial scale due to its structural simplicity and ease of operation. The thickness of the liquid film applied by the blade coating process is determined by the interaction of various forces acting on the coating liquid, such as the viscous force exerted on the fluid during the process, the capillary force at the menisci, and the gravitational force exerted on the coating solution.

In high-speed blade coating processes in industrial manufacturing, the coating flow can be analyzed with a simple hydrodynamic model that neglects capillary forces because the viscous force derived from the movement of the substrate is dominant. However, capillary forces dominate low-speed blade coating processes, making the classical hydrodynamic model invalid for analysis. In addition, most of the hydrodynamic models are based on two-dimensional flow analysis assuming uniformity of the lateral flow, which is unable to identify various coating defects caused by lateral inhomogeneities.

This thesis aims to investigate the blade coating process in various applications by combining experimental, numerical simulation, and theoretical approaches and to solve the defects in the coating process utilizing these approaches. First, a novel continuous coating process was introduced to improve the performance uniformity of organic semiconductor devices fabricated at a laboratory scale. A study on process design for the fabrication of highly uniform organic semiconductor devices was conducted by analyzing the threedimensional flow analysis of the coating process based on numerical simulation and the visualization approach of the crystallization phenomena of organic semiconductor thin films.

Second, a high-speed blade coating process was used to fabricate battery anodes by applying battery anode slurry, which is a complex fluid, and analyzing the edge elevation phenomenon, a lateral defect that occurs in the battery electrode coating process. In this study, we experimentally observed the defects of battery electrodes fabricated by varying the process parameters and compared them by considering the viscoelastic behavior of the slurry concerning shear strain using linear viscoelastic modeling and analyzed the edge elevation phenomenon in the coating process from a rheological point of view in terms of the shear strain applied to the slurry and the viscoelastic deformation of the slurry for the shear stress. We also experimentally confirmed that the reduction of edge defects by controlling the process parameters can be performed without degrading the performance of the battery electrode from an electrochemical point of view.

Keyword : Blade coating, Finite element method, Coating defect, microfluidic channel, Complex fluid, Viscoelastic fluid **Student Number :** 2018-21745

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Chapter 1.

Introduction

1.1. Background

The coating is the process of applying a thin liquid layer to a substrate using an applicator to form a uniform liquid layer on the substrate Weinstein, 2004.In general, the final product of a coating process is a uniform thin film on a substrate that performs its intended function, for example, adhesive tape, battery electrode for electric vehicles, transparent conducting film for displays, and flexible circuits for wearable devices. By forming a uniform thin liquid film, due to the capillarity of the coating solution used in the coating process, the applied liquid layer has the nature to spontaneously level out, which is a great advantage in achieving good quality of the final product. In addition, the coating process is one of the representative processes widely used in various fields, from laboratory scale for scientific research to industrial manufacturing, because it is easy to mass production by continuously supplying the coating solution to the moving substrate.

Figure 1.1 is a schematic illustration of the continuous liquid coating process. First, the coating liquid is prepared by mixing various functional materials with a solvent depending on the final product to provide a uniform composition. The prepared coating liquid is supplied to the coating station by transporting it through a pipe, and the coating station applies the supplied coating solution as a uniform thin liquid layer of desired thickness. The applied liquid layer moves to the drying or curing unit to remove the solvent or solidify it to form a solid thin film. After that, it goes through subsequent processes such as calendaring and lamination to obtain the final product we want to manufacture.



Figure 1.1: Schematic diagram of the continuous liquid coating process.

To apply a uniform thin film liquid layer to a substrate, numerous types of liquid applicators have been developed and used in the coating process. Figure 1.2 shows the liquid applicators used to apply coating liquid at a coating station. Coating processes can be broadly categorized into two types according to which liquid applicator is used: In post-metered coating method, the thickness of the coated liquid film is determined by the interplay of liquid properties, substrate speed, and geometry. In contrast, in pre-metered coating methods, the thickness of the coated film is controlled independently of the parameters mentioned above by applying only the intended volume of coating liquid to the substrate. Because of their different metering mechanisms, much research has been done to understand and control them over the years (Weinstein, 2004; Diao *et al.*, 2014; Ding *et al.*, 2016; Patidar *et al.*, 2020).

Post-metered coating method



(a) Rigid knife coating.





(b) Flexible blade coating. (c) Rod, bar coating.

Pre-metered coating methods







(d) slide fed curtain coating.

(e) Slide coating.

(f) Slot die coating.

Figure 1.2: Schematic of various liquid applicators in the coating process (From Scriven, 2005).

1.2. Blade coating process

Blade coating, also called knife coating, applies a thin liquid film to a substrate by removing excess coating liquid on a moving substrate through a liquid applicator called a blade or knife. Since blade coating is one of the simplest coating methods that can produce a uniform thin liquid film, it is widely used and has been studied in various fields, from the production of functional films such as organic thin films for organic field effect transistors at the laboratory scale to the production of paper or adhesive tapes in the industrial field.

Blade coating is one of the representative coating methods categorized as a post-metered coating. Hence, the thickness of the coated liquid film is determined by the balance of various forces exerted on the coating liquid. Figure 1.3 shows the main forces in a blade coating. The final wet film thickness is determined by the interplay of the viscous force caused by the substrate movement, the capillary force caused by the surface tension of the upstream and downstream menisci formed between the coating liquid and the blade, and the gravitational force acting on the coating liquid. Because of this metering mechanism, it is difficult to control the precise wet film thickness compared with pre-metered coating methods. In laboratory scale operation, the gravity force and capillary force affect the coating flow dominantly. In contrast, the viscous force dominates other forces in industrial-scale operations.



Figure 1.3: Forces exerted on the blade coating.

1.3. Scientific research on flows in blade coating

As mentioned above, the blade coating process has been studied for several decades due to its simple structural features. In addition, as the types of solutions used as coating liquids have become more complex and contain a large number of functional particles, the properties of coating liquids are no longer limited to Newtonian fluids, but have non-Newtonian properties such as viscoelasticity and viscoplasticity. As a result, hydrodynamic models have been developed to analyze the coating flow in blade coating for various coating liquids. The early studies on blade coatings were mainly conducted on high-speed blade coatings for industrial manufacturing. Yehuda Greener, 1974 analyzed the dynamics of blade coating of Newtonian and viscoelastic fluid onto a moving substrate using lubrication approximation. Hwang, 1979 and I. K. Dien, 1983 studied the simple and complete analysis of Newtonian hydrodynamics in blade coating to predict the coated liquid film thickness as a function of process parameters like coating gap and material properties like surface tension, viscosity, and density. Timothy M. Sullivan, 1986 also performed asymptotic analysis with Reynods number and geometrical parameter to predict the film thickness of viscous and viscoelastic liquids. Ross et al., 1999 re-examine the approximate solution of Hwang and Dien & Elrod's previous studies and make a detailed comparison between their predictions and exact solution. Some previous researches are focused on the process design perspective. Tong C. Hsu, 1985 examined the separating forces in blade coating of viscous and viscoelastic liquids both theoretically and experimentally. Kim et al., 2006 studied a coating flow for a beveled blade configuration as a one-dimensional flow.

At the laboratory scale, blade coating is mainly studied on lowspeed applications because it is used for the experimental analysis of various materials, and the classical hydrodynamic models are not suitable for analyzing the coating flow of low-speed blade coatings. In this case, the substrate moves at a slow speed to precisely control the reactions and physico-chemical phenomena occurring during the fabrication process. In particular, in the fabrication of organic thin films for organic field effect transistor (OFET) manufacturing, Brédas et al., 2002 and Giri et al., 2011 confirmed that achieving well-aligned crystal domains in organic small molecule crystallization process is an important criterion to improve the electron and hole transfer rate in OFETs. After that, studies have been devoted to controlling the crystallinity inside OFETs and improving their performance through low-speed blade coating from a process perspective (Giri *et al.*, 2011; Diao et al., 2013; Giri et al., 2014; He et al., 2017). Maël Le Berre, 2009 theoretically examined the low-speed blade coating, and it classified the low-speed blade coating into two distinct operating regimes based on the substrate speed. Yim & Nam, 2022 also examined the shape of a puddle under the assumption of equilibrium, where the viscous force is negligible. Their analysis classified the shape of the puddle into three types based on the wedge shape, contact angles, material properties, and puddle size. However, to the best of our knowledge, most of the previous studies have focused on the twodimensional flow assuming uniformity in the transverse direction, and only theoretical analyses or experimental observations have been considered, which has the limitation that no in-depth analysis has been attempted for the phenomenon where complex transport phenomena occur.

1.4. Final remarks

Despite the many studies conducted on blade coatings, there are still many unexplained coating failures due to complex coating solution properties and process complexity. Therefore, the main objective of this study is to investigate the blade coating process in various applications by combining experimental, numerical simulation, and theoretical approaches and to solve the defects in the coating process utilizing these approaches. Chapter 2 presented an innovative continuous coating method designed to enhance the performance uniformity of organic semiconductor devices produced on a laboratory scale. The research explored a process design to manufacture highly uniform organic semiconductor devices. It was conducted by analyzing the three-dimensional flow analysis of the coating process based on numerical simulation and the visualization approach of the crystallization phenomena of organic semiconductor thin films.

In chapter 3, a high-speed blade coating process was used to fabricate battery anodes by applying battery anode slurry and analyzing the edge elevation phenomenon, a lateral defect that occurs in the battery electrode coating process. In this study, we experimentally observed the defects of battery electrodes fabricated by varying the process parameters and compared them from a rheological point of view.

Chapter 2.

Solution shearing process for OFETS

2.1. Study background

Solution-based coating has many positive attributes such as highthroughput manufacturability, processability at ambient temperature and pressure, and large-area scalability (Sun *et al.*, 2015; Gu *et al.*, 2018). this regard, solution-processed organic thin-film transistors (OTFTs) have been deemed as a highly promising technology because it can be applied to various applications such as large-area displays and sensor arrays (Klauk, 2010; Zhang *et al.*, 2010; Guo *et al.*, 2017). Contrary to vacuum deposition, the liquid-to-solid transition in solution-based coating is intricately dependent on the fluid dynamics in the vicinity of the liquid-solid boundary (Wang *et al.*, 2016). Therefore, the precise control of thin-film properties necessitates careful tuning of flow behavior and the understanding of how it influences the crystallization process and the thin-film properties.

Thus far, optimization of OTFTs has generally been conducted by trial and error without full discernment of the underlying fluid dynamics and its relation to the crystallization mechanism and thin-film properties (Diao *et al.*, 2014; Gu *et al.*, 2018). The crystallization process of organic thin-films occurs at the tens of nanometer to several micrometer scale, and the manipulation of flow behavior at such length scales is difficult. Furthermore, due to the complex interdependence of experimental parameters (Lamberti, 2014; Janneck *et al.*, 2016; Lee *et al.*, 2019), independent control of flow

behavior is challenging, rendering it difficult to elucidate the connection between flow behavior and thin-film properties. Numerical simulations have been utilized to study the effect of flow behavior on the thin-film properties. However, these simulations did not properly reflect the actual experiments, as the size of the computation domains was limited, transient effects were not considered, or simplified 2D flows were assumed (Peng *et al.*, 2016; Zhang *et al.*, 2017; Kyung Sun Park, 2019). Also, numerical simulations were conducted within a limited region, not fully considering the entire flow path, which restricts the interpretation of the relation between flow behavior, crystallization, and thin-film properties (Diao *et al.*, 2013). To overcome the limitations of computational analysis, in situ microscopy has been used to observe the crystallization process in real-time (Hu *et al.*, 2017). However, the connection between flow behavior and crystallization has not been elucidated.

2.2. Purpose of research

The main objective of this research is to introduce continuous solution shearing process for large-area organic thin-film manufacturing (chapter 2.3). In addition, the changes due to design variations of the introduced process are analyzed through numerical simulation and experimental analysis, and the effects of each part of the continuous solution shearing process on the subsequent process and their correlation are analyzed to elucidate the connection between flow behavior and crystallization of thin-film and achieve high uniformity large-area device production. To achieve this, we observe the microchannel feed regions with three different pattern designs and analyzed the effect of variation in pattern design on the flow kinematics of the flow developing inside the microchannel in Chapter 2.4. In chapter 2.5, an analysis based on numerical simulations and inverted phase optical microscopy was performed to investigate how differences in flow kinematics developed in the feed region led to differences in the puddle where the solution is distributed. In chapter 2.6, the effect of the observed differences in distribution tendency in the distribution region on crystal alignment in the crystallization that occurs inside the thin-film upon drying was observed through optical microscopy based visualization experiments. Finally, a comparison of the degree of orientation of the crystals inside the thin-film and the performance of OFETs fabricated using thin-film was performed in chapter 2.7.

2.3. Continuous solution shearing process

In this research, we introduce continuous flow microfluidic channel-based meniscus-guided coating (CoMiC), a system that enables precise control of flow behavior and comprehensive analysis connecting flow behavior, crystallization, and thin-film properties. Figure 2.1 is overall schematics of CoMiC. A microfluidic chip was utilized to continuously supply solution toward a substrate, and using microfluidic channels embedded with 3D structures, flow pattern was manipulated. The extruded solution forms a meniscus (curved airliquid interface) between the microfluidic chip and the substrate, and thin-film crystallization occurs near the edge of the meniscus at the liquid-solid boundary. As the substrate moves, crystallization progresses across the substrate. Using 3D numerical simulations and in situ microscopy particle-tracking analysis, the flow pattern was analyzed from within the microfluidic channel to the outlet where the solution extruded out onto the substrate. Furthermore, using in situ microscopy, crystallization process at the liquid-solid boundary was directly observed in real-time. For this work, CoMiC was specifically utilized to address the most critical requirement for the commercialization of OTFTs: device-to-device uniformity. Over the past several decades, the performance (e.g., field-effect mobility) of OTFTs has increased significantly, exceeding the requirements needed for many commercial applications $(1-10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ (Guo *et al.*, 2017; Paterson *et al.*, 2018). However, without ensuring sufficient device-to-device uniformity, OTFTs cannot operate concertedly to carry out circuit functionalities (Guo *et al.*, 2017), rendering high device performance meaningless.



Figure 2.1: Schematic diagram of CoMiC-based comprehensive analytical system along the entire flow path connecting flow pattern, crystallization, and thin-film properties.

The ink solution for CoMiC was formulated by dispersing TIPSpentacene and tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ p-dopant in mesitylene. $B(C_6F_5)_3$ is a Lewis acid p-dopant that forms an adduct complex with TIPS-pentacene,[14] which was shown to increase the mobility and reduce the threshold voltage (V_{th}) (Paterson *et al.*, 2018).

The microfluidic chip was made using polyimide due to its high resistance to temperature, pressure, and organic solvents (Heejin Kim, 2016). The PI-film stacked CoMiC blade was fabricated by the UV laser ablation previously reported (Heejin Kim, 2016). PI films were ablated by laser to pattern the inlet, outlet, Y channel, and various microfluidic patterns (SGM and SHM). After ablation, the top layer of each PI film was spin-coated (1000 rpm for 30 s) with FEP dispersed in aqueous medium, through which 3 µm FEP nanopowders were uniformly deposited after evaporation of solvent at 100 °C for 10 min. For alignment of stacked PI film, 4 holes with 1 mm diameter at corners were passed through pins in the metal plate. 3–4 stacked PI films were pressed at 350 °C under the pressure of 10 kPa for 3 h. The fabricated CoMiC blade was coated with 5 nm Cr/50 nm Au by electron beam evaporation and immersed in a 10 mm ethanolic solution of 1H,1H,2H,2H perfluorodecanethiol (PFDT) for 1 h to make surface hydrophobic. OSC solution was injected to microchannel via syringe pumps (PHD ULTRA, Harvard Apparatus).



Figure 2.2: Side-view in situ image analysis of meniscus shape variation during the coating of conventional solution shearing (left) and CoMiC without 3D structures (right).

One of the features of CoMiC is the continuous supply of solution during coating, which is on the contrary to conventional solution shearing, where a fixed amount of solution is inserted between the blade and the substrate prior to thin-film coating (Giri *et al.*, 2011). Figure 2.2 is side-view high-resolution in situ images of the meniscus during coating for solution shearing and CoMiC (here, the microfluidic channel did not have any 3D structuring), respectively. Videos S1 and S2, Supporting Information, are the corresponding in situ videos. Since solution volume progressively depletes for solution shearing due to the evaporating solvent and depositing thin-film, the shape of the meniscus gradually changes. On the other hand, for CoMiC, shape of the meniscus remains the same during coating due to the maintenance of steady state, where the evaporating solvent and depositing thinfilm are replenished by the constant supply of solution. Figure 2.3 is transfer characteristics of OTFTs made with solution shearing and CoMiC, respectively. For each condition, 70 OTFTs were

characterized. For solution shearing, there is significant variation in transistor properties compared to that of CoMiC. The solution volume and the meniscus shape are correlated to solvent evaporation rate (Goto *et al.*, 2012; Kyung Sun Park, 2019), which is in turn correlated to the crystallization process and thin-film morphology. Therefore, for solution shearing, higher variability in OTFTs is expected compared to that of CoMiC. This result strongly suggests that continuous supply of solution itself improves device-to-device uniformity.



Figure 2.3: The transfer characteristics of doped TIPS-pentacene thin-film transistors fabricated by conventional solution shearing (left) and CoMiC without 3D structures (right)

Figure 2.4 is close-up schematic of the CoMiC process. The flow pattern was tracked along the three designated regions (the feed, distribution, and film-formation regions) where the flow environment greatly differs. The feed region is the microfluidic channel, and the distribution region is where the solution flows out of the microfluidic channel onto the substrate. The film formation region is near the solution/thin-film boundary, where thin-film crystallization occurs. In this work, the computational and/or in situ analysis were conducted in each of the three regions to connect flow pattern to crystallization and thin-film properties.



Figure 2.4: Close-up schematic diagram of the CoMiC that consists of three regions; the feed, distribution, and film-formation regions.



Figure 2.5: Schematic illustration of the microfluidic channel with labeled directions (left). Three types of microfluidic channels (e.g., flat microfluidic channel [FM], slanted groove microfluidic channel [SGM], and staggered herringbone microfluidic channel [SHM]) and the corresponding flow patterns (right). The main channel height, width, and depth of the groove are 125, 500, and 125 µm, respectively.

