Butterflies and Batteries: Advances in Liquid Repellent Surfaces by Anisotropic Wetting and Lubricant Impregnation

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2016

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Abstract

Recent advances in creating liquid-repellent surfaces have focused on decreasing the interaction between a liquid and a solid surface by modifying the surface’s chemistry and cleverly designing its geometry on nano- and millimetric length scales. This thesis explores two advances to control a liquid’s interaction with a surface: 1) deflectable structures that influence anisotropic wetting properties and 2) lubricant impregnated surfaces comprised of a porous surface and liquid lubricant. Through experimental characterization the mechanism by which deflectable scales on a butterfly wing cause anisotropic drop repellency is investigated. The design of lubricant impregnated surfaces is reviewed and expanded by demonstrating their potential for drag reduction and incorporation into electrochemical systems.

The first part of this thesis characterizes how the unique structure of a butterfly’s wings contributes to its anisotropic wetting properties. In particular, a water drop placed on the surface of a butterfly’s wing will easily roll away from the butterfly’s body, but will roll off at much higher angles toward the body. This phenomenon is observed and quantified using environmental electron microscopy and confocal microscopy. A theory that takes into account the deflection of the butterfly’s scales explains the observed anisotropy and correlates with the observed roll-off on a wide range of butterfly species. Such deflectable surface structures offer a new way to tune the wetting properties of a surface.

The second part of this thesis reviews and expands on lubricant impregnated surfaces. It explains how to achieve a stable lubricant impregnated surface and discusses its basic features including the wetting ridge and lubricant cloak. Motivated by the slippery nature of these surfaces, the potential of lubricant impregnated surfaces to reduce drag is detailed. A scaling model that incorporates the viscosity of the lubricant and elucidates the dependence of drag reduction on the ratio of the viscosity of the working fluid to that of the lubricant is presented. The model is validated by experiments conducted in a cone and plate rheometer where a drag reduction of 16% is measured.
Finally, lubricant impregnated surfaces are applied to electrochemical systems. Measurements quantify how lubricant impregnated surfaces improve the flowability of a non-Newtonian lithium polysulfide flow electrode in which electronic conductivity is imparted by carbon particles. A framework for the design of such surfaces for a wide range of flow electrode solvents is used to incorporate lubricant impregnated surfaces into a Gravity Induced Flow Cell (GIFCell) prototype to enable the flow of highly conductive suspension.

Thesis Supervisor: Kripa K. Varanasi
Title: Associate Professor of Mechanical Engineering
Acknowledgments

I am forever grateful for the opportunity Professor Kripa K. Varanasi provided me to spend five years in his lab and at MIT. I am grateful for his undying optimism and faith in me. I would also like to thank Professor Gareth H. McKinley and Professor Yet-Ming Chiang for serving on my thesis committee. Also thanks to Lauren Wolinsky for making the lab and my work run as smoothly as possible.

I thank the MIT Energy Initiative, Shell Oil Company, the Martin Family Society of Fellows for Sustainability, and the Joint Center for Energy Storage Research for funding me throughout my graduate career.

During my first few years at MIT living in Ashdown I was welcomed with open arms into a loving community. Itai Stein, Frank “Noble” Permenter, My Vu, Troy Niekamp, Chris Johnson, Andrea Carney, and others made the building that I called home special. I’m blessed to have many friends from college overlap my time in Boston and value my long lasting friendships with Lakshya, Harold, Henry, Alan, and Sarah.

I am especially grateful for getting to know everyone in my lab. Seyed Mahmoudi’s unique outlook is a breath of fresh air. My work would not be possible without the help of Leonid Rapoport whose level-headedness and maturity has always impressed me. As a young researcher I especially looked up to the work of Dave Smith, Adam Paxson, Sushant Anand, and Gisele Azimi.

All my roommates during my time in Boston were also Ph.D. students, and it was great
to live with Itai Stein, Justin Beroz, Joshua Martin, and Alec Walker who all managed very well-balanced lifestyles and maintained healthy outlooks on their academic careers. Also, special thanks to Taylor Farnham and Jessica Bernier who helped me immensely with last minute edits on my thesis.