2.4. Flow kinematics of feed region

2.4.1. Types of microfluidic channels

Figure 2.5 depicts the three types of microfluidic channels that were tested for this study and in previous research (Abraham D. Stroock, 2002): the flat microfluidic channel (FM), slanted groove microfluidic channel (SGM), and staggered herringbone microfluidic channel (SHM) (see Figure 2.6). For ease of explanation, we have designated the direction along the microfluidic channel (along the main flow direction) as the *x*-axis, and the transverse directions to the main flow direction as the y-axis (along the width of the microfluidic channel) and z-axis (along the depth of the microfluidic channel). In the case of FM, the channel consisted of no 3D structures. SGM consisted of slanted grooves (recessed regions along the z-axis) oriented at 45° with respect to the x-axis and y-axis, but parallel to the z-axis. SHM consisted of asymmetric V-shaped grooves that were parallel to the *z*-axis. Here, the position of the V groove tips alternated periodically to the left and right along the y-axis (at every five grooves). For SGM and SHM, the grooves occupied half of the distance along the z-axis, meaning that half of the yz-plane cross-section consisted of grooves (named as grooved region) while the other half did not (named as main channel region). We have designated ten grooves as one cycle, and each microfluidic channel consisted of five cycles (i.e., a total of 50 grooves for each microfluidic channel).

2.4.2. Numerical method for numerical experiments

Figure 2.6 represents geometries which were used in the numerical simulations. In this study, two types of geometry were used to conduct the simulations. One is the microchannel system with staggered herringbone, slanted groove patterns, and that without any

pattern (Figure 2.6a). The analysis of flow patterns inside of the channel and the assessment of both qualitative and quantitative assessment of mixing was conducted using these microchannel systems. Each microchannel except for FM has five cycles of grooves, and each cycle consists of 10 grooves. The channel height, width, and depth of the groove are 125 μ m, 500 μ m, and 125 μ m, respectively. The length of each pattern is 100 μ m, the distance between each pattern is 100 μ m, and the distance between each cycle is 100 μ m. In SHM, the tip of herringbone grooves positioned at a distance 1/3 of channel width from each side wall at each half-cycle. In SGM, the angle of slanted grooves is 45°. The number of elements was 2,404,259 for SHM, and 2,903,736 for SGM, and 2,891,020 for FM.

Another type of geometry is the truncated domains of the CoMiC systems (Figure 2.6b). The domains are the large enough to examine lateral mass transport phenomena in detail but small enough to be handled by the parallel computing facility that we can used. The width of the truncated distribution region is 1.5 mm, and the length of this region is also 1.5 mm. This domain can cover 50 percent of the total width of the microfluidic chip (3 mm), and 50 percent of the full length from the end of the outlet to the end of the microfluidic chip (1 mm). Again, the size of the truncated domains is large enough to analyze the difference between SGM and SHM feed because of the boundary layer estimation, which is discussed in chapter 2.5. The angle between the microfluidic chip and the substrate is 8 degrees, and the speed of the substrate is $500 \,\mu$ m/sec in all numerical experiments. The number of elements was 3,283910 for SHM-CoMiC, and 3,314,086 for SGM-CoMiC.



Figure 2.6: (a) Geometries of SHM, SGM, and FM used in numerical computations. Each geometry consists with 5 cycle. (b) Geometry of SHM-CoMiC used in numerical experiments. Red, blue, and ivory-colored planes represent inlet, outlet, substrate each. (c),(d) Top- and front- view schematic illustration of dimensions of SHM (c) and SGM (d).

The Reynolds number inside of the microfluidic channel can be calculated by the definition as follows:

$$Re = \frac{D_{\rm H}u}{\nu}, \quad D_{\rm H} = \frac{4A}{P} \tag{2.1}$$

where $D_{\rm H}$, u, v, A, and P denote the hydraulic diameter of the channel, the mean velocity, the kinematic viscosity, the cross-sectional area, and the wetted perimeter. The value of Reynolds number that inside of the microfluidic channel is about 0.32, and it is decreased when the solution flows to the distribution and film-formation regions. Hence, flows in this system are laminar.

The Péclet number is decreased from about 930 to about 70 at the end of the truncated distribution region, i.e., the mass transfer in this system still depends on the advection of the solution dominantly even though the effect of diffusion is increased. The value of the diffusion coefficient used in this study is $7.1 \times 10-4$ mm2/sec, which is the diffusion coefficient of TIPS-pentacene in toluene as the reference (Alharbi, 2017). Here, we assume that the value of the diffusion coefficient of TIPS-pentacene in mesitylene is similar to that of TIPS-pentacene in toluene.

In this study, we considered an isothermal flow of an incompressible, Newtonian fluid with constant density ρ , viscosity μ , and kinematic viscosity \mathbf{v} . The gravitational force is ignored because the flow inside of the microchannel is mainly driven by the pressure gradient. The steady-state mass and momentum balance equations are represented by

 $\nabla \cdot \boldsymbol{u} = \boldsymbol{0} \quad \text{on } \boldsymbol{\Omega} \tag{2.2}$

$$\rho(\boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u}) - \boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = \boldsymbol{0} \quad \text{on } \Omega \tag{2.3}$$

 $\boldsymbol{\sigma} = -p\boldsymbol{I} + \boldsymbol{T} \tag{2.4}$

$$\boldsymbol{T} = 2\boldsymbol{\mu}\boldsymbol{\varepsilon}(\boldsymbol{u}) \tag{2.5}$$

$$\boldsymbol{\varepsilon}(\boldsymbol{u}) = \frac{1}{2} (\boldsymbol{\nabla} \boldsymbol{u} + (\boldsymbol{\nabla} \boldsymbol{u})^T)$$
(2.6)

where \boldsymbol{u} is the velocity vector, \boldsymbol{n} is the outward normal vector to the boundary surface, $\boldsymbol{\sigma}$ is the Cauchy stress tensor, \mathbf{T} is the deviatoric stress tensor, $\boldsymbol{\varepsilon}$ is the rate of strain tensor and \boldsymbol{p} is the pressure.

The no-slip boundary condition is imposed at the surface of the microchannel. A uniform inlet velocity (\overline{u}) is imposed at the inlet with the same flow rate in the solution shearing process. Traction-free boundary condition is applied at the outlet surfaces. These boundary conditions can be represented by

$$\boldsymbol{u} = \boldsymbol{0} \quad \text{on } \boldsymbol{\Gamma}_{\boldsymbol{w}} \tag{2.7}$$

$$\boldsymbol{u} = \boldsymbol{u}_s \quad \text{on } \boldsymbol{\Gamma}_s \tag{2.8}$$

 $-\boldsymbol{n}_i \cdot \boldsymbol{u} = \bar{\boldsymbol{u}} \quad \text{on } \Gamma_i \tag{2.9}$

$$\boldsymbol{n_o} \cdot \boldsymbol{\sigma} = \boldsymbol{t} = \boldsymbol{0} \quad \text{on } \boldsymbol{\Gamma_o}. \tag{2.10}$$

In above equations, Ω , Γ_w , Γ_s , Γ_i , Γ_o , and t denote the entire computational domain, the wall boundary, the substrate boundary, the inlet boundary, the outlet boundary, and the traction force.

The stabilized Galerkin Least-Squared (GLS) finite element method was used to solve the governing equations. The detailed procedures are described elsewhere (Behr & Tezduyar, 1994). We summarize the main points here. The weak form of the GLS method is represented as follows:

$$\rho \int_{\Omega^{h}} w^{h} \cdot (u^{h} \cdot \nabla u^{h}) d\Omega - \int_{\Omega^{h}} p \nabla \cdot w^{h} d\Omega + \mu \int_{\Omega^{h}} \nabla w^{h} : \nabla u^{h} d\Omega + \sum_{e=1}^{n_{el}} \int_{\Omega^{e}} \tau_{MOM} [\rho(u^{h} \cdot \nabla w^{h}) - \nabla \cdot \sigma(q^{h}, w^{h})]$$
(2.11)
$$\cdot [\rho(u^{h} \cdot \nabla u^{h}) - \nabla \cdot \sigma(p^{h}, u)] d\Omega + \sum_{e=1}^{n_{el}} \int_{\Omega^{e}} \tau_{CONT} \nabla \cdot w^{h} \rho \nabla \cdot u^{h} d\Omega = \int_{\Gamma^{h}} w^{h} \cdot t d\Gamma \int_{\Omega} q (\nabla \cdot v) d\Omega = 0$$
(2.12)

where the w^h and q^h are the test functions for velocity and pressure and Ω^e , n_{el} denotes the interior of the element e and the number of elements. The stabilization parameter τ_{MOM} and τ_{CONT} follow the definition given in Pauli et al (Pauli *et al.*, 2015).

The approximated solutions \boldsymbol{u}^h and p^h for velocity and pressure respectively are chosen from the finite dimensional function spaces \boldsymbol{S}^h , $\boldsymbol{\mathcal{V}}^h$, and $\boldsymbol{\mathcal{Q}}^h$ as given in

$$S^{h} = \left\{ u^{h} \in \mathcal{H}^{1h}(\Omega) \middle| u^{h} = u^{h}_{D} \text{ on } \Gamma_{\text{Dirichlet}} \right\}$$
(2.13)

$$\boldsymbol{\mathcal{V}}^{h} = \{ \boldsymbol{w}^{h} \in \boldsymbol{\mathcal{H}}^{1h}(\Omega) \big| \boldsymbol{w}^{h} = \boldsymbol{0} \text{ on } \boldsymbol{\Gamma}_{\text{Dirichlet}} \}$$
(2.14)

$$\mathcal{Q}^h = \{ p^h \in \mathcal{H}^{1h}(\Omega) \}$$
(2.15)

where the superscript h indicates an approximation, $\mathcal{H}^{1h}(\Omega)$ is a finite dimensional subset of the Sobolev space \mathcal{H}^1 on Ω . The Dirichlet boundaries and Neumann boundary are $\Gamma_D = \Gamma_w \cap \Gamma_s \cap \Gamma_i$, $\Gamma_N = \Gamma_o$. The global velocity and pressure field were approximated by the firstorder polynomial basis functions over the element domain. In this study, the hexahedral element with eight nodes was chosen, and trilinear basis functions, $\phi_j(\mathbf{x})$ defined at the *j* th node for both velocity and pressure fields. Hence, the approximated solutions can be represented by

$$u^h = \sum_{j=1}^8 u_j \phi_j(x)$$
 (2.16)

$$p^{h} = \sum_{j=1}^{8} p_{j} \phi_{j}(\mathbf{x})$$
 (2.17)

where u_j and p_j are unknown coefficients. They can be obtained by solving the system of equations, which are formulated by the stabilized GLS method in this study (Thomas J.R. Hughes, 1986; Leopoldo P. Franca, 1992; T.E. Tezduyar, 1992).

The concentration distribution of TIPS-pentacene is calculated by solving an advection-diffusion equation using the velocity field obtained from the above differential equations.

$$\frac{\partial c}{\partial t} + u \cdot \nabla c - D \nabla^2 c = 0 \quad \text{on } \Omega$$
 (2.18)

$$c = c_i \quad \text{on } \Gamma_i \tag{2.19}$$

$$\boldsymbol{n_o} \cdot \boldsymbol{\nabla} c = 0 \quad \text{on } \boldsymbol{\Gamma}_o \tag{2.20}$$

$$c = c_0 \quad \text{on } \Omega \text{ at } t_0 \tag{2.21}$$

where u is the advective velocity, D is the diffusivity of TIPSpentacene in toluene, $c_i = 2.5 \, mM$ is the concentration of TIPSpentacene, and $c_0 = 0$ is the initial concentration in the entire domain. The stabilized space-time formulation of the advection-diffusion equation can be expressed as follows

$$\int_{Q_n} \psi \left(\frac{\partial c}{\partial t} + u \cdot \nabla c \right) dQ + \int_{Q_n} \nabla \psi \cdot D\nabla c \, dQ + \int_{\Omega_n} \psi((c)_n^+ - (c)_n^-) \, d\Omega + \sum_{e=1}^{n_{el}} \int_{Q_n^e} \left(\frac{\partial \psi}{\partial t} + u \cdot \nabla \psi - D\nabla^2 \psi \right) \tau \left(\frac{\partial c}{\partial t} + u \cdot \nabla c \right) - D\nabla^2 c \, dQ = 0$$
(2.22)

where Q_n is the nth space-time slab at subintervals $I_n = (t_n, t_{n+1})$, which divides the time interval. Q_{t_n} consists of enclosing surfaces, t_n , t_{n+1} and the surface described by P_{t_n} as time t transverses I_n . In equation (2.22), c and ψ denote the approximated concentration and the basis function, i.e., $c = c^h \in S^h \subset \mathcal{H}^{1h}(\Omega)$ such that $\forall \psi = \psi^h \in$ $\mathcal{V}^h \subset \mathcal{H}_0^{1h}(\Omega)$. The following notation is used in equation (2.22):

$$(c)_n^+ = \lim_{\varepsilon \to 0} c(t_n \pm \varepsilon)$$
(2.23)

$$\int_{Q_n} \cdots \, dQ = \int_{I_n} \int_{\Omega_t^h} \cdots \, d\Omega \, dt \tag{2.24}$$

In this study, three-dimensional space-time hexahedral elements were used, and the concentration field is represented by trilinear basis functions $\phi_j(\mathbf{x})$ defined at the jth node. The approximated solutions are

$$c^{h} = \sum_{j=1}^{16} c_{j} \phi_{j}(x, t)$$
 (2.25)

2.4.3. Particle tracking methods

The colored particle tracking method was used to visualize the mixing of fluids inside the microchannel. This method calculates the numerical trajectories of fluid particles that travel in the flow field, and It was widely used on previous studies (O. Byrde, 1999; Kang & Kwon, 2004; Camesasca *et al.*, 2005). In this study, we used a backward particle tracking method to obtain uniformly distributed particle images.

The trajectories of particles were calculated by solving the equation as follows:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = u \tag{2.26}$$

Where **x** is the position vector of particle, **u** is the velocity of the particle, and *t* is the time. In this study, the 4th-order Runge-Kutta method was used to integrate this ordinary differential equation. The length of the cell is used as the step unit, and the initial step size, minimum step size, and maximum step size are assigned as 0.2, 0.01, 0.5 each. The full illustration of the mixing of FM, SGM, and SHM from the inlet to the end of the 5th cycle is discussed in chapter 2.4.4. Total of 40,000 particles (20,000 red-colored particles and 20,000 blue-colored particles each) was used to express the mixing profiles at the end of each channel. Because the particle tracking method only considers the effect advection when expressing the mixing profile, the particles are perfectly separated in FM.

2.4.4. Flow kinematics in microfluidic channels

For all our numerical simulations, fluids exhibited steady flow, meaning that flow patterns are time invariant. Figure 2.7 is the top view cross-section (xy-plane) of the pressure gradient contour plot for SHM. The lines on the contour plot indicate regions of equal pressure. The color indicates different pressure levels (red for high and blue for low pressure). Since fluid flows from high pressure to low pressure under the absence of external forces, and no flow occurs along the contour line of pressure, the flow behavior can be roughly estimated from the pressure gradient contour plot. For FM, only straight contour lines along the y-axis are observed, meaning that unidirectional laminar flow along the x-axis is expected (Figure 2.8a). In SHM, however, the asymmetric V-grooves induce transverse pressure gradient along the *y*-axis, perturbing the unidirectional flow. This is characterized by the curved contour lines. Figure 2.7 indicates that inside the grooves, the contour lines are nearly parallel to the xaxis, and the pressure is the lowest at the tip of the V-grooves. This suggests that fluid flows inward toward the tip from regions 1 and 2 to region 3. Figure 2.7 is the cross-sectional view (yz-plane) of the velocity vector field, which shows that fluids from regions 1 and 2 are rotating inward toward the tip of the V-groove (region 3). Such a fluidic behavior can be characterized as "asymmetric counter-rotating helical flows," where the asymmetricity comes from the asymmetric V-grooves. For SGM, the pressure gradient contour plot and the velocity vector field plot indicate that fluid rotates in toward the center from one side, generating a large helical flow (Figure 2.8b).


Figure 2.7: The pressure distribution within the SHM and corresponding cross-sectional velocity vector field. The transversal pressure gradient is induced due to the groove pattern.



Figure 2.8: (a) The pressure distribution within the FM (top) and velocity vector field (bottom). (b) The pressure distribution within the SGM (top) and cross-sectional velocity vector field (bottom).

To further analyze the flow patterns within SGM and SHM, particle pathlines were calculated and visualized (Kang & Kwon, 2004), as seen in Figure 2.9a. Since we have steady flow, the streamlines (lines tangent to the velocity vectors) and the pathlines are the same. Two hundred particles were initially assembled along the z-axis, and the particle paths were tracked as indicated by the blue lines. In SGM, helically shaped flow pattern is observed; whereas, in SHM, asymmetric counter-rotating helical flow pattern can be observed. Figure 2.9b is cross-sectional (yz-plane) views of particle pathlines after one cycle for the SGM and SHM, respectively. The grev region covering top half of the cross-sectional area indicates the grooved region. The red horizontal line is the boundary between the grooved and the main channel region, and the wobbling pathlines in the main channel region for both SGM and SHM are due to rotation caused by shear stress applied to the fluid at this boundary. In SGM, the flow pattern shows concentric circular paths around the center of the stirring vortex, indicated as red circle. In SHM, multiple concentric circular paths are seen due to the presence of multiple centers of the stirring vortex. When the position of the V-groove tips change, the center of the stirring vortex moves. This causes the rotational flows to be divided up into smaller flows. As fluid progresses through the microfluidic channel, the generation of many small rotational flows ultimately results in chaotic flows, which has stretching and folding properties. These properties induce the stochastic motions of a tracer particle in a fully deterministic velocity field, which turns initially smooth particle distribution into complex patterns without large energy input as required by turbulent flows; this is often referred as chaotic advection (Aref, 1984; Aref et al., 2017).



Figure 2.9: (a) Pathlines of fluid markers through the SGM (left) and the SHM (right) using numerical analysis. (b) Cross-sectional projection of the trajectories of particles inside the SGM (up) and the SHM (down). The gray region and the red circles indicate the grooved region and the center of stirring vortex, respectively.

2.4.5. Mixing in microfluidic channels

The disturbance of unidirectional laminar flow due to the presence of grooves in SGM and SHM can be effective in mixing different fluids together. In SGM and SHM, advection is stronger than diffusion, as indicated by a large Péclet number (Pe), which is defined as Ul/D, where U is the average flow velocity, l is the characteristic length (the channel width in this case), and D is the diffusivity (Abraham D. Stroock, 2002). Figure 2.10 and 2.11 are the simulation of two fluids being mixed (blue and red) in FM, SGM, and SHM. Initially, the two fluids are completely separated as they enter from two different inlets. However, with increasing number of cycles, the increase in the degree of mixing is evident. The degree of mixing can be quantitatively

represented as Shannon entropy (S_l) .



Figure 2.10: The mixing profile visualization of two fluids (blue and red) being mixed along five cycles in SHM.



Figure 2.11: The evolution of mixing profile at the end of 1st, 2nd, 3rd, 4th, and 5th cycles: (a) FM, (b), SGM, and (c) SHM. All mixing profiles acquired by using the backward particle tracking method. The number of particles is 40,000 for the three microchannels.

The Shannon information entropy has been widely used because it can measure the disorder or lack of information of system (Shannon, 1948; Kim *et al.*, 2016; Franke *et al.*, 2017). In this study, the lack of information means how uncertain to predict what is the color of the particle if we pick a particle at each bin. The degree of mixing is measured via the Shannon entropy following the antecedent study, and the details about mathematical backgrounds are described in Camesasca *et al.*, 2006. The entropy can be calculated by the equation as follows:

$$S = -\sum_{j=1}^{M} \sum_{c=1}^{C} p_{j,c} \ln p_{j,c}$$
(2.27)

and

$$p_{j,c} = \frac{\frac{n_{j,c}}{P_c}}{\sum_{i=1}^{M} \sum_{c=1}^{C} \frac{n_{i,c}}{P_c}}$$
(2.28)

In above equations, P_c , $n_{j,c}$, and $p_{j,c}$ denote the total number of particles of species c in the overall system, the number of particles of species c in j th bin, and the joint probability to find a group/complex of P_c particles of species c is in bin j. In this study, two species of particle, red and blue-colored particles, were used, which means C = 2 in this system.

From the fourth Shannon-Khinchin's axiom, the total entropy *S* can be expressed the sum of two other entropies as follows:

$S = S_{\text{location}}(\text{species}) + S(\text{location})$ (2.29)

where $S_{\text{location}}(\text{species})$ is the conditional entropy and S(location)is the entropy of the spatial distribution. Note that the conditional entropy $S_{\text{location}}(\text{species})$, expressed as S_{l} in the main text, is the average of the entropy of mixing the *C* species conditional on bin location:

$$S_{\text{location}}(\text{species}) = \sum_{j=1}^{M} p_j S_j(\text{species})$$
 (2.30)

and
$$S_j(\text{species}) = -\sum_{c=1}^{C} p_{c/j} \ln p_{c/j}$$
 (2.31)

where p_j is the number of particles in bin *j* irrespective of species, and $p_{c/j}$ is the conditional probability to find a particle of species *c* conditioned on being on bin *j*. These probabilities are estimated as follows:

$$p_{c/j} = \frac{\frac{n_{j,c}}{P_c}}{\sum_{c=1}^{C} \frac{n_{j,c}}{P_c}}$$
(2.32)

$$p_{j} = \frac{\sum_{c=1}^{C} \frac{n_{j,c}}{P_{c}}}{\sum_{i=1}^{M} \sum_{c=1}^{C} \frac{n_{i,c}}{P_{c}}}$$
(2.33)

S(location) can be related to the spatial distribution of particles regardless of species:

$$S(\text{location}) = -\sum_{j=1}^{M} p_j \ln p_j. \qquad (2.34)$$

Hence, the total entropy quantifies both how particles of species well mixed at each bin and how particles evenly distributed in the overall system regardless of species. The values of $S_{\text{location}}(\text{species})$ and S(location) can be normalized by $\ln C$ and $\ln M$, respectively.

Figure 2.12 illustrates the mesh geometries for the assessment of mixing in this study. The scale of observation can be varied by

changing the number of bins. The value of Normalized S(location) is almost same as shown in Figure 2.13 because we use the backward particle tracking method to obtain the mixing profile. Hence, the mixing efficiencies of three microchannels can be analyzed by comparing the values of the normalized $S_{\text{location}}(\text{species})$, which shown in Figure 2.14.



Figure 2.12: The mesh geometries for the assessment of mixing: Each geometry contains (a) 16 bins, (b) 64 bins, (c) 256 bins, (d) 1024 bins, (e) 4096 bins, and (f) 16384 bins. All bins inside of the mesh are square shaped. The mesh which consist of 1024 bins was used in the analysis of S_l (colored particles).



Figure 2.13: The normalized *S*(location) for three microchannels at different number of bins: (a) 16 bins, (b) 64 bins, (c) 256 bins, (d) 1024 bins, (e) 4096 bins, and (f) 16384 bins. All normalized *S*(location) have values very close to 1.



Figure 2.14: Comparison of quantified mixing efficiency between FM, SGM, and SHM using Shannon entropy.

Figure 2.14 is a plot of normalized Shannon entropy (1 representing perfectly mixed particles) as a function of number of cycles, which shows that SHM yields the highest Shannon entropy. The *x*-axis of Figure 3b can also be represented as a fraction of L_{diff} , which is the distance needed to perfectly mix particles purely by diffusion under unidirectional flow, and is defined as $(Ul^2)/D$ (such mixing is the case for FM). L_{diff} for our system was calculated to be ≈ 470 mm. The dimensionless channel length in Figure 2.14 is the actual length of the microfluidic channel (26 mm) divided by L_{diff} . This means that just at 5.5% of L_{diff} , the SHM has a similar mixing effect as that of purely diffusional mixing. These results confirm that chaotic advection is the most efficient in mixing two fluids together.

To experimentally test the mixing effect of different microfluidic channels, we have fabricated OTFTs by injecting pure TIPSpentacene solution and another solution consisting of 1 mol% of $B(C_6F_5)_3$ in TIPS-pentacene into two separate inlets and let the two solutions mix within the microfluidic channel (non-premixed), as depicted in Figure 2.14. The 1:1 perfect mixture of the two solutions would yield 0.5 mol% of $B(C_6F_5)_3$ in TIPS-pentacene, which was the optimized dopant concentration. Hence, depending on the degree of mixing, the performance of the OTFTs should vary. As control experiments, we have made OTFTs by flowing in premixed solution of 0.5 mol% of $B(C_6F_5)_3$ in TIPS-pentacene through the three types of microfluidic channels. As seen in Figure 3c and in the inset, in the case of FM, non-premixed solution yielded lower average mobility and higher coefficient of variation (CV) compared to that of premixed solution. For FM, unidirectional flow is expected within the microfluidic channel, where the two solutions would mix purely by diffusion. As explained in Figure 3b, the length of the microfluidic channel is too short for mixing to occur by diffusion. The lower average mobility can therefore be attributed to a majority of OTFTs with non-optimized dopant concentration, and the higher CV can be attributed to the large variation of dopant concentration in OTFTs. SHM yielded nearly the same average mobility and CV between the premixed and non-premixed solutions since chaotic advection induced by SHM yields the highest degree of mixing amongst the three microfluidic channels. These mixer-based CoMiC systems can be used in a variety of materials systems where sediments are formed due to poor solubility, and where rapid reaction between species prevents the premixing of solutions. Figure 2.15 also indicates that SHM yields the highest mobility and lowest CV (for both premixed and non-premixed solutions) compared to that of FM and SGM. To explain such a trend, it is necessary to analyze how the difference in the flow patterns within the microfluidic channels affects particle/solute motion in the distribution region. The experimental results in subsequent sections are all based on premixed solutions.



Figure 2.15: The mobility values of doped TIPS-pentacene transistors (70 devices for each condition) fabricated by the three types of CoMiC. For each condition, a premixed (shaded) and a non-premixed TIPS-pentacene: $B(C_6F_5)_3$ solution were injected. The inset image shows the difference in the CV of mobility for each pattern.

2.5. Flows in distribution region

The important question to answer is whether the complex flow pattern of the fluid coming out of the microfluidic channel changes the movement of particles/solute in the distribution region, since this will ultimately determine whether the thin-film crystallization process will be affected by the manipulation of fluid dynamics in the microfluidic channel. To answer this question, we have visualized the motion of tracer particles experimentally and predicted concentration profiles computationally in the distribution region. The truncated distribution region depicted on the left side of Figure 2.16 is the computational domain within which simulation was conducted. The right side of Figure 4a depicts where the movement of fluorescent particles was experimentally observed via optical microscopy (red box) and where the predicted concentration profile was observed (blue box).



Figure 2.16: Schematic illustration of fluid flow from feed to distribution region (left), and the observed region via optical microscopy (red box, right) and numerical simulation (blue box, right).

2.5.1. Visualization experiment

Figure 2.17 is image of fluorescent particles at millisecond time interval for SGM-CoMiC and SHM-CoMiC. The arrows represent instantaneous velocity vector field, which was acquired via particle image velocimetry (PIV). This experiment was conducted without moving the substrate to effectively capture small-scale flow patterns. Since in SGM-CoMiC, large helical flow is generated, when the movement of particles is observed locally in a restricted area over a short time frame, the direction of particle movement does not significantly change. This results in negligible change in the velocity vector field with time. SHM-CoMiC, on the other hand, undergoes significant change in velocity vector field with time due chaotic flow (i.e., many small rotational flows). Real-time videos and description of the particle movement for SGM-CoMiC and SHM-CoMiC are in Figure S8 and Videos S5–S8, Supporting Information, respectively. In the case of SHM-CoMiC, the chaotic movement of particles manifests as periodic fluctuations in the fluid. These observations confirm that the manipulation of flow pattern within the microfluidic channel indeed affects the flow pattern in the distribution region.

SGM

SHM



Figure 2.17: The particle image velocimetry (PIV) analysis for SGM (left) and SHM (right) in the distribution region. The time step between each image is 1 ms and the substrate is stationary.

2.5.2. Numerical simulations

Figure 2.18 is concentration profiles at different times for SGM-CoMiC and SHM-CoMiC. Here, the substrate is in motion but the depletion of solute and the evaporation of solvent due to thin-film crystallization were ignored. Red indicates regions of high concentration, and blue indicates regions of low concentration. The vertical direction is parallel to the main flow direction (x-axis) and the horizontal direction is parallel to the transverse direction (y-axis). The computational domain was initially filled with pure solvent. Then, solution containing solute was fed into the microfluidic channel, which eventually flowed into the distribution region. The Péclet number in the distribution region was calculated to be ≈ 70 , which implies that advection dominates over diffusion. For SGM-CoMiC, concentration spreads more rapidly along the main flow direction but less so in the transverse direction. For SHM-CoMiC, on the contrary, the concentration spreads out more rapidly compared to that of SGM-CoMiC (as indicated by darker red color), and more evenly along both main flow and transverse directions. These results suggest that chaotic flow induced by SHM-CoMiC enhances mass transport rate in multiple directions.



Figure 2.18: Concentration change of OSC solution at different times at $\Delta t = 0.3$, 2.3, and 4.3 s. The substrate moves from the bottom to the top of the images.

2.6. Crystallization in film formation region

Using in situ microscopy (1000 frames per second), thin-film crystallization process was directly observed and analyzed in realtime. Toward the edge of the meniscus, the liquid layer gets thinner, which consequently results in the solvent being evaporated away faster. Crystallization of thin-film is therefore induced near the edge of the meniscus, forming a solution/thin-film boundary that moves along with the moving substrate. In other words, thin-film growth is thought to occur simultaneously along with the moving solution/thinfilm boundary (i.e., this is a characteristic of coating being conducted in the evaporative regime, where the solvent evaporation rate at the meniscus occurs on a similar time scale to that of the coating speed) (Maël Le Berre, 2009). TIPS-pentacene generally grows as ribbons along the coating direction (Diao et al., 2013; Kim et al., 2018). It has been theorized that the growth of ribbons occurs due to the solution maintaining a "saturation state" near the solution/thin-film boundary during coating, at which crystal growth is promoted and nucleation is suppressed (Goto et al., 2012; Park et al., 2015). Despite the common convention, such an idealized thin-film growth process is not exactly what happens without the aid of chaotic advection, as depicted in Figure 2.19a,b. In the case of FM-CoMiC, we have observed that in some regions, the growth of ribbons does not occur concurrently with the moving solution/thin-film boundary. Rather, the liquid solution layer protrudes out away from the solution/thin-film boundary, generating a time lag in the thin-film formation. In some cases, the liquid solution layer gets trapped within the thin-film, forming an island (Figure 2.19b, see the yellow box at $t_0 + 0.4$ s). The liquid layer then quickly crystallizes, catching back up to the solution/thin-film boundary. Such a "lag behind/ catch up process" repeats consistently during coating. The rapid crystal growth in the protruded liquid layer region yields isotropic growth, generating misaligned dendritic crystals. Surprisingly, in the case of SHM-CoMiC, the "lag behind/catch up process" did not occur; ribbons in all regions grew concurrently with the moving solution/thin-film boundary (Figure 2.19c,d). Such a difference in the crystallization process can be explained by the difference in the mass transport rate. Crystal growth in the saturation state is dependent on sufficient and rapid supply of solute to the growing face of crystals. In the case of FM-CoMiC, poor mass transport rate yields the lack of sufficient supply of solute needed to keep the crystals growing, thereby ceasing their growth. Then, as the solvent evaporates in the protruded liquid solution layer, concentration increases to the state of supersaturation, where nucleation and rapid isotropic crystal growth is promoted. As mentioned above, for SHM-CoMiC, the chaotic advection enhances the mass transport rate in all directions via small rotational flows. Therefore, there is always a sufficient supply of solute to keep the crystal growing, which results in the idealized evaporative regime process of simultaneous ribbon growth with the moving solution/ thinfilm boundary.



Figure 2.19: a–d) Schematic illustration and in situ microscopy images showing the variation of solution/thin-film boundary and crystallization process of doped TIPS-pentacene using the FM-CoMiC (a,b) and the SHM-CoMiC (c,d). The yellow box in (b) represents the generation of a solution island, leading to rapid crystallization. The arrows indicate the substrate moving direction, and scale bars are 30 μ m.

Figure 2.20 is cross-polarized microscopy images of thin-film generated with conventional solution shearing (referred to as reference film) (top) and SHM-CoMiC (bottom). For SHM-CoMiC, the thin-film completely extinguishes upon substrate rotation, suggesting high degree of crystal alignment. The reference film, on the contrary, consisted of misaligned crystals and high density of grain boundaries. Figure 5f is grazing incident X-ray diffraction (GIXD) images of the reference thin-film (top) and thin-film generated with SHM-CoMiC (bottom). Incident X-ray beam was exposed with an incident angle of 0.11° parallel (left) and perpendicular (right) to the coating directio n. (001) peaks were detected at $q_z = 0.379$ on both reference film and SHM-CoMiC based film, which corresponds to a *d*-spacing of 16.58 Å; this is in agreement with edge-on TIPS-pentacene crystal structure (Giri et al., 2011; Kim et al., 2019). The film generated with SHM-CoMiC was observed to have in-plane anisotropic orientation (i.e., highly textured), where (h0l) Bragg peaks were detected when the incident X-ray was parallel to the coating direction. This implies that the *a*-axis of TIPS-pentacene crystal lattice is oriented perpendicular to the coating direction. On the other hand, for incident X-ray beams perpendicular to the coating direction, (0kl) diffraction patterns were detected, indicating that the b-axis (i.e., which has been shown to have higher charge transport rate) (John E. Anthony, 2001; Mannsfeld et al., 2011; Kim *et al.*, 2019) is aligned parallel to the coating direction. For the reference film, on the other hand, various Bragg peaks were observed regardless of the substrate orientation, indicating that the degree of texturing had been reduced. These results corroborate the observed crystal growth process in Figure 2.19b.



Figure 2.20: (a) Polarized optical microscopy images of doped TIPSpentacene thin-film coated by solution shearing (top) and SHM-CoMiC (bottom). Substrate temperature and coating speed are 130 °C and 0.5 mm s-1, respectively. (b) GIXD patterns of thin-films coated by solution shearing (top) and SHM-CoMiC system (bottom), with the incident beam parallel and perpendicular to the coating direction.

We have fabricated bottom gate top contact OTFTs using conventional solution shearing (designated as reference) and using CoMiC with the three types of microfluidic channels. Au source and drain electrodes were used with the channel length and width of 80 and 400 µm, respectively. Heavily doped silicon wafer with a 300 nm SiO2 layer was used as the gate electrode and the dielectric layer, respectively. As seen in Figure 2.21a, the transfer characteristics of 70 OTFTs fabricated with SHM-CoMiC exhibited superior uniformity, compared to that of the reference OTFTs and FM-CoMiC (Figure 2.3). Figure 2.21b-d compares the statistical analysis of different types of OTFTs (based on 70 OTFTs for each type) in regards to mobility, threshold voltage ($V_{\rm th}$), and on-off current ratio ($I_{\rm on}/I_{\rm off}$), respectively. OTFTs fabricated using SHM-CoMiC exhibited the highest average mobility and lowest CV of 2.04 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 7.3%, respectively. To the best of our knowledge, this is the lowest CV achieved amongst organic solution-based coating techniques. On the other hand, reference OTFTs had an average mobility of $1.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a significantly higher CV of 61.2%. As mentioned above in Figure 2.20b, chaotic advection causes anisotropic ribbon growth with the fast transport axis aligned along the coating direction, which is also the direction along the OTFT channel length. This explains the observed high average mobility and low CV.

Even with uniform mobility, high variability in $V_{\rm th}$ will limit transistors' circuit operation. For instance, variation in $V_{\rm th}$ degrades noise tolerance in logic gates (Neamen, 2003), rendering it difficult to design and carry out logic functionalities. Furthermore, in display applications, $V_{\rm th}$ variation causes dissimilarities in pixel brightness (Paterson & Anthopoulos, 2018). On-off current ratio is another important parameter in transistors as it allows proper logic circuit operations and switching of pixels in display applications (Neamen, 2003; Zhang *et al.*, 2010). As seen in Figure 2.21c, d, CV of both $V_{\rm th}$ and $\log (I_{on}/I_{off})$ are the lowest for OTFTs fabricated with SHM-CoMiC. Vth was calculated using linear extrapolation (LE) method. CV for $V_{\rm th}$ was omitted since both positive and negative values exist in the sample. The huge difference in CV of transistor characteristics between SHM-CoMiC and solution shearing was statistically noteworthy with low p value for F-test of equality of variance. Such high device-to-device uniformity in transistor parameters, along with large-area scalability of our coating process, opens up the possibility of various solution-processed electronic applications such as lowcost flexible OLED displays (Zhou et al., 2006) and logic circuits (Matsui et al., 2019).