And finally thanks to my family for always being supportive of my path in life and being there to lighten the mood. Thanks to my two brothers and our friendship that will continue to grow for the rest of our lives. I’m blessed to have a life full of amazing people that encourage and believe in my potential.
# Contents

<table>
<thead>
<tr>
<th>Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 Introduction</strong></td>
<td>25</td>
</tr>
<tr>
<td><strong>2 Deflection of Butterfly Scales and Anisotropic Roll-off</strong></td>
<td>27</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>27</td>
</tr>
<tr>
<td>2.2 Literature Review</td>
<td>27</td>
</tr>
<tr>
<td>2.3 Experimental Observations</td>
<td>29</td>
</tr>
<tr>
<td>2.3.1 Roll-off Anisotropy</td>
<td>29</td>
</tr>
<tr>
<td>2.3.2 Hysteresis</td>
<td>31</td>
</tr>
<tr>
<td>2.3.3 Roll-off of Many Species</td>
<td>33</td>
</tr>
<tr>
<td>2.3.4 Optical Microscopy</td>
<td>33</td>
</tr>
<tr>
<td>2.3.5 Environmental Scanning Electron Microscopy</td>
<td>34</td>
</tr>
<tr>
<td>2.3.6 Confocal Microscopy</td>
<td>36</td>
</tr>
<tr>
<td>2.4 Discussion</td>
<td>38</td>
</tr>
<tr>
<td>2.4.1 Deflection of <em>Morpho aega</em> Scales</td>
<td>38</td>
</tr>
<tr>
<td>2.4.2 Modeling Pinning Force</td>
<td>39</td>
</tr>
<tr>
<td>2.5 Synthetic Replication</td>
<td>42</td>
</tr>
<tr>
<td>2.6 Outlook</td>
<td>45</td>
</tr>
<tr>
<td><strong>3 Lubricant Impregnated Surfaces</strong></td>
<td>47</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>47</td>
</tr>
<tr>
<td>3.2 Fundamentals</td>
<td>47</td>
</tr>
</tbody>
</table>

7
5.2.3 Cyclic Voltammetry Experiments for Measuring Electrochemical Stability of Lubricant ........................................... 99
5.2.4 Cycling Experiments in Non-flowing Half-cells ..................... 100
5.2.5 Assembly of GIFCell with Lubricant Impregnated Surfaces ...... 100
5.3 Design of Lubricant Impregnated Surfaces for Electrochemical Devices .................................................. 101
5.4 Application of Lubricant Impregnated Surfaces to the GIFCell .............................................................. 105
5.5 Characterizing Slip ................................................................. 108
  5.5.1 As-Mixed Suspension ...................................................... 108
  5.5.2 Discharged Suspension .................................................. 111
5.6 Outlook ............................................................................ 114

6 Conclusions and Future Work ........................................ 115

References ........................................................................ 119
List of Figures

2.1 (a) Image of a male *Morpho aega* butterfly. (b) SEM image of scales on the wing of *Morpho aega*. (c) Image of a male *Papilio cresphontes* butterfly. (d) SEM image of scales on the wing of *Papilio cresphontes*. The red arrows denotes the direction of scales. Scale bars: (a, c) 1 cm (b, d) 100 µm.

2.2 Hierarchical micro- and nanostructures on the surface of the wings. (a, b) SEM images of the periodic arrangement of overlappingscales on the wings and nano-stripes on the scales. Scale bars: (a) 100 mm (b) 100 nm. c, d) AFM images of the overlapping micro-scale and nano-stripe structures. The black lines present the respective cross-section profiles at the bottom. Reproduced from Ref [1] with permission of The Royal Society of Chemistry.

2.3 The proposed model by Zheng et al. to explain roll-off anisotropy on the wings of *Morpho aega*. (a) When the wing is tilted away from the butterfly’s the morphology of the contact line is different than when the wing is tilted against the scales. Reproduced from Ref [1] with permission of The Royal Society of Chemistry.