Figure 2.21: (a) Transfer curves for 70 devices fabricated by SHM-CoMiC. Injection flow rate is 8 μ L min⁻¹. (b–d) Comparison of electrical characteristics for transistors fabricated by solution shearing and FM-, SGM-, SHM-CoMiC: (b) mobility, (c) threshold voltage, (d) on-off current ratio. Coefficient of variation (%) for each condition is italicized.

2.7. Final remarks

In summary, continuous-flow microfluidic channel based meniscus -guided coating (CoMiC) is introduced, which enabled the manipulation and systematic analysis of flow pattern and crystallization process. The flow pattern was determined to be maintained in the distribution region and affected the crystallization process. In particular, chaotic advection resulted in high device performance and device-to-device uniformity. We project that CoMiC will be critical for in-depth understanding of solution-based thin-film processing, through which the properties of OTFTs and other types of devices such as solar cells and displays can be further optimized.

Chapter 3.

High-speed blade coating for battery electrode

3.1. Study Background

Due to the growth of the market size of products with lithium-ion battery (LIB) as the core component, such as Electric vehicle (EV), energy storage system (ESS), etc., the demand for LIB has increased rapidly (2020). This demand has increased the necessity to improve the performance of LIBs, in particular, increasing energy density is a challenge for next-generation LIBs. From a manufacturing perspective, to attain high energy density LIBs, it is important to make high quality electrodes based on a deep understanding of the electrode manufacturing process and fabricate them effectively to make cells.

Battery electrodes are basically made by coating a battery electrode slurry on a conductive substrate such as copper or aluminum foil (Claus Daniel, 2011). To make a high quality battery electrode, the active materials and other functional solid particles such as polymer binders or conductive additives in the battery electrode slurry should be dispersed uniformly without agglomeration (Du *et al.*, 2017; Hawley & Li, 2019). The slurry is applied to the substrate through various coating equipment such as slot-die coater, comma coater, and doctor blade coater. Among these, slot die coating is the most common coating method for battery electrode manufacturing because it has high precision and reliability, whereas blade coating is often used in electrode research in laboratory scale (Du *et al.*, 2017; Hawley & Li, 2019; Saraka *et al.*, 2020).

In the battery electrode coating process, it is important to avoid various defects that may occur during coating, such as ribbing, dripping, and air entrainment (Ding *et al.*, 2016). A phenomenon called heavy edge, also known as side-edge elevation, is a type of coating defect where the thickness of the wet film at the edge is thicker than the thickness at the center (Ding et al., 2016). Such edge defects in the electrode coating process occur in the form of side superelevation on the left and right sides during continuous processing, and additionally occur at the leading and trailing edges where the wet film begins and ends during intermittent coating for producing rectangular patch-shaped products (Schmitt et al., 2015; Maza & Carvalho, 2017; Tan *et al.*, 2020). The presence of heavy edge can be a cause of cell defects in later cell packaging processes or long-term cell use, where stress is concentrated on the edge due to inhomogeneous stress distribution (Edgar B. Gutoff, 2006; Schmitt, 2016; Spiegel et al., 2022). To improve such process problems, some previous studies have attempted to solve the problem of heavy edge formation through various approaches such as the design of slot die shim geometry and changes in process parameters (Han et al., 2014; Schmitt et al., 2014; Spiegel et al., 2022; Spiegel et al., 2022). So far, there is a lack of studies that have analyzed the principles of heavy edge formation from a rheological perspective, and previous studies have mainly interpreted it is determined by the interplay of wetting phenomena between the slurry and substrate and neck-in phenomena caused by retraction due to surface tension, viscoelastic die swelling and film stretching (T. Dobroth, 1986; Schmitt et al., 2014; Schmitt, 2016; Jalaal *et al.*, 2019; Spiegel *et al.*, 2022; Spiegel *et al.*, 2022).

In several industrial coating processes, including slot die coating and blade coating, the flow in a narrow gap between a stationary solid surface and a solid surface moving at a constant velocity is one of the main flows we can observe. The flow formed in such areas is called Couette-Poiseuille flow (C-P flow), and the flow configuration is determined by the viscous force generated by the moving substrate and the influence of the pressure gradient formed within the area (R. W. Flumerfelt, 1969; Kwak & Nam, 2020). Commercially, the viscous force due to shear deformation is dominant compared to other forces in the blade coating process because the substrate speed is operated at a high speed. On the other hand, in slot die coating, various forms of C-P flow are developed depending on the relative magnitudes of the shear force and pressure gradient formed by the vacuum chamber, pressure jump at the upstream and downstream menisci, etc.

3.2. Purpose of Research

In this study, we aimed to understand the heavy edge phenomenon that caused by shear deformation during battery electrode manufacturing process by implementing blade coating experiment with various process parameters corresponding to the commercial mass production condition and suggest strategies to improve it. To analyze this, we made a battery electrode by coating the battery anode slurry using a specially designed blade coating apparatus and measured the wet thickness profile of the battery electrode using a displacement sensor. The heavy edge defect was quantified by using the coating quality parameters based on the measured wet thickness profile. Subsequently, we selected the process parameters that significantly affect the coating quality among various process conditions through statistical analysis. Furthermore, we measured the rheological properties of the battery anode slurry and interpreted the trend of heavy edge formation from a rheological perspective through linear viscoelastic modeling. Finally, we confirmed that the coating quality problem about heavy edge can be solved without compromising the electrochemical performance of the cell through electrochemical experiments. The results of this study provide a direction for solving problems in the commercial mass production process of battery

electrodes by analyzing the shear deformation and response of complex fluids such as battery slurry to shear flow in the form of C-P flow, which is one of the main flows occurring in various coating processes such as slot coating and blade coating, using experimental and theoretical methods.

3.3. Experimental

3.3.1. Slurry preparation

The multicomponent slurries prepared in this study consisted of an active material, conductive additive, and Polymer binder. Spherical graphite (SG-BH8, Ito Graphite Co., Ltd., Japan) with a median particle diameter of 8.8 μ m, specific surface area of 8.80 m²g⁻¹ and density of 2.23 g ml⁻¹ was used as the active material. Carbon black (CB, EQ-Lib_SuperC65, MTI Korea, Korea) with a primary particle size of less than 50 nm and a specific surface area of 62 m²g⁻¹ was used as a conductive additive. Carboxymethyl cellulose (CMC) is a cellulose derivative thickener, stabilizer, and binder. The average molecular weight (M_w) and degree of substitution of CMC powder (Sigma Aldrich, Germany) was 20 kg mol⁻¹ and 0.7, respectively. The solvent used is a deionized water.

The slurry preparation was follows: CMC powder was dissolved in deionized water at 3 wt% concentration using a magnetic stirrer at 500 rpm for one day. CB and graphite were added to the CMC solution and mixed to prepare an anode slurry. To sufficiently disperse the CB powder and prevent damage to the graphite, the CB particles were dispersed at 7000 rpm using a homogenizer (T50 digital ultra, IKA) for 12 min before the graphite was added. Graphite was pre-mixed using an overhead stirrer (HOT-50DX, Daehan Scientific) with a sawtooth impeller at 1000 rpm for 10 min to disperse large agglomerates. The

graphite was subsequently completely dispersed using a planetary mixer (PLM-0.6, Daehwa Tech) at orbital and rotational speeds of 150 and 300 rpm, respectively, for 60 min. The planetary mixer provided a sufficiently uniform dispersion of solid contents up to 500 ml without dead zones.

3.3.2. Rheological measurement

The rheological properties were measured using a stresscontrolled rheometer (Discovery HR-2, TA Instruments Inc.). The solution was loaded onto a parallel plate with a diameter of 40 mm and a gap size of 1 mm. To minimize the influence of device inertia, an aluminum plate was utilized. Additionally, an acrylic solvent trap was employed to reduce the evaporation during the experiment. Prior to each experiment, a preshear at a rate of 1 s⁻¹ was applied for 20 seconds, followed by a 120 seconds relaxation. The viscosity curve was obtained by increasing the shear rate from 0.01 to 1000 s⁻¹ and then decreasing it. A 7-second equilibration time was given at each data point, and the viscosity value was obtained by averaging the data over 5 seconds. Furthermore, a frequency sweep test was performed by increasing the angular frequency within a range of 0.1–100 rad/s, while maintaining a strain of 1%.

3.3.3. Blade coating experiment

Figure 3.1a is a schematic of the blade coating system for the blade coating experiment. The blade coating system consists of three main elements: a coating blade with a stand, a linear stage for moving the substrate, and a laser displacement sensor with a moving mount stage. The coating blade used in this study was designed to have a geometry similar to the downstream lip of the slot die. The coating

blade is made of stainless steel (SUS630) and was custom-made by Changsung Tech (Figure 3.1b). In the blade coating experiment, two different coating blades with blade lip lengths (d_l) of 1000 μ m and 2000 μm, respectively, were used to fabricate battery electrodes. A battery anode slurry was deposited on Cu foil mounted on a high-precision linear motor (V-508, Physik Instrumente GmbH & Co. Kg, Karlsruhe, Germany) with metal plate. The linear stage was able to observe the coating phenomena occurring under conditions similar to those used in commercial battery electrode manufacturing process by accurately controlling the substrate speed up to 600 mm/sec. The laser displacement sensor can measure the anode slurry thickness deposited on the copper foil by measuring the displacement of the coating layer surface through the laser triangulation method (example of measured thickness profile is shown in Figure 3.1d). Since the laser displacement sensor can only measure displacement about a point, we measured the cross-web thickness profile of the anode slurry wet film using a moving mount stage that allows the displacement sensor to perform cross-web directional movement (Measured position is shown in Figure 3.1c as a red-colored dashed line).



Figure 3.1: (a) Experimental setup for blade coating (omit blade stand). (b) Rigid coating blade used in a battery electrode coating. Blade lip length (d_1) can be changed to control the area of C-P flow region. (c) Anode electrode sample manufactured by blade coating process. Red dashed line illustrates a cross-web directional region where a thickness profile of anode slurry wet film measured. (d) Partial cross-web thickness profile of anode slurry wet film at side heavy edge and definition of lengths for coating quality parameters.

3.3.4. Statistical analysis and spectral clustering

To understand the effects of the operating variables, we conducted statistical analyses based on factorial design (Lazić, 2004). The factorial design can be used for categorial, qualitative, and/or quantitative types of data types to be applied for the choice of factors (or process parameters in this study) and estimation of main effects and interactions between factors. Although it requires an extensive number of experiments for the analysis as the number of factors and levels for the factors exponentially, the resolution of the analyses is fully informative compared with other designs of experiment methods. Note that the number of factors and levels of the experiments considered in this study is not that large. Hence full factorial design is a good candidate for the analyses. The analyses were performed via Minitab 19.

Spectral clustering is one kind of method to cluster data into a specific number of groups based on a similarity graph, i.e., a directionless graph where each node and edge represents the data point and distance between the data, respectively (Bishop, 2006). In this study, MATLAB 2022a was used, and the clustering was conducted using MATLAB's built-in function "spectralcluster." Herein we used the default values for the clustering, but normalized symmetric Laplacian matrix (Andrew Y. Ng, 2001) was manipulated as a similarity graph of the data, and various distance criteria were considered, such as Euclidean distance, semi-Euclidean distance, Mahalanobis distance, and radial based distance.

3.3.5. Electrochemical cell fabrication and Electrochemical characterization

In order to examine the effect of operational variables on the electrochemical performance, galvanostatic experiments were performed using 2032 type-coin cells with a lithium metal counter electrode, and a 1.0 M solution of lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate, ethyl methyl carbonate/ dimethyl carbonate (with a volume ratio of 3:7, Soulbrain Co. Ltd.). Fluoroethylene carbonate (FEC, Sigma Aldrich, \geq 99%) was used as an electrolyte additive (2 wt%). The graphite electrode deposited on a Cu foil substrate was dried overnight at a temperature of 120°C under vacuum conditions. Coin cells were assembled in an argon-filled glove box. The amount of the electrolyte was 0.1 mL. The galvanostatic charge-discharge cycling tests were performed by a battery cycler system (TOYO, Japan) connected to a coin cell climate chamber, which was set at 25 °C. The cycle retention of a graphite electrode was

evaluated in a voltage range of 0.01-2 V versus Li/Li⁺ at a 0.1 C rate (36 mA g⁻¹) after 3 formation cycles at a 0.05 C rate (18 mA g⁻¹).

3.4. Result and discussion

3.4.1. Influence of process parameters for the heavy edge

3.4.1.1. Blade coating as a simplified model process

As mentioned earlier, the slot die coating is the most common coating method for battery electrode manufacturing. The slot die coating process is a pre-measured coating method, which allows for the regulation of coating thicknesses by adjusting the process conditions like flow rate, coating gap, substrate speed, and pressure in a vacuum chamber. Due to its unique features, the slot die coating process has advantages such as high productivity, uniformity, precision, and reliability and it is widely applied in the rechargeable battery manufacturing industry (Schmitt et al., 2014; Li et al., 2022). The blade coating process is a post-metered coating method in which the coating thickness is determined by the balance among forces such as the viscous, gravity, and the capillary force (Yim, 2021). The blade coating process has an advantage in that the number of units constituting the process is small and the structure is simple compared to the slot die coating process, hence, it is also widely used in various industry (Weinstein, 2004; Reynolds *et al.*, 2021).



Figure 3.2: Schematic illustration of slot die coating and blade coating process (a and b). Side edge elevations are formed in both electrode manufacturing processes. Representative C-P flow regions in a side-view of slot die coating (c) and blade coating (d). Shear deformation of fluid is occurred by moving substrate and pressure gradients in these C-P flow region.

Despite having structural and operational differences between the two coating processes, they are characterized by very similar flows in the main areas of the processes. In particular, as seen in Figure 3.2, the area between the downstream die lip of the slot die and the moving substrate in the slot die coating (Figure 3.2c) and between the blade lip of the blade and the moving substrate in the blade coating (Figure 3.2d) have in common that the flow is formed by the flow through a narrow gap between one stationary process element (slot die, blade) and a substrate moving at a constant speed (Stephan F. Kistler, 1997; Gates, 1999; Ji *et al.*, 2016; Maillard *et al.*, 2016; Kwak & Nam, 2020). The flow formed in such areas is called Couette-Poiseuille flow (C-P

flow), and the flow configuration is determined by the viscous force generated by the moving substrate and the influence of the pressure gradient formed within the area (R. W. Flumerfelt, 1969; Kwak & Nam, 2020).

For a Newtonian fluid, the mathematical model for twodimensional C-P flow in a narrow channel is obtained by solving the Navier-Stokes equations by

$$\mathbf{u}(\mathbf{y}) = \frac{\Delta \mathbf{P}}{2\mu L} \mathbf{y}(\mathbf{H} - \mathbf{y}) + \left(\mathbf{U} - \frac{\mathbf{U}}{\mathbf{H}}\mathbf{y}\right)$$
(3.1)

where u, ΔP , μ , *L*, *H*, and *U* are fluid velocity, pressure gradient along the x-direction, the viscosity of fluid, the channel length, the channel height, and the speed of substrate. The first term in Equation (3.1) represents the pressure-driven flow (Poiseuille flow) and the second term presents the shear-driven flow (Couette flow). The shape of C-P flow is determined by superimposing the two terms. The mathematical expression of C-P flow for Generalized Newtonian fluid or non-Newtonian fluid is derived in different forms depending on the properties of the considered fluid. Nevertheless, the features of the velocity profile mentioned above are similarly observed (R. W. Flumerfelt, 1969; Rajeev Malik, 1991; Tsuda, 2010; Kwak & Nam, 2020).

In high-speed operation of blade coating process, the pressuredriven flow contribution from hydrostatic pressure in the puddle and pressure difference from downstream menisci in the blade coating process is reduced to negligible and the viscous force is more dominant than other forces. As a result, the C-P flow in the blade coating process becomes very close to the Couette flow (Hwang, 1979; Loest *et al.*, 1994; Kim *et al.*, 2006; Yim, 2021). On the other hand, in the slot coating process, the presence of a pressure gradient due to the pressure difference at upstream and downstream menisci and the pressure in a vacuum chamber leads to the formation of a C-P flow that differs from the Couette flow, except when the coating thickness is half the coating gap (Sartor, 1990; Liu & Zhu, 2010; Tsuda, 2010; Kwak & Nam, 2020). Therefore, the blade coating process has the advantage of being able to evaluate the effect of shear deformation more directly because the C-P flow in a blade coating approximates a simple shear flow compared to the slot die coating process. Additionally, compared to the slot die coating process, the blade coating process has advantages in process complexity and capital cost because the blade coating process has fewer types and numbers of units constituting the process compared to the slot die coating process. These feature makes it relatively favorable to observe the changes in heavy edges caused by shear deformation under various process conditions in the blade coating process. Hence, we utilized a specially designed blade coating apparatus, which shown in Figure 1a and b, as a simplified model process to produce and analyze rechargeable battery electrodes. Through this research, we investigate the influence of process conditions and rheological properties of battery anode slurry on the shape of the wet film developed after it is deformed through shear flow, which is mainly observed in the coating process. In particular, we analyze the effect of changing process conditions on the superelevation of wet film edge and examine how to use process condition changes to mitigate edge defects in battery electrode fabrication.

3.4.1.2. Effects of the process parameters in heavy edge.

Figure 3.1d shows the cross-web directional thickness profile of the right half of the anode slurry wet film produced through the experimental setup for blade coating. Due to the occurrence of heavy edges on the wet film side, the height of the superelevated edge, H_{edge} , has a value greater than the bulk height H, which represents the thickness of the wet film center area. Additionally, the width of the
heavy edge that rises higher than the bulk height H and the total width of the edge formed from the end of the coating layer to the bulk height are defined as B_{edge} and B_{step} , respectively.

In this study, three dimensionless parameters are defined as coating quality parameters to quantify the shape of the side edge for the quality assessment of side edge superelevation. First, the dimensionless edge height, H^* , is proposed and used in previous studies (T. Dobroth, 1986; Schmitt *et al.*, 2014; Spiegel *et al.*, 2022)

$$H^* = \frac{H_{\text{edge}}}{H} \tag{3.2}$$

and we define a dimensionless edge width B^* as

$$\boldsymbol{B}^* = \frac{\boldsymbol{B}_{edge}}{\boldsymbol{\lambda}_c} \tag{3.3}$$

where $\lambda_c = \kappa^{-1} = \sqrt{\gamma/\rho g}$ is capillary length of anode slurry and κ , γ , ρ , g are curvature of meniscus, surface tension, density of anode slurry and gravitational acceleration (Pierre-Gilles Gennes 2004). B^* is defined as the dimensionless edge width using the capillary length instead of the bulk height H, in order to quantify the heavy edge width consistently even when the wet film height changes significantly. Since the surface tension and density of the anode slurry at 20°C are 65.48 dyn/cm and 1.405 g/ml, respectively, a capillary length of 2.18 mm was used for the anode slurry.

The ratio of edge height and step width can be defined by the edge gradient R^* and it also proposed and used in previous studies

$$\boldsymbol{R}^* = \frac{\boldsymbol{H}}{\boldsymbol{B}_{\text{step}} - \boldsymbol{B}_{\text{edge}}} \tag{3.4}$$

We investigate the heavy edge morphology variation in response

to process parameter changes through the coating quality parameters. As for the process parameters, we selected three process parameters that are commonly used in industrial coating processes and have a significant impact on the rheological properties of the slurry: a blade die lip length d_1 , a coating gap h_g , and a substrate speed u_w . These coating parameters that mainly affect the flow of battery slurry in the C-P flow region, shown in red shading in Figure 3.2c and 3.2d, which is commonly developed in both blade coating and slot die coating processes. Therefore, we expect that the results obtained through this experiment can also be applied to the analysis of heavy edge phenomena occurring in other processes, such as slot die coating, where C-P flow is formed.

Here, we assume the shear rate $\dot{\gamma}$, residence time t_r , and the aspect ratio of the C-P flow region α as

$$\dot{\gamma} = \frac{u_{\rm w}}{h_{\rm g}} \tag{3.5}$$

$$t_{\rm r} = \frac{d_{\rm l}}{u_{\rm w}} \tag{3.6}$$

and

$$\boldsymbol{\alpha} = \frac{\boldsymbol{d}_{\mathbf{l}}}{\boldsymbol{h}_{\mathbf{g}}} \tag{3.7}$$

to simply characterize the flow developing inside the C-P flow region (Mezger, 2014; Maillard *et al.*, 2016; Kwak & Nam, 2021). This assumption is valid because in a high-speed blade coating process, the viscous force dominates over the other forces, which causes the C-P flow to approach Couette flow. Hence, changes in process parameters can be simplified and represented in terms of the shear rate, residence time, and the aspect ratio that the battery slurry experiences in the C-P flow region.

Expt #	<i>d</i> ₁ [μm]	<i>h</i> g [μm]	u _w [mm]	Shear rate (γ) [sec ⁻¹]	Residence time (t _r) [× 10 ⁻³ sec]	Aspect ratio (α)
1	1000	100	250	2,500	4	10
2	1000	100	350	3,500	2.857	10
3	1000	100	500	5,000	2	10
4	1000	200	500	2,500	2	5
5	2000	200	500	2,500	4	10
6	1000	50	500	10,000	2	20
7	2000	100	500	5,000	4	20

Table 3.1: Experimental conditions of blade coating experiment

Table 3.1 shows the experimental conditions of the blade coating process in which the battery anode was fabricated. Each condition was designed to consider the changes in the shear rate $(\dot{\gamma})$, residence time (t_r) and the aspect ratio (α) formed in the C-P flow region according to the three process parameters: blade lip length d_l , coating gap h_g , and substrate speed u_w , to observe their impact on the heavy edge. For each experimental condition, 20 anode electrodes were coated, and the thickness profile of the coated anode slurry wet film was measured. The coating quality parameter was quantified and analyzed for the measured thickness profile, i.e., 40 heavy edges were used in the analysis for each experimental condition.



Figure 3.3: Schematic Boxplot of coating quality parameters for experiment conditions in Table 1 (a, b, and c). d) Normalized coating profile of anode slurry wet film with various coating gap h_g e) Normalized coating profile of anode slurry wet film with various aspect ratio α .

Figure 3.3 is a boxplot that shows the coating quality parameter distribution quantifying the heavy edge morphology formed on the anode slurry wet films coated under the process conditions listed in Table 3.1. By examining the changes in the coating quality parameters for various process parameter variations, we can assess the influence of process conditions on anode slurry coating. Experiments # 1, 2, and 3 are designed to check the change of coating quality parameters under the condition of the same blade lip length d_1 and the same coating gap h_g , when only the substrate speed u_w is varied. In detail, experiments # 1, 2, and 3 were all conducted using the same blade $(d_l = 1000 \ \mu m)$ to coat anode slurry under the same coating gap condition (h_g =100 µm) while varying the substrate speed u_w to 250, 350, and 500 mm/sec, respectively. In these experiments, the aspect ratio remains constant since the geometry of the C-P flow region remains the same. However, the shear rate and residence time in the C-P flow region change with the substrate speed. Therefore, we can identify the effect of shear rate changes on the morphology of the heavy edge under the same aspect ratio condition in the C-P flow region by comparing experiments # 1, 2, and 3. As shown in Figure 3.3a-c, despite a twofold change in substrate speed for the shear rate, the three coating quality parameters showed no significant differences in the observed experimental conditions. This confirms that changes in the substrate speed do not significantly affect the heavy edge morphology in the shear deformation that occurs in the C-P flow region of battery anode slurry, which is consistent with previous studies using slot die coatings (Schmitt *et al.*, 2014).

Experiments # 3, 4, 5, 6 and 7 are experiments that observe the changes in coating quality parameters where the blade length d_1 and the coating gap h_g change while maintaining the same substrate speed u_w . In these experiments, the shear rate and aspect ratio are correlated, making it is not possible to observe the effect of changing only one specific condition. However, based on the results of experiments # 1, 2, and 3, we assumed that the change in shear rate within the observed process conditions does not cause significant changes in the morphology of heavy edge. Therefore, by comparing the experimental results of experiments # 3, 4, 5, 6 and 7, we can confirm the influence of aspect ratio on the heavy edge when the battery anode slurry is coated. In a macroscopic point of view, H^* and B^* values tend to be higher as the coating gap h_g increases. Additionally, when h_g remains constant, the values of H^* and B^* tend to decrease as the blade lip length d_1 increases.

of change in H^* and B^* values due to the change in blade lip length d_1 is smaller than the amount of change due to the change in coating gap h_g . In the case of R^* , it is the most clearly grouped by the coating gap h_g among the three coating quality parameters, and its value increases as h_g increases.

Based on the experimental results above, we can reach a few conclusions. First, all three coating quality parameters H^* , B^* , and R^* tend to have a positive correlation with the coating gap h_g , and the change in the coating gap has the most significant impact compared to other process condition changes. In other words, the heavy edge of the anode slurry wet film tends to be worse when the coating gap becomes larger as shown in Figure 3.3d. In particular, the value of R^* was most significantly affected by the coating gap. Second, the three coating quality parameters tend to decrease as the aspect ratio of the C-P flow region α increases. In other words, the heavy edge tends to decrease as the aspect ratio of the C-P flow region increases by increasement of blade length d_1 . However, the magnitude of the change caused by the aspect ratio is smaller than the change in the coating gap. These observations are shown in Figure 3.3e.

As mentioned earlier, the main interpretation is that the heavy edge is determined by the interplay of neck-in and wetting phenomena caused by surface tension, viscoelasticity, and film stretching (T. Dobroth, 1986; Schmitt et al., 2014; Schmitt, 2016; Jalaal et al., 2019; Spiegel et al., 2022). Based on the experimental results, it is believed that for the anode slurry wet film we used, the initial meniscus shape of the side coating bead formed between the coating gap and the substrate has a major influence on the shape and scale of the heavy edge that develops during the subsequent coating process, and the viscoelastic properties of the anode slurry have a subordinate influence. The rheological interpretation of the heavy edge will be discussed in а subsequent section. Before the rheological interpretation, we conduct statistical analysis to confirm our experimental observations.

3.4.2. Statistical analysis and spectral clustering

3.4.2.1. Statistical analysis

Based on the 2 × 2 full factorial design, we analyzed the effects of the two process parameters (h_g and d_1) on the coating quality parameters (H^* , B^* and R^*). In this study, we used Experiments # 3, 4, 5, and 7: the substrate speed ($u_w = 500 \text{ mm/sec}$) is a constant. Meanwhile, the other two parameters were obtained under two coating gaps ($h_g = 100$ and 200 µm) and two downstream die lip lengths ($d_1 =$ 1000 and 2000 µm), i.e., 2 × 2 full factorial design. Herein, we investigated the main effects and the interactions between factors to the coating quality parameters (H^*, B^* , and R^*).

It should be mentioned that the 2×2 full factorial experiments could not elucidate the fundamental details behind the heavy edge phenomena. However, if obtaining data is limited, such as in our experiments, the 2×2 full factorial design analysis is the effective way to identify the trends of output variables with respect to operating variables. The results of the analyses are summarized in Figure 3.4 and Table S1 to S6 in the Supporting Information.



Figure 3.4: Contour plot of coating quality parameters with respect to two process parameters (H_g and d_l). The plot was obtained by factorial regression (Tables B.2, B.4, and B.6 in the Supporting Information), where the P-value of the coefficient less than 0.05 was used for the plots.

Figure 3.4 presents the contour plot for the three coating quality parameters based on the results of the factorial design. In a nutshell, the analysis of variance (Table B.1, B.3, and B.5) and Figure 3.4 illustrate that H_g and d_1 independently affect the value of H^* and R^* , as shown in Figure 3.4a and b. It can be identified by which the contours are represented as straight lines. However, interestingly, the value of B^* is affected by the interaction of h_g and d_1 as well as h_g and d_1 themselves, e.g., see the contour lines in Figure 4c lie as curves and p-values in Table B.4. It should be emphasized that the effect of h_g on the coating quality parameters is much more significant than that of d_1 , according to F-statistics, see Table B.1, B.3, and B.5. That means a coating gap h_g is the significant operation parameter for controlling the coating quality at a given substrate speed. This coincides with Figure 3.3 as well, such as one can compare experiment # 3, 5, and 6 for identifying the effect of the coating gap on coating quality parameters. Another observation from the analyses is that the value B^* shows a relatively rapid change with respect to h_g and d_l compared to other coating quality parameters. The result also coincides with Figure 3.3, where Figure 3.3b shows the largest value difference among the three coating quality parameters.



Figure 3.5: 3-dimensional scatter plot with respect to the coating quality parameters for (a) groups by experiments and (b) groups after clustering.

3.4.2.2. Spectral clustering

The purpose of the clustering is to investigate how the operating variables $(h_{g} \text{ and } d_{l})$ affect the coating quality parameters H^{*}, B^{*} , and R^{*} . In this study, we used experiments # 3, 4, 5, 6, and 7 shown in Table 1. Here, the data of experiments # 3, 4, and 6 were obtained under the constant d_{l} and u_{w} , but h_{g} was varied. Meanwhile, those of experiments # 4 and 5 and experiments # 3 and 7 were obtained under the constant u_{w} and h_{g} , but d_{l} was different.

Figure 3.5a shows the 3-dimensional scatter plot of the experimental data with respect to the three coating quality parameters. One can recognize that the data are aligned with respect to R^* . Based on the statistical analyses in chapter 3.4.2.1, we claim that the h_g is a

crucial operating variable to determine the coating quality R^* . Also, as shown in Figure 3.5a, experiments # 4 and 5 and experiments # 3 and 7 are distinguished with respect to downstream die lip length d_1 , although some of the data are overlapped each other.

Figure 3.5b shows the result of spectral clustering of experiments # 3, 4, 5, 6, and 7. In this analysis, note that the data are represented by the coating quality parameters H^*, B^* , and R^* , not by the operating parameters $(u_w, h_g, \text{ and } d_l)$. In this study, we used the Laplacian matrix as the similarity estimation (roughly speaking, the distance between each data point). Since the scale of the H^*, B^* , and R^* are not even, we used standardized Euclidean distance as a distance matric, i.e., each coordinate was scaled by dividing the value with the standard deviation of the corresponding coordinates. Otherwise, the clustering could be affected by the large-scale variable only, and resulting in a bad clustering.

Clustering analysis is the study of how data can be grouped based on their similarity, where the data could be represented by various parameters, e.g., three coating quality parameters. If the given parameters are not suitable to represent the experiment, the results of clustering would greatly deviate from data grouped according to the experiment batches. On the other hand, if the results of clustering are close to those grouped by experiment batches, it suggests that the parameters are suitable to describe the experiment and data.

Interestingly, As shown in Figure 3.5b, the matching percent was 81.86%, which is the ratio of data points where the majority of the data points in the cluster matched with an experiment batch out of the total amount of data. Given that some of the experimental data shown in Figure 5a are overlapped each other, the matching percent value quite encourages because almost all clustering results coincide with experiment batches. Therefore, we can "statistically" certify that the parameters H^* , B^* , and R^* are suitable for explaining the coating quality.

Last but not least, the relation between the operating variables $(h_g, \text{and } d_l)$ and the coating quality parameters $(H^*, B^*, \text{ and } R^*)$ should be investigated. As shown in Figure 3.5, one can see the three large data bundles aligned along R^* : [brown (exp #6)], [black (exp #3), light blue (exp #7)], and [red (exp #4), blue (exp #5)]. According to Table 1, the gap heights (h_g) of the data sets are 50 μm , 100 μm , and 200 μm , respectively. Therefore, gap height more significantly affects the coating quality parameters, and again it coincides with Figures 3 and 4. Also noteworthy, d_l can distinguish two data clusters at the similar R^* values, by which it varies other two coating quality parameters $(H^* \text{and } B^*)$. Therefore, it can be confirmed that d_l also definitely affects the coating quality.

Shortly, chapter 3.4.2 statistically described the relation between coating quality parameters and operating parameters. We expect that the idea will be expanded to machine learning or statistical analysis to mine the fundamental information from the data. Also, one could apply generative models, such as the Gaussian process, to this system for generating numerous data from a small number of experimental data. Note that statistical analyses dealt with in this section give insights into the parameters but there is no physical interpretation. The following section describes the physical relation between the parameters based on rheology.

3.4.3. Linear viscoelastic modeling

In the battery industry field, it has been shown that the anode slurry exhibits various non-Newtonian fluid properties such as thixotropy and viscoelasticity through previous research (Cho *et al.*, 2013; Kwon *et al.*, 2014; Zhao *et al.*, 2022). The thixotropy of anode slurry, the time-dependent property, means that the rheological property can be changed during the coating process with the construction or destruction of its internal microstructure (Mewis, 1979; Barnes, 1997). Also, viscoelasticity of anode slurry means when the anode slurry undergoes deformation, some of the deformation is restored and the other is dissipative (Ferry, 1980; Lakes, 2009). In recent research about the above two rheological properties, it has been reported that the material which has thixotropy and viscoelasticity, the viscoelastic property plays a main role in a relatively short time scale. In contrast, the thixotropy property predominates on a long-time scale because of its time evolution of microstructure (Agarwal et al., 2021; Choi et al., 2021; Yilin Wang, 2022). The coating profile was measured in seconds, the thixotropy property can be considered negligible in this coating system. From this point of view, this study aims to analyze the results by focusing on the viscoelastic property of anode slurry, where the coating process is conducted in short-time and also the drying process is proceeded in the industrial coating process before the thixotropy can play a significant role.



Figure 3.6: (a) Four-mode Maxwell model, (b) variation in storage and loss modulus of anode slurry with frequency and adjustment of Eq. (3.8), (3.9). Storage and loss modulus are plotted as black and red line, respectively. The solid line (-) with circle means the experimental data, and the dashed lines (--) are for the 4-mode Maxwell model modulus value with fitted parameter set (G_i , η_i).

From the experimental results, the effect of the coating gap was analyzed. Therefore, the further analysis in this section will focus on the die lip length, and the substrate speed. In the previous study, several viscoelastic models such as standard linear viscoelastic, generalized Maxwell, and multimode Maxwell models are used to fit the experimental result in the linear viscoelastic region (Gupta et al., 1997; Vilmin & Raphael, 2006; Benmouffok-Benbelkacem et al., 2010; Jaishankar et al., 2011). In this study, the multimode Maxwell model is used to analyze the effect of viscoelasticity. While it could not be claimed that the multimode Maxwell model represents all the characteristics of anode slurry, it is deemed sufficient to explain in terms of a simple analysis in viscoelastic aspect for the anode slurry. The parameter set for the multimode Maxwell model can be obtained by comparing the experimental result from the frequency sweep test, and storage and loss modulus equations used for the multimode Maxwell model, the most common measures of linear rheology, as follows

$$G' = \sum_{i} G_i \frac{(\lambda_i w)^2}{1 + (\lambda_i w)^2}$$
(3.8)

$$G'' = \sum_{i} G_i \frac{\lambda_i w}{1 + (\lambda_i w)^2}$$
(3.9)

where $\lambda_i = \frac{n_i}{G_i}$ is the relaxation time of i-th Maxwell unit, G_i is the modulus of i-th Maxwell unit, and w is the frequency. In this study, the fitting was conducted for the N = 2, 3, 4 in the N-mode Maxwell model, and the resulting parameter sets are listed in Appendix A. From the experimental data and parameter fitting results, the storage modulus (G') in the low-frequency region, which best characterizes material property, did not correlate well for N =2, 3. However, as it is indicated in Figure 3.6b., the N-mode Maxwell model provided a good fit for N \geq 4. Thus, we proceeded further analysis of anode slurry

used in our study in the aspect of viscoelastic with the four-mode Maxwell model, the simplest model within the N-mode Maxwell model. If the composition of anode slurry varied, it is necessary to redetermine a suitable parameter set with the above N-mode Maxwell model fitting.

Using the above model and parameters, the C-P flow region in the blade coating near the blade lip is possible to represent the shear deformation that the anode slurry exerted through the die lip within a temporal time. In other words, the anode slurry passing through the C-P flow region will be exposed to the high shear rate for a certain period of time due to the shear deformation. From previous study, the anode slurry exhibits the shear-thinning behavior of a Generalized Newtonian fluid (GNF) at high shear rate region (Lee *et al.*, 2022). Thus, we represented its behavior as a GNF model during the C-P flow region in Figure 3.2d, and as a four-mode Maxwell fluid after passing the die lip C-P flow region. The response strain with the 4-mode Maxwell model can be represented as the recovery test of viscoelastic material. Thus, the stress can be expressed as follows

$$\dot{\gamma}(t) = \dot{\gamma}_0 \left(H(t) - H(t - t_{\text{coating}}) \right)$$
(3.10)

$$\tau(t) = \eta \dot{\gamma}(t) \tag{3.11}$$

$$\tau_{tot} = \int_0^{t_{\text{coating}}} \tau(t) dt \qquad (3.12)$$

where $\dot{\gamma}_0$ is the shear rate from the shear deformation, H(t) is the Heaviside function, and t_{coating} is the stress applied time. The stress $\tau(t)$ to the anode slurry can be obtained from Eq. (3.10) and Eq. (3.11). As the shear rate $\dot{\gamma}_0$ during the coating process is the same, stress is a kind of step function. The temporal deformation of anode slurry $\gamma(t)$ can be obtained by solving the constitutive equation of four-mode Maxwell model for a given stress in Eq. (3.11). The total stress applied

to the anode slurry also can be obtained using Eq. (3.12).