2.4 (a) A *Morpho aega* butterfly in which scales on the surface of the wings are directed radially outward. (b) SEM image of the scales. A drop placed on the wing rolls of at (c) 42.4° against the scales or (d) 15.6° with the scales. (e) A *Papilio cresphontes* butterfly also decorated with scaled. (f) SEM of *Papilio cresphontes* scales. (g) A water drop placed on the surface of *Papilio cresphontes* rolls off at 0° in all directions. Scale bars: (a, e) 1 cm (b, f) 100 µm (c, d, g) 1 mm.
2.5 Depiction of a drop of a tilted surface when capillary pinning forces balance gravity. The front edge makes an angle $\theta_a$, and the back edge angle and angle $\theta_r$. ................................................................. 31

2.6 Advancing and receding angles in the direction with the scales measured for seven butterfly species. ................................................................. 32

2.7 Advancing and receding angles in the direction against the scales measured for seven butterfly species. ................................................................. 32

2.8 Roll-off angles of seven butterfly species with scales and against scales. In all cases, the roll-off against scales is as least as large as the roll-off with scales. The two species Danaus plexippus and Papilio cresphontes both show 0° roll-off in all directions. Scale bars: 1 cm. ......................... 33

2.9 (a) Schematic for the images shown in (c) showing the drop moving into the page against the scales. b) Schematic for (d) showing the drop moving to the left against the scales. (c, d) Orthogonal views of a drop moving against scales where scale deflection is clearly visible. Scale bar: 200 $\mu$m. .......................... 34

2.10 (a) Experimental apparatus within an ESEM chamber. A 10 $\mu$L drop is held in place by a copper wire fixed to a rotating stage. (b) Illustration of electron beam imaging area with respect to droplet contact line. (c) Single frame from movie of water droplet receding on superhydrophobic pillars as the drop is moved in the x direction. Scale bar: 10 $\mu$m. Reproduced from Ref [2] under the CC BY-NC-SA 3.0 license. ................................. 35

2.11 Phase diagram for water. The triple point occurs at 600 Pa and 0.05 °C . . . 35

2.12 Environmental scanning electron microscopy setup viewing from the direction that the electron beam travels and the backscatter detector. A chilled water line provides cooling to the chamber. The wing sample is fixed to a copper plate that is held in place by a custom fixture screwed into the stage. 36

2.13 Frames from ESEM videos collected at one frame per second as a drop translates against the direction of scales. Scale bars: 100 $\mu$m. .................. 37

2.14 A schematic of a confocal microscopy setup in which water is put between the butterfly wing and a coverslip held up by a 1 mm spacer. ................. 37
2.15 SEM images (top row) and confocal microscopy images (bottom row) for several butterfly species. For the confocal microscopy images, the scales are imaged through a cover slip and water. The air-water interface reflects light strongly. Scale bar: 100 µm.

2.16 Frames from ESEM videos collected at one frame per second as a drop translates (a) with the direction and scales and (b) against the direction of scales. The total receding angle \( \tilde{\theta}_r \) is the angle the water drop makes with the horizontal. (c, d) Schematics showing the total angle \( \tilde{\theta}_r \) decomposed into a scale deflection angle \( \alpha \) and intrinsic receding angle \( \theta_r \). Scale bar: 100 µm.

2.17 (a, b) ESEM images of a drop moving against the scales of *Morpho aega* and *Papilio cresphontes* respectively. (c, d) SEM images showing the density of scales of *Morpho aega* and *Papilio cresphontes* respectively. (e, f) Confocal microscopy images of *Morpho aega* and *Papilio cresphontes* respectively. The air-water interface strongly reflects light.

2.18 Model parameters measured for seven butterfly species.

2.19 Roll-off difference vs. estimated pinning force. The roll-off data is also presented in Figure 2.8 and the estimated pinning force presented in Equation 2.2.

2.20 Fabrication method in which first underlayers of titanium nitride and silicon dioxide that are 80 nm in thickness are applied via lithography. Next, an Fe/Al₂O₃ catalyst is patterned. Finally, carbon nanotubes are growth, and the rate of growth depends on the underlying substrate. The SEM image confirms that carbon nanotube forests with a silicon dioxide underlayer grows faster than those with a titanium nitride underlayer. Scale bar: 40 µm. Reproduced from Ref [3] with permission of Macmillan Publishers Ltd: Nature Communications (Copyright 2014).
2.21 Micropillars are grown from catalyst rectangles partially overlapping titanium nitride (shown as green layer in the inset) and bend towards