FEniCS, open-source platform solving the partial differential equations based on Finite Element Method (FEM), is used for the sake of analyzing the results with a numerical point of view. This numerical approach can be one of the methods to solve the problem as the analytical solution cannot be easily obtained because of the complexity of the multimode Maxwell model. The formulated system in this numerical approach can be found in Appendix B. and τ_0 , t_0 are selected on a similar scale compared to the experimental condition. Initially, the validation was conducted for the two-mode Maxwell model by comparing its analytical solution and numerical solution from FEniCS (the validation results are attached in Appendix B). The numerical solutions in Figure 3.7. were obtained by enlarging it to four-mode Maxwell model.



Figure 3.7: Response strain $\gamma(t)$ of the GNF, and four-mode Maxwell model to the stress $\tau(t)$ and shear rate $\dot{\gamma}(t)$. (a), (c), (e) Under the same total stress (τ_{tot}) with varying shear rates and time periods. (b), (d), (f) Under increased total stress with the same shear rate, yet with different time periods. Region I, II, and III represent the anode slurry's rest state, under shear deformation, and recovery state, respectively.

The numerically obtained response strains, $\gamma(t)$, of anode slurry represented with GNF fluid and four-mode Maxwell fluid are plotted in Figure 3.7. Figure 3.7a and b show the shear rate that the anode slurry undergoes through the C-P flow region. In this region, region II, the anode slurry responses as a GNF fluid because of its high shear rate. Thus, the stress in Figure 3.7c and d show a step function to the given shear rate condition in Figure 3.7a and b, respectively. This can be represented as Eq. (3.10) and (3.11). When the coating is done, high shear rate is removed, then the anode slurry behaves as a four-mode Maxwell model. The response strain in Figure 3.7e and f can be divided into two parts: region II, which exhibits GNF-model, and region III, where the four-mode Maxwell model is applied. t = 0 means the time when the anode slurry enters to the die lip region where the coating begins.

More specifically, the same total stress (τ_{tot}) is applied with different shear rate in the case of Figure 3.7a. The step stress with different time period for each case A, B, and C is τ_0 for t_0 , $\frac{\tau_0}{2}$ for $2t_0$, and $\frac{\tau_0}{3}$ for $3t_0$, respectively. The response strain for each condition is plotted in Figure 3.7e and its subplot which show the change of shear rate $(\dot{\gamma})$ with the same total stress. In other words, these results correspond to the change of the shear rate from substrate speed change with same die lip length during the coating process. The process condition change in Figure 3.7a is consistent with the experimental conditions for experiment # 1, 2, and 3 in Table 1. In other case, shear rate, stress, and strain when the same shear rate is applied with different time period are plotted in Figure 3.7b, d, and f, respectively. The same step shear rate $\dot{\gamma}_0$ is applied during t_0 , $2t_0$, $3t_0$ in case 1, 2, and 3, respectively. This process condition change in Figure 3.7b. represents that the usage of different die lip length with the same substrate speed, and this corresponds to the experimental conditions for experiment #4 and 5 or #3 and 7 in Table 3.1.

In the viscoelastic perspective, the reason of development in edge bead can be interpreted as the viscoelastic recovery that the anode slurry tends to return its initial structure in region I. As anode slurry passes through region I, II, and III, it becomes to align to the C–P flow direction. Thus, the response strain means the deviation between the initial and final coating profile of anode slurry. The larger this value is, the better the coating profile formed in region II is sustained.

From the results, we were able to draw two significant conclusions. First, the change of die lip length will affect more significantly to the heavy edge than the change of substrate speed. In the subplots in Figure 3.7e and f, the differences in response strain between each case are much larger in Figure 3.7f than in Figure 3.7d at later times. These numerical results exhibit a comparable tendency similar to the experimental results. As a side note, the subplot in Figure 3.7e shows that, unlike the experimental results, substrate speed also seems to affect the heavy edges. However, the differences in each case are relatively small, so the discrepancies could potentially be minimized or eliminated when consider the surface tension, capillary force, and other material properties of anode slurry. Second, the long-time behavior of strain in Figure 3.7f shows that the longer the die lip length induces, the less heavy edge appears. As aforementioned above, the larger strain means the better of coating profile by suppressing the elevating heavy edge with sustaining its deformed shape in region II. That means the case 3 will show the smallest heavy edge and these numerical results are correspond to the experimental results.

The numerical analysis conducted within a viscoelastic framework, utilizing a multi-Maxwell model, effectively corroborates the experimental results. It has been demonstrated that the aspect ratio from the operating conditions, significantly influences the coating profiles. Although further research is required to better understand the behavior of anode slurry in relation to its additional material properties and process parameters, this preliminary analysis employing a viscoelastic model successfully captures the primary characteristics of anode slurry behavior.



Figure 3.8: (a) The cycling performance of the graphite/Li cells using electrode expt #4, #2, and #7 that charge-discharge rate was 0.1C in the potential range of 0.01-2 V at 25 °C. (b) Error bars, and standard deviations of the normalized capacity retention (50 cycles) from three samples.

3.4.4. Electrochemical performance

To investigate the effect of the process conditions on electrochemical performance in manufacturing conditions, we conducted electrochemical tests using the fabricated electrodes under different aspect ratio conditions by manipulating the process conditions for manufacturing battery anodes as described above. Figure 8 shows the capacity retention using graphite electrodes fabricated under various aspect ratio conditions. Figure 8a shows the normalized capacity retention through cycle test during the 100 cycles for each sample. Additionally, to verify the effects of shear stress, multiple cells were assembled under the same conditions. Figure 8b illustrates the standard deviations of the normalized capacity retention for 50 cycles in each sample, allowing for a detailed comparison of the conditions within each cell. Samples 1, 2, and 3 exhibited cycle retentions of 99.194% (with a standard deviation of 0.573), 99.434%(with a standard deviation of 0.385), and 99.062% (with a standard deviation of 0.682), respectively. These results indicate that as the shear strain increases during the slurry coating process, a similar performance is observed in terms of the electrochemical test.

It is important to note that electrochemical performance measurement and comparisons through rate tests are dependent on the amount of active material that is loaded on the electrode (electrode thickness). Further studies under thickness-controlled conditions with various shear thickness are required.

3.5. Final remarks

This research aimed to observe and investigate how to improve the side heavy edge, which is one of the defects that occurs in the battery electrode mass production process. In particular, we wanted to understand the heavy edge based on the properties of the slurry from a rheological point of view, which is one of the reasons for the formation of the heavy edge. To analyze this, we coated battery anode slurry using a high speed blade coating process to make anodes under different process conditions and measured the morphology of the heavy edge formed using displacement sensors.

From the experimental observations, we found that the heavy edge changes its size most significantly with the coating gap which is a common process parameter, and we observed that the heavy edge defect intensifies as the coating gap increases. In addition, we found that the heavy edge defect is mitigated as the aspect ratio of the C-P flow region, which exerts shear deformation on the slurry due to the increase in blade lip length, increases. However, the coating speed seemed not to cause any significant difference in the morphology of the heavy edge. Statistical analysis on the experiment results statistically verified these tendencies, and in particular, spectral clustering results showed that coating gap and blade lip length significantly changed the coating quality parameter.

Furthermore, the experimental results were interpreted from a rheological point of view through linear viscoelastic modeling. The coating of anode slurry through the blade coating process can be interpreted as a linear viscoelastic behavior in which the slurry experiences shear deformation and then some of the deformation is recovered as the stress is removed. As a result, it was found that the slurry deformation due to the change in the aspect ratio of the area where the slurry undergoes deformation due to the change in blade lip length has a larger magnitude than the difference in slurry deformation due to the change in coating speed.

Finally, through the electrochemical performance evaluation of the fabricated anode, it was confirmed that the electrochemical performance of the fabricated anode remained constant even if the process conditions were changed to improve the heavy edge defect.

The work presented in this study is meaningful as it provides a basis for research on how to understand and regulate heavy edge defects in depth from a rheological point of view by conducting a primitive analysis of heavy edge phenomena, which has not been properly analyzed theoretically so far.

Chapter 4.

Concluding remarks

In this dissertation, investigation for the blade coating process in various applications was examined by combining experimental, numerical simulation, and theoretical approaches and to solve the defects in the coating process utilizing these approaches. Firstly, a novel continuous coating process was introduced to improve the performance uniformity of organic semiconductor devices fabricated at a laboratory scale. This process, which is called as CoMiC process, enabled the manipulation of coating flows by varying the patterns inside microfluidic feed region. Examination on process design for the fabrication of highly uniform organic semiconductor devices was conducted by analyzing the three-dimensional flow analysis of the coating process based on numerical simulation and the visualization approach of the crystallization phenomena of organic semiconductor thin films. This analysis confirmed that a shape-perturbed coating flow could be developed by placing a pattern inside the microfluidic channel used for coating liquid supply in a continuous blade coating process. Depending on the characteristics of the developed coating flow, it is possible to control the transverse feeding tendency from the puddle formed by the coating liquid, and due to the improved transverse feeding flow uniformity, it is possible to reduce the isotropic crystal defects occurring in the crystallization process and achieve high uniformity organic semiconductor fabrication. This study is valuable for suggesting a new process utilization by using the patterned microchannel system, which has been used only from the perspective

of a passive microfluidic mixer, to control the subsequent process.

Secondly, we investigated how to improve the side heavy edge defects that occurs in the battery electrode mass production process. Experimental investigation was conducted by manufacturing the battery electrodes under process parameter variation and statistical analysis on the experimental results. We found that the heavy edge changes its size most significantly with the coating gap which is a common process parameter, and we observed that the heavy edge defect intensifies as the coating gap increases. In addition, we found that the heavy edge defect is mitigated as the aspect ratio of the C-P flow region, which exerts shear deformation on the slurry due to the increase in blade lip length, increases. We have analyzed these phenomenological correlations from a rheological perspective using linear viscoelastic modeling, it was found that the slurry deformation due to the change in the aspect ratio of the area where the slurry undergoes deformation due to the change in blade lip length has a larger magnitude than the difference in slurry deformation due to the change in coating speed. This study holds significant value as it lays the groundwork for comprehending and controlling heavy edge defects more thoroughly from a rheological perspective. This has been achieved through an initial analysis of the heavy edge phenomena, an area that has previously lacked substantial theoretical examination.

There are still many unexplored aspects of the coating process even though many researchers have been conducting various studies on it for a long time because many types of products are manufactured by the liquid coating process in the industry, and the coating liquids used to produce them have increasingly complex properties. I hope that the piece of the research described in this thesis will be helpful for future engineers to reveal the remaining unexplored areas.

Bibliography

Abraham D. Stroock, S. K. W. D., Armand Ajdari, Igor Mezi[']c, Howard A. Stone, George M. Whitesides. 2002 Chaotic Mixer for Microchannels. *Science* **295**(5555), 647-651.

Agarwal, M., S. Sharma, V. Shankar and Y. M. Joshi. 2021 Distinguishing thixotropy from viscoelasticity. *Journal of Rheology* **65**(4), 663-680.

Alharbi, A. M. (2017). Applied Analytical Techniques to Study Solution Behaviour of TIPS-pentacene and 1,6-bis(pyren-1-ylthio)hexane, University of Manchester.

Andrew Y. Ng, M. I. J., Yair Weiss (2001). On Spectral Clustering: Analysis and an algorithm. 14th International Conference on Neural Information Processing Systems.

Aref, H. 1984 Stirring by chaotic advection. Journal of Fluid Mechanics 143 1-21.

Aref, H., J. R. Blake, M. Budišić, S. S. S. Cardoso, J. H. E. Cartwright, H. J. H.
Clercx, K. El Omari, U. Feudel, R. Golestanian, E. Gouillart, G. F. van Heijst, T. S.
Krasnopolskaya, Y. Le Guer, R. S. MacKay, V. V. Meleshko, G. Metcalfe, I. Mezić,
A. P. S. de Moura, O. Piro, M. F. M. Speetjens, R. Sturman, J.-L. Thiffeault and I.
Tuval. 2017 Frontiers of chaotic advection. *Reviews of Modern Physics* 89(2).

Barnes, H. A. 1997 Thixotropy—a review. *Journal of Non-Newtonian Fluid Mechanics* **70**(1-2), 1-33.

Behr, M. and T. E. Tezduyar. 1994 Finite element solution strategies for large-scale flow simulations. *Computer Methods in Applied Mechanics and Engineering* **112**(1-

4), 3-24.

Benmouffok-Benbelkacem, G., F. Caton, C. Baravian and S. Skali-Lami. 2010 Nonlinear viscoelasticity and temporal behavior of typical yield stress fluids: Carbopol, Xanthan and Ketchup. *Rheologica Acta* **49**(3), 305-314.

Bishop, C. M. 2006 Pattern Recognition and Machine Learning. Springer New York.

Brédas, J. L., J. P. Calbert, D. A. da Silva Filho and J. Cornil. 2002 Organic semiconductors: a theoretical characterization of the basic parameters governing charge transport. *Proceedings of the National Academy of Sciences* **99**(9), 5804-5809.

Camesasca, M., M. Kaufman and I. Manas-Zloczower. 2006 Quantifying Fluid Mixing with the Shannon Entropy. *Macromolecular Theory and Simulations* **15**(8), 595-607.

Camesasca, M., I. Manas-Zloczower and M. Kaufman. 2005 Entropic characterization of mixing in microchannels. *Journal of Micromechanics and Microengineering* **15**(11), 2038-2044.

Cho, K. Y., Y. I. Kwon, J. R. Youn and Y. S. Song. 2013 Evaluation of slurry characteristics for rechargeable lithium-ion batteries. *Materials Research Bulletin* **48**(8), 2922-2926.

Choi, J., M. Armstrong and S. A. Rogers. 2021 The role of elasticity in thixotropy: Transient elastic stress during stepwise reduction in shear rate. *Physics of Fluids* **33**(3).

Claus Daniel, J. O. B. 2011 Handbook of Battery Materials. Wiley-VCH Verlag

GmbH & Co. KGaA.

Diao, Y., L. Shaw, Z. Bao and S. C. B. Mannsfeld. 2014 Morphology control strategies for solution-processed organic semiconductor thin films. *Energy Environmental Science* **7**(7), 2145-2159.

Diao, Y., B. C. Tee, G. Giri, J. Xu, D. H. Kim, H. A. Becerril, R. M. Stoltenberg, T. H. Lee, G. Xue, S. C. Mannsfeld and Z. Bao. 2013 Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains. *Nature Materials* **12**(7), 665-671.

Ding, X., J. Liu and T. A. L. Harris. 2016 A review of the operating limits in slot die coating processes. *AIChE Journal* **62**(7), 2508-2524.

Du, C.-F., Q. Liang, Y. Luo, Y. Zheng and Q. Yan. 2017 Recent advances in printable secondary batteries. *Journal of Materials Chemistry A* **5**(43), 22442-22458.

Edgar B. Gutoff, E. D. C. 2006 *Coating and Drying Defects: Troubleshooting Operating Problems*. Wiley.

Ferry, J. D. 1980 Viscoelastic Properties of Polymers. Wiley.

Franke, D., M. V. Petoukhov, P. V. Konarev, A. Panjkovich, A. Tuukkanen, H. D. T. Mertens, A. G. Kikhney, N. R. Hajizadeh, J. M. Franklin, C. M. Jeffries and D. I. Svergun. 2017 ATSAS 2.8: a comprehensive data analysis suite for small-angle scattering from macromolecular solutions. *Journal of Applied Crystallography* 50(Pt 4), 1212-1225.

Gates, I. D. (1999). SLOT COATING FLOWS: FEASIBILITY, QUALITY VOLUME 1, University of Minnesota.

Giri, G., S. Park, M. Vosgueritchian, M. M. Shulaker and Z. Bao. 2014 High-mobility, aligned crystalline domains of TIPS-pentacene with metastable polymorphs through lateral confinement of crystal growth. *Advanced Materials* **26**(3), 487-493.

Giri, G., E. Verploegen, S. C. Mannsfeld, S. Atahan-Evrenk, D. H. Kim, S. Y. Lee, H. A. Becerril, A. Aspuru-Guzik, M. F. Toney and Z. Bao. 2011 Tuning charge transport in solution-sheared organic semiconductors using lattice strain. *Nature* **480**(7378), 504-508.

Lithium-ion Battery Market Size, Share & Trends Analysis Report by Product (LCO, LFP, NCA, LMO, LTO, NMC), by Application (Consumer Electronics, Energy Storage Systems, Industrial), by Region, and Segment Forecasts, 2020-2027. 2020 *Research and Markets*.

Goto, O., S. Tomiya, Y. Murakami, A. Shinozaki, A. Toda, J. Kasahara and D. Hobara. 2012 Organic single-crystal arrays from solution-phase growth using micropattern with nucleation control region. *Advanced Materials* **24**(8), 1117-1122.

Gu, X., L. Shaw, K. Gu, M. F. Toney and Z. Bao. 2018 The meniscus-guided deposition of semiconducting polymers. *Nature Communications* **9**(1), 534.

Guo, X., Y. Xu, S. Ogier, T. N. Ng, M. Caironi, A. Perinot, L. Li, J. Zhao, W. Tang, R. A. Sporea, A. Nejim, J. Carrabina, P. Cain and F. Yan. 2017 Current Status and Opportunities of Organic Thin-Film Transistor Technologies. *IEEE Transactions on Electron Devices* **64**(5), 1906-1921.

Gupta, M., C. A. Hieber and K. K. Wang. 1997 Viscoelastic Modelling of Entrance Flow Using Multimode Leonov Model. *International Journal for Numerical Methods in Fluids* **24**(5), 493-517. Han, G. H., S. H. Lee, W.-G. Ahn, J. Nam and H. W. Jung. 2014 Effect of shim configuration on flow dynamics and operability windows in stripe slot coating process. *Journal of Coatings Technology and Research* **11**(1), 19-29.

Hawley, W. B. and J. Li. 2019 Electrode manufacturing for lithium-ion batteries— Analysis of current and next generation processing. *Journal of Energy Storage* 25.

He, M., B. Li, X. Cui, B. Jiang, Y. He, Y. Chen, D. O'Neil, P. Szymanski, M. A. Ei-Sayed, J. Huang and Z. Lin. 2017 Meniscus-assisted solution printing of largegrained perovskite films for high-efficiency solar cells. *Nature Communications* **8** 16045.

Heejin Kim, K.-I. M., Keita Inoue, Do Jin Im, Dong-Pyo Kim, Jun-ichi Yoshida. 2016 Submillisecond organic synthesis: Outpacing Fries rearrangement through microfluidic rapid mixing. *Science* **352**(6286), 691-694.

Hu, Q., L. Zhao, J. Wu, K. Gao, D. Luo, Y. Jiang, Z. Zhang, C. Zhu, E. Schaible, A. Hexemer, C. Wang, Y. Liu, W. Zhang, M. Gratzel, F. Liu, T. P. Russell, R. Zhu and Q. Gong. 2017 In situ dynamic observations of perovskite crystallisation and microstructure evolution intermediated from [PbI(6)](4-) cage nanoparticles. *Nature Communications* **8** 15688.

Hwang, S. S. 1979 Hydrodynamic analyses of blade coaters. *Chemical Engineering Science* **34**(2), 181-189.

I. K. Dien, H. G. E. 1983 A Generalized Steady-State Reynolds Equation for Non-Newtonian Fluids, With Application to Journal Bearings. *Journal of Tribology* **105**(3), 385-390.

Jaishankar, A., V. Sharma and G. H. McKinley. 2011 Interfacial viscoelasticity, yielding and creep ringing of globular protein–surfactant mixtures. *Soft Matter* **7**(17).

Jalaal, M., C. Seyfert and J. H. Snoeijer. 2019 Capillary ripples in thin viscous films. *Journal of Fluid Mechanics* **880** 430-440.

Janneck, R., F. Vercesi, P. Heremans, J. Genoe and C. Rolin. 2016 Predictive Model for the Meniscus-Guided Coating of High-Quality Organic Single-Crystalline Thin Films. *Advanced Materials* **28**(36), 8007-8013.

Ji, H. S., W.-G. Ahn, I. Kwon, J. Nam and H. W. Jung. 2016 Operability coating window of dual-layer slot coating process using viscocapillary model. *Chemical Engineering Science* **143** 122-129.

John E. Anthony, J. S. B., David L. Eaton, Sean R. Parkin. 2001 Functionalized Pentacene: Improved Electronic Properties from Control of Solid-State Order. *Journal of the American Chemical Society* **123**(38), 9482-9483.

Kang, T. G. and T. H. Kwon. 2004 Colored particle tracking method for mixing analysis of chaotic micromixers. *Journal of Micromechanics and Microengineering* **14**(7), 891-899.

Kim, D., J. Choi and J. Nam. 2016 Entropy-assisted image segmentation for nanoand micro-sized networks. *Journal of Microscopy* **262**(3), 274-294.

Kim, D., S. Lee, W. Hong, H. Lee, S. Jeon, S. Han and J. Nam. 2019 Image Segmentation for FIB-SEM Serial Sectioning of a Si/C-Graphite Composite Anode Microstructure Based on Preprocessing and Global Thresholding. *Microscopy and Microanalysis* **25**(5), 1139-1154. Kim, H. J., M. J. M. Krane, K. P. Trumble and K. J. Bowman. 2006 Analytical Fluid Flow Models for Tape Casting. *Journal of the American Ceramic Society* **89**(9), 2769-2775.

Kim, J. O., J. C. Lee, M. J. Kim, H. Noh, H. I. Yeom, J. B. Ko, T. H. Lee, S. H. Ko Park, D. P. Kim and S. Park. 2018 Inorganic Polymer Micropillar-Based Solution Shearing of Large-Area Organic Semiconductor Thin Films with Pillar-Size-Dependent Crystal Size. *Advanced Materials* e1800647.

Kim, K., J. Hong, S. G. Hahm, Y. Rho, T. K. An, S. H. Kim and C. E. Park. 2019 Facile and Microcontrolled Blade Coating of Organic Semiconductor Blends for Uniaxial Crystal Alignment and Reliable Flexible Organic Field-Effect Transistors. *ACS Applied Materials & Interfaces* **11**(14), 13481-13490.

Klauk, H. 2010 Organic thin-film transistors. *Chemical Society Reviews* **39**(7), 2643-2666.

Kwak, H. and J. Nam. 2020 Simple criterion for vortex formation in the channel flow of power-law fluids. *Journal of Non-Newtonian Fluid Mechanics* **284**.

Kwak, H. and J. Nam. 2021 Simple methods for obtaining flow reversal conditions in Couette–Poiseuille flows. *Journal of Rheology* **65**(5), 1023-1033.

Kwon, Y. I., J. D. Kim and Y. S. Song. 2014 Agitation Effect on the Rheological Behavior of Lithium-Ion Battery Slurries. *Journal of Electronic Materials* **44**(1), 475-481.

Kyung Sun Park, J. J. K., Rishat Dilmurat, Ge Qu, Prapti Kafle, Xuyi Luo, Seok-Heon Jung, Yoann Olivier, Jin-Kyun Lee, Jianguo Mei, David Beljonne, Ying Diao. 2019 Tuning conformation, assembly, and charge transport properties of conjugated polymers by printing flow. *Science Advances* **5**(8), eaaw7757. Lakes, R. 2009 *Viscoelastic Materials*. Cambridge University Press.

Lamberti, G. 2014 Flow induced crystallisation of polymers. *Chemical Socicety Reviews* **43**(7), 2240-2252.

Lazić, ž. R. 2004 Design of Experiments in Chemical Engineering. WILEY-VCH.

Lee, J.-C., J.-O. Kim, H.-J. Lee, B. Shin and S. Park. 2019 Meniscus-Guided Control of Supersaturation for the Crystallization of High Quality Metal Organic Framework Thin Films. *Chemistry of Materials* **31**(18), 7377-7385.

Lee, M., H. Jung, M. Lee, H. Kwak and J. Nam. 2022 Model fluid for coating flows of Li-ion battery anode slurry. *Journal of Materials Science* **57**(38), 17935-17945.

Leopoldo P. Franca, S. L. F. 1992 Stabilized finite element methods: II. The incompressible Navier-Stokes equations. *Computer Methods in Applied Mechanics and Engineering* **99**(2-3), 209-233.

Li, J., J. Fleetwood, W. B. Hawley and W. Kays. 2022 From Materials to Cell: Stateof-the-Art and Prospective Technologies for Lithium-Ion Battery Electrode Processing. *Chemical Reviews* **122**(1), 903-956.

Liu, Y.-Q. and K.-Q. Zhu. 2010 Axial Couette–Poiseuille flow of Bingham fluids through concentric annuli. *Journal of Non-Newtonian Fluid Mechanics* **165**(21-22), 1494-1504.

Loest, H., R. Lipp and E. Mitsoulis. 1994 Numerical Flow Simulation of Viscoplastic Slurries and Design Criteria for a Tape Casting Unit. *Journal of the American Ceramic Society* **77**(1), 254-262.

Maël Le Berre, Y. C., and Damien Baigl. 2009 From Convective Assembly to Landau-Levich Deposition of Multilayered Phospholipid Films of Controlled Thickness. *Langmuir* **25** 2554-2557.

Maillard, M., C. Mézière, P. Moucheront, C. Courrier and P. Coussot. 2016 Bladecoating of yield stress fluids. *Journal of Non-Newtonian Fluid Mechanics* 237 16-25.

Mannsfeld, S. C., M. L. Tang and Z. Bao. 2011 Thin film structure of triisopropylsilylethynyl-functionalized pentacene and tetraceno[2,3-b]thiophene from grazing incidence X-ray diffraction. *Advanced Materials* **23**(1), 127-131.

Matsui, H., Y. Takeda and S. Tokito. 2019 Flexible and printed organic transistors: From materials to integrated circuits. *Organic Electronics* **75**.

Maza, D. and M. S. Carvalho. 2017 Trailing edge formation during slot coating of rectangular patches. *Journal of Coatings Technology and Research* **14**(5), 1003-1013.

Mewis, J. 1979 Thixotropy - a general review. *Journal of Non-Newtonian Fluid Mechanics* **6**(1), 1-20.

Mezger, T. 2014 The Rheology Handbook. Vincentz Network.

Neamen, D. A. 2003 Semiconductor physics and devices: Basic principles. McGraw-Hill.

O. Byrde, M. L. S. 1999 Optimization of a Kenics static mixer for non-creeping ⁻ow conditions. *Chemical Engineering Journal* **72** 163-169.

Park, S., G. Giri, L. Shaw, G. Pitner, J. Ha, J. H. Koo, X. Gu, J. Park, T. H. Lee, J. H. Nam, Y. Hong and Z. Bao. 2015 Large-area formation of self-aligned crystalline domains of organic semiconductors on transistor channels using CONNECT. *Proceedings of the National Academy of Sciences* **112**(18), 5561-5566.

Paterson, A. F. and T. D. Anthopoulos. 2018 Enabling thin-film transistor technologies and the device metrics that matter. *Nature Communications* 9(1), 5264.

Paterson, A. F., S. Singh, K. J. Fallon, T. Hodsden, Y. Han, B. C. Schroeder, H. Bronstein, M. Heeney, I. McCulloch and T. D. Anthopoulos. 2018 Recent Progress in High-Mobility Organic Transistors: A Reality Check. *Advanced Materials* e1801079.

Patidar, R., D. Burkitt, K. Hooper, D. Richards and T. Watson. 2020 Slot-die coating of perovskite solar cells: An overview. *Materials Today Communications* **22**.

Pauli, L., J. W. Both and M. Behr. 2015 Stabilized finite element method for flows with multiple reference frames. *International Journal for Numerical Methods in Fluids* **78**(11), 657-669.

Peng, B., Z. Wang and P. K. L. Chan. 2016 A simulation-assisted solution-processing method for a large-area, high-performance C10-DNTT organic semiconductor crystal. *Journal of Materials Chemistry C* **4**(37), 8628-8633.

Pierre-Gilles Gennes , F. B.-W., David Quéré. 2004 *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves.* Springer.

R. W. Flumerfelt, M. W. P., S. L. Cooper, R. B. Bird. 1969 Generalized Plane Couette Flow of a Non-Newtonian Fluid. *Industrial & Engineering Chemistry Fundamentals* **8**(2), 354-357.

Rajeev Malik, U. V. S. 1991 Generalized annular Couette flow of a power-law fluid. *Industrial & Engineering Chemistry Research* **30**(8), 1950-1954.

Rényi, A. 1955 On a new axiomatic theory of probability. *Acta Mathematica Academiae Scientiarum Hungarica* **6** 285-335.

Rényi, A. 1961 On Measures of Entropy and Information. *Proceedings of the 4th Berkeley Symposium on Mathematical, Statistics and Probability* 547.

Reynolds, C. D., P. R. Slater, S. D. Hare, M. J. H. Simmons and E. Kendrick. 2021 A review of metrology in lithium-ion electrode coating processes. *Materials & Design* **209**.

Ross, A. B., S. K. Wilson and B. R. Duffy. 1999 Blade coating of a power-law fluid. *Physics of Fluids* **11**(5), 958-970.

Saraka, R. M., S. L. Morelly, M. H. Tang and N. J. Alvarez. 2020 Correlating Processing Conditions to Short- and Long-Range Order in Coating and Drying Lithium-Ion Batteries. *ACS Applied Energy Materials* **3**(12), 11681-11689.

Sartor, L. (1990). Slot coating: Fluid mechanics and die design, University of Minnesota.

Schmitt, M. (2016). Slot die coating of lithium-ion battery electrodes, Karlsruher Institut für Technologie.

Schmitt, M., R. Diehm, P. Scharfer and W. Schabel. 2015 An experimental and analytical study on intermittent slot die coating of viscoelastic battery slurries.

Journal of Coatings Technology and Research **12**(5), 927-938.

Schmitt, M., P. Scharfer and W. Schabel. 2014 Slot die coating of lithium-ion battery electrodes: investigations on edge effect issues for stripe and pattern coatings. *Journal of Coatings Technology and Research* **11**(1), 57-63.

Scriven, L. E. 2005 *Fine-Structured Materials by Continous Coating and Drying or Curing of Liquid Precursors.* Wiley.

Shannon, C. E. 1948 A mathematical theory of communication. *The Bell System Technical Journal* **27**(3), 379-423.

Spiegel, S., T. Heckmann, A. Altvater, R. Diehm, P. Scharfer and W. Schabel. 2022 Investigation of edge formation during the coating process of Li-ion battery electrodes. *Journal of Coatings Technology and Research* **19**(1), 121-130.

Spiegel, S., A. Hoffmann, J. Klemens, P. Scharfer and W. Schabel. 2022 Optimization of Edge Quality in the Slot-Die Coating Process of High-Capacity Lithium-Ion Battery Electrodes. *Energy Technology* **11**(5).

Stephan F. Kistler, P. M. S. 1997 *Liquid Film Coating: Scientific principles and their technological implications*. Springer.

Sun, H., Q. Wang, J. Qian, Y. Yin, Y. Shi and Y. Li. 2015 Unidirectional coating technology for organic field-effect transistors: materials and methods. *Semiconductor Science and Technology* **30**(5).

T. Dobroth, L. E. 1986 Causes of edge beads in cast films. *Polymer Engineering and Science* **26**(7), 462-467.
T.E. Tezduyar, S. M., S.E. Ray, R. Shih. 1992 Incompressible flow computations with stabilized bilinear and linear equal-order-interpolation velocity-pressure elements. *Computer Methods in Applied Mechanics and Engineering* **95**(2), 221-242.

Tan, P., S. Diao, T. Huang, Z. Yang, H. Zhou and Y. Zhang. 2020 Mechanism and Control of the Trailing Edge in Intermittent Slot Die Coating. *Industrial & Engineering Chemistry Research* **59**(35), 15758-15767.

Thomas J.R. Hughes, L. P. F., Marc Balestra. 1986 A new finite element formulation for computational fluid dynamics: V. Circumventing the babuška-brezzi condition: a stable Petrov-Galerkin formulation of the stokes problem accommodating equalorder interpolations. *Computer Methods in Applied Mechanics and Engineering* **59**(1), 85-99.

Timothy M. Sullivan, S. M. 1986 Film thickness in blade coating of viscous and viscoelastic liquids. *Journal of Non-Newtonian Fluid Mechanics* **21**(1), 13-38. Tong C. Hsu, M. M., R.L. Laurence, Stanley Middleman. 1985 Separating forces in blade coating of viscous and viscoelastic liquids. *Journal of Non-Newtonian Fluid Mechanics* **18**(3), 273-294.

Tsuda, T. 2010 Coating Flows of Power-Law Non-Newtonian Fluids in Slot Coating. *Nihon Reoroji Gakkaishi* **38**(4-5), 223-230.

Vilmin, T. and E. Raphael. 2006 Dewetting of thin polymer films. *European Physical Journal E: Soft Matter and Biological Physics* **21**(2), 161-174.

Wang, Z., Z. Ma and L. Li. 2016 Flow-Induced Crystallization of Polymers: Molecular and Thermodynamic Considerations. *Macromolecules* **49**(5), 1505-1517. Weinstein, S. J. 2004 Coating Flows. *Annual Review of Fluid Mechanics* **36**(1), 29-53.

Yehuda Greener, S. M. 1974 Blade-coating of a viscoelastic fluid. *Polymer Engineering and Science* **14**(11), 791-796.

Yilin Wang, R. H. E. 2022 Distinguishing thixotropy, anti-thixotropy, and viscoelasticity using hysteresis. *ArXiv* 2212.07572.

Yim, H. (2021). Analyses and modeling of the low-speed blade coating flows, Seoul National University.

Yim, H. and J. Nam. 2022 Classification of static cylindrical menisci confined in a wedge. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **634**.

Zhang, L., C.-a. Di, G. Yu and Y. Liu. 2010 Solution processed organic field-effect transistors and their application in printed logic circuits. *Journal of Materials Chemistry* **20**(34).

Zhang, Z., B. Peng, X. Ji, K. Pei and P. K. L. Chan. 2017 Marangoni-Effect-Assisted Bar-Coating Method for High-Quality Organic Crystals with Compressive and Tensile Strains. *Advanced Functional Materials* **27**(37).

Zhao, B., D. Yin, Y. Gao and J. Ren. 2022 Concentration dependence of yield stress, thixotropy, and viscoelasticity rheological behavior of lithium-ion battery slurry. *Ceramics International* **48**(13), 19073-19080.

Zhou, L., A. Wanga, S.-C. Wu, J. Sun, S. Park and T. N. Jackson. 2006 All-organic active matrix flexible display. *Applied Physics Letters* **88**(8).

Appendix A

Assessment of segregation within mixing system and microstructures

A.1. Study Background

In the research conducted in Chapter 1, we dealt with the quantitative analysis of the unique mixing profiles generated by different pattern designs inside the microfluidic channel. For three microchannels (flat microchannel. different slanted groove microchannel, and staggered herringbone microchannel, as shown in Figure 2.5), the results obtained through numerical simulation and the mixing profile obtained through backward particle tracking are shown in Figure 2.11. In addition, to quantitatively compare each mixing profile, which qualitatively visualizes the mixing state, we analyzed a kind of information entropy called Shannon entropy as a quantitative indicator, and the result is shown in Figure 2.14. However. The results in Figure 2.14 have several limitations because we have analyzed the mix from the distribution perspective. First, in the final mixing profile of SGM, we can recognize that mixing the two substances is not performed adequately in some areas in the center (see Figure 2.11b). Still, nevertheless, it has high quantitative index values that are not significantly lower than expected compared to the quantitative index values for the mixing profile of SHM, which qualitatively achieved a very high level of mixing. Second, when considering the quantitative metric values obtained in Figure 2.14, it is difficult to intuitively recognize what level of mixing the system has achieved. In other

words, the quantitative metric values have a limitation in that they lack a baseline indicator of the state they represent.

In general, mixing is analyzed in two ways: from a distribution perspective, which is how uniformly the substances are distributed in the system being observed, and from a dispersion perspective, which is how well the substances in the system are separated from each other, as shown in Figure A.1. However, most of the previous work devoted to the quantification of mixing has focused on the analysis and quantification from the distribution perspective.



Figure A.1: Various mixing state in terms of distribution and dispersion.

A.2. Purpose of Research

In order to achieve high performance of products, coating fluids used in the liquid coating process are increasingly contained with various types of functional particles in higher concentrations. Therefore, if the mixing is not adequate during the coating fluid preparation process, the particles are not sufficiently dispersed, which leads to agglomeration, which causes various defects in the subsequent process. Therefore, the main objective of this research is to develop quantitative indicators to quantitatively evaluate the microstructure of various systems, including the mixing state, from the dispersion perspective. To achieve this, we aim to select appropriate methods for quantification and develop a unique algorithm to analyze them. Furthermore, we will analyze the mixing profile in a patterned microchannel as an example, performed in Chapter 2, to identify the features, pros, and cons of the proposed quantitative method.

A.3. Information entropy

Information entropy is a concept invented by Claude Shannon to quantify the uncertainty of an observed system. The Shannon entropy S, the simplest form of information entropy, is expressed as follows (Shannon, 1948):

$$S(X(p)) = -\sum_{i=1}^{M} p_i \ln (p_i)$$
(A.1)

and

$$\boldsymbol{X}(\boldsymbol{p}) = (\boldsymbol{p}_1, \boldsymbol{p}_2, \cdots, \boldsymbol{p}_M) \tag{A.2}$$

where X(p) is a discrete probability distribution of M elements such that $\sum_{i=1}^{M} p_i = 1$. The Rényi entropy, R_q , is a common generalization of the Shannon entropy, which defined as follows

$$R_q(X(p)) = \frac{1}{1-q} \ln\left(\sum_{i=1}^M p_i^q\right) \tag{A.3}$$

where the positive constant q is called Rényi parameter (Rényi, 1955; Rényi, 1961). Note that the limet of $q \rightarrow 1$ the Rényi endtropy becomes the Shannon entropy. The value of Rényi entropy is characterized by its value generally varying with the value of the Rényi parameter. We utilize Rényi entropy to quantify a probability distribution X(p) that reflects the characteristics of the system we want to observe and thus quantify the aggregation of the system.



Figure A.2: 168 by 168 Checker-board system with two segregations.

A.4. Probability distribution for observed system

For correct quantification using Rényi entropy, we need to determine a probability distribution X(p) that reflects the various states of dispersion in the system we observe. If the obtained probability distribution X(p) does not correctly reflect the information

regarding the dispersion that we intuitively perceive, the quantitative index obtained based on it will not correctly quantify the state of the system.



Figure A.3: (a) Checker-board system with two by two grid-shape filter. (b) Checker-board system with four by four grid-shape filter.

For example, suppose the system we are examining is an image of 168 by 168 pixels, as shown in Figure A.2, where the black pixels in the image represent aggregated particles and the white pixels represent empty space. For this system, we divide the area of interest through a grid-shaped filter that divides the system into two by two, as shown in Figure A.3a, and calculate the ratio of the number of particles in each region to the number of particles in the total, so that the probability distribution X(p) of having elements is as follows

$$X(p) = \left(\frac{1}{2}, \frac{1}{2}, 0, 0\right)$$
 (A.4)

By substituting the obtained probability distribution, equation (A.4), into equation (A.3) and calculating the Rényi entropy value for the case q=5, the quantitative measure for the system is quantified as $R_5(X(p)) \approx 0.3$. However, for a grid-shaped filter that divides the

system into four by four, as shown in Figure A.3b, the probability distribution X(p) obtained by the same method is as follows.

$$X(p) = \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, \frac{1}{8}, 0, 0, 0, 0, 0, 0, 0, 0, 0\right)$$
(A.5)

In this case, by substituting the obtained probability distribution, equation (A.5), into equation (A.3) and calculating the Rényi entropy value for the same q=5 case, the quantitative measure for the system is quantified as $R_5(X(p)) \approx 2.08$. As shown in the above two cases, even if the same system is examined, the values of the quantitative measures will differ depending on the method used to obtain the probability distribution X(p) for the system. Therefore, we can infer that for a multiscale-dispersion system with particles aggregated in various sizes, as shown in Figure A.4, obtaining a probability distribution of aggregation is an essential factor in the quantification of aggregation based on information entropy.



Figure A.4: Examples of multiscale-segregation system and the proper probability distributions for each example.

A.5. Algorithm for probability acquisition

As mentioned in Appendix A.4, obtaining an appropriate probability distribution X(p) for the system under investigation is one of the most essential factors in this study. In order to obtain the probability distribution X(p), we proposed an algorithm that uses a multiscale filter to classify segregations of different structures.

Figure A.5 shows an example of how the algorithm works for a physical mixture system. For a mixture of multiscale components, we can first separate the largest components from the mixture through a coarse sieve, denoted as filter 1. Then, we can use a dense sieve with a smaller filter size, denoted as filter 2, to sort out the smaller components. By repeating this sequentially down to the smallest size filter, we can classify the particles filtered out by each filter by size.

Assuming that the particles all have the same density, we can obtain a probability distribution X(p) by calculating the mass fraction of the sorted particles relative to the total mixture mass.



Figure A.5: Classification of multiscale component mixture system.

Since the object of this research is not a physically classifiable system, but a numerical simulation result or an image obtained from analysis equipment, we developed an algorithm that can virtually perform the process that is physically performed in the previous example. Figure A.6 shows the flowchart of the algorithm proposed in this study. The algorithm first performs data preparation for analysis by performing appropriate preprocessing on the raw data, such as numerical simulation data or images obtained from the analysis equipment. This study used the mixing profile data analyzed in Chapter 2.4. Each mixing profile consists of 40,000 particles, of which 20,000 are blue, and 20,000 are red. In this example, blue particles were selected as the object of observation. For the data obtained by preprocessing, a multiscale filter is sequentially used to detect the segmentation which is captured by the filter, and the detected segmentation is added as an element of the probability distribution X(p), which is obtained by calculating the number fraction of the detected segmented particles to the total number of particles. The particles used for probability distribution are excluded from the algorithm's subsequent observations to avoid repeated consideration of particles. Particles that are not captured even after applying the smallest filter are considered to be single particles that are not aggregated and added to the probability distribution. The resulting probability distribution is finally quantified using the Rényi entropy.



Figure A.6: Flow chart of the algorithm.

For the algorithm proposed above, there are no restrictions on the size, number, and shape of the multiscale filters used as long as there is no problem applying the algorithm. Since the microstructure geometry to be analyzed in this study has a 4:1 width to height ratio, a square-shaped multiscale filter is used, reflecting the relative length of the microchannels to their height. Figure A.7 shows the multiscale filters used in this study, and a red square represents each filter unit that moves inside the system to observe segregation. The largest filter

has half of the microchannel height as a length of the filter unit (as shown in Figure A.7a), and the filter unit, labeled in red, moves inside the system to detect aggregation. The filter unit of the lower filter is smaller than the previous filter unit with half the size of the previous filter unit. This study uses six multiscale filters, which we define as F_1 through F_6 in order from largest to smallest.



Figure A.7: Multiscale filters used in the algorithm.



Figure A.8: Algorithm result for mixing profile of SHM at 1st cycle (Figure 2.10) by using multiscale filters.

Let $N_{ref,i}$ be the number of particles that can be inside the filter unit F_i , and the values of $N_{ref,1}$ to $N_{ref,6}$ are 2500, 625, 156, 39, 9, and 2, respectively. However, in practice, when the algorithm is applied, all the particles inside the filter unit are rarely the same kind of particles, so we choose a tolerance for $N_{\text{ref},i}$ that enables the filter to detect aggregation at that scale even if a few different kinds of particles are present. For example, with a tolerance of 10%, filter F_1 in Figure A.7a detects an aggregation containing more than $N_{\rm ref,1} \times 0.9 = 2250$ particles and determines it to be an aggregation of filter F_1 size, and reflects the number fraction of such aggregations as an element of the probability distribution X(p). Figure A.8 is a schematic illustration of applying the algorithm to the mixing profile after 1 cycle for the staggered herringbone microchannel (SHM) analyzed in Chater 2.4. When the algorithm is performed for blue particles and a tolerance of 10% is applied, two aggregates are identified with the largest filter F_1 and a set P_1 is obtained by the algorithm whose elements are the number fractions of those cases. Sequentially, the algorithm identifies eight agglomerations by filter F_2 and obtains P_2 . The final probability distribution X(p) is the union of all the sets P_1 through P_6 obtained for all filters.

Figure A.9 and Figure A.10 show the algorithm's results for mixing profiles from 1 cycle to 5 cycles for SGM and SHM, respectively, and for blue particles in each mixing profile. As we can see, for mixing profiles that arbitrarily exist in various scales and shapes, the algorithm characterizes the state in which the particles are made by a combination of multiscale filters, which is the criteria for segregation. Based on this, the probability distribution X(p) reflecting each mixing profile is obtained.



Figure A.9: The mixing profiles and corresponding algorithm result for slanted groove microchannel (SGM).



Figure A.10: The mixing profiles and corresponding algorithm result for staggered herringbone microchannel (SHM).

A.6. Quantification using the Rényi entropy

Based on the information entropy introduced in Appendix A.3, especially the Rényi entropy, and the probability distribution X(p) obtained in Appendix A.5, we can quantify the system we observe in terms of dispersion. This study uses the normalized Rényi entopy for the probability distribution X(p) to define the resulting quantitative index, the segregation index, I_q , as follows.

$$I_q(X(p)) = \frac{R_q(X(p))}{R_{\text{max}}}$$
(A.6)

where

$$R_{\max} = \frac{1}{1-q} \ln \left(\sum_{i=1}^{N} \left(\frac{1}{N} \right)^{q} \right)$$
(A.7)

...

 R_{max} in Equation (A.7) refers to the Rényi entropy value for the state where all particles are completely dispersed without aggregating together, and since the Rényi entropy value in this case is the maximum value the system can have, the segregation index I_q is normalized by dividing the Rényi entropy value of the observed system by R_{max} . Thus, $I_q = 0$ means a perfectly segregated system and $I_q = 1$ means a perfectly dispersed system. Also, as shown in equation (A.3), the segregation index generally changes its value as the Rényi parameter q changes.

The segregation index I_q has a unique property for special cases. In the case of the six checker-board systems shown in Figure A.11, where the objects to be observed are in clusters of the same size as the filter used in this study, the probability distribution obtained by applying the algorithm to each system is characterized by the fact that they all consist of elements with the same value, and in this case the dependence on the Rényi parameter q is eliminated. Figure A.12 shows the values of the segregation index I_q for the six checkerboard systems in Figure A.11 for varying Rényi parameter q ranges. The segregation index I_q remains constant despite varying the value of the Rényi parameter q, which can be used as an important criterion to evaluate the system in subsequent analyses.

Figure A.13 shows the value of the segregation index I_q for the mixing profile of SGM from 1 cycle to 5 cycles for various Rényi parameter q ranges. As mentioned earlier, we can see that the value of the segregation index I_q varies with the value of the Rényi parameter q, which characterizes the segregation index I_q proposed in this study. In the high q value region, we can see that the segregation index I_q for each mixing profile converges to a certain value. In this case, the converging values are the values of the segregation index for the checker-board system presented in Figure A.12. Comparing the results of the algorithm in Figure A.9 with the converging values of the segregation index in Figure A.13, we can see that in the high q range, the segregation index converges to the segregation index value for a uniformly distributed system, which corresponds to the largest aggregation that exists in the system we observe. For example, the segregation index values for cycles 1 through 4 converge to a, which is the segregation index value for a checker-board system with particles aggregated into clusters of size F_1 . Furthermore, the segregation index value of cycle 5 converges to b, which is the segregation index value of the checker-board system with size F_2 .

Furthermore, as shown in Figure A.9, the mixing profiles of the first and fourth cycles inside the SGM show that although the maximum size of the aggregation is the same, the fourth cycle achieves a higher level of dispersion in the substructure aggregations than the first cycle. This difference is reflected in the difference in segregation index in the low q range in Figure A.13. Since the dispersion of lower scales in the mixing profile of the fourth cycle is better than that of the first cycle, we can see that the segregation index values in the low q range

are higher for the fourth cycle than for the first cycle.

This analysis shows that the segregation index I_q we proposed depends on the Rényi parameter. First, the segregation index I_q converges to a certain value in the high q range, and this converging value is the value of the segregation index I_q of a uniformly distributed reference system (shown in Figure A.11) with a scale corresponding to the largest aggregation inside the observing system. Thus, it is intuitive that the largest aggregation present in the observing system is characterized by the value of segregation Index I_q in the high q range. Conversely, segregation index I_q values in the low q range lead to increased contributions from smaller-scale aggregates, making it possible to perform relative comparisons of lower-scale aggregates.



Figure A.11: The checker-board system which has same segregation scale with each filters. The length written in figure means the physical length scale of segregation based on the microchannel geometry.



Figure A.12: The segregation indices for the six checker-board systems represented at Figure A.11.

Figure A.14 shows the values of the segregation index I_q for the mixing of SHM from 1 cycle to 5 cycles for various Rényi parameter q ranges. Comparing the values of segregation index I_q in the high q range, it can be seen that SHM can reduce the size of the largest aggregates to the size of F_3 in the end. Furthermore, as we can see in Figure A.10, cycle four and cycle five achieve almost similar levels of mixing qualitatively. They also seem to have almost the same values of segregation index I_q over the entire q range. It means that the segregation index I_q we proposed can effectively quantify the qualitatively perceptible state of dispersion. And from a dispersion perspective, we can see that SHM has already achieved the highest level of mixing that can be achieved in cycle 4.

Comparing the segregation index I_q values in Figure A.13 and Figure A.14, we can conclude that SHM has a higher value in the overall q range compared to SGM, indicating that it is a well-mixed process from a dispersion perspective, both in terms of the largest agglomeration size and sub-scale dispersion.



Figure A.13: The segregation indices for mixing profiles of SGM with various q range.



Figure A.14: The segregation indices for mixing profiles of SHM with various q range.

A.7. Final remarks

In this research, we developed an algorithm and a quantitative index to evaluate a system with multiscale segregation from the perspective of dispersion. Rényi entropy, a type of information entropy, is used to define the quantitative index, and an algorithm is designed to capture various sizes of dispersion using multiscale filters to effectively obtain the probability distribution X(p) required for quantification. The obtained probability distribution X(p) was finally quantified using the segregation index defined by the normalized Rényi entropy.

In addition, we evaluated the mixing profile inside the patterned microfluidic channel obtained in the previous study from the perspective of dispersion using the proposed quantitative index. The segregation index shows its advantages in determining the scale of the largest-scale aggregation present in the observed system in the high q range. In contrast, in the low q range, it can effectively perform a relative evaluation of the lower-scale aggregation. By comparing the segregation indices for two patterned microfluidic channels (SGM, SHM), we could evaluate that SHM is a relatively efficient process from a dispersion perspective.

The segregation index devised in this study can be widely utilized for mixing systems and microstructure systems where dispersion is essential. In addition, it is expected to be applied to various fields because, by expanding the dimensions, it is possible to analyze not only two-dimensional structures but also three-dimensional structures composed of multiple materials, such as battery electrodes analyzed in a previous study by Kim *et al.*, 2019.

국문 초록

블레이드 코팅 공정은 기재 위에 균일한 두께의 액체 박막을 도포하는 코팅 공정 중 후계량 방식의 대표적인 코팅 공정의 한 종류로, 구조적 간결성과 동작의 용이성으로 인해 실험실 규모에서 산업의 대량 생산 규모에 이르기까지 다양한 분야에서 널리 사용되는 공정이다. 블레이드 코팅 공정을 통해 도포되는 액체 박막의 두께는 공정에서 유체에 작용하는 점성력과 코팅 용액이 형성하는 계면의 모세관 힘, 코팅 용액에 작용하는 중력 등 공정에 작용하는 다양한 힘들의 복합적인 상호작용에 의해 결정된다.

대량 생산 공정에서 수행되는 고속 블레이드 코팅 공정은 기재의 움직임에서 기인한 점성력이 지배적으로 작용하기 때문에 모세관 힘을 배제한 간단한 형태의 유체역학 모델로 코팅 유동을 분석할 수 있다. 그러나 실험실 규모에서 주로 수행되는 저속 블레이드 코팅 공정의 경우, 모세관 힘이 지배적으로 작용함에 따라 기존의 유체역학 모델에 기반한 현상의 예측이 유효하지 않게 된다. 또한, 대부분의 유체역학 모델들은 폭방향 유동의 균일성을 가정한 2차원 유동 분석을 분석의 대상으로 하였기 때문에, 폭방향 불균일성에서 기인한 다양한 코팅 공정의 불량을 규명할 수 없다는 한계점이 존재한다.

이 논문은 실험, 전산모사, 이론적 접근법을 결합하여 다양한 분야에서 사용되는 블레이드 코팅 공정을 분석하고, 이를 기반으로 공정에서 발생하는 불량을 해결하는 것을 목적으로 한다. 첫 번째로, 실험실 규모에서 제작되는 유기 반도체 소자의 성능 균일성 향상을 위해 새로운 형태의 연속형 코팅 공정을 고안하고, 전산모사 기반의 코팅 공정의 3차원 유동 분석과 유기 반도체 박막의 결정화 현상을 시각화 기법으로 분석하여 고 균일성 유기 반도체 소자 생산을 위한 공정 설계 연구를 수행하였다.

두 번째로, 고속 블레이드 코팅 공정을 통해 복잡 유체인 배터리

음극 슬러리를 도포하여 배터리 음극을 제작하고, 배터리 전극 코팅 공정에서 발생하는 폭방향 불량 현상인 모서리 부풀음 현상을 분석하였다. 또한, 다양한 공정 인자 변화를 통해 제작된 배터리 전극의 불량 현상을 실험적으로 관측하고 이를 선형 점탄성 모델링을 통해 전단 변형에 대한 슬러리의 점탄성 거동을 계산하여 비교하였고, 이를 통해 슬러리에 가해지는 전단 변형과 전단 응력에 대한 슬러리의 점탄성 변형의 관점에서 코팅 공정에서 발생하는 모서리 부풀음 현상을 유변학적 관점에서 분석하였다. 또한, 공정 인자 제어를 통한 모서리 불량의 개선이 전기화학적 관점에서 배터리 전극의 성능 저하 없이 수행될 수 있음을 실험적으로 확인하였다.

주요어: 블레이드 코팅, 유한요소법, 코팅 불량, 마이크로채널, 유동 시각화, 점탄성 유체 **학번**: 2018-21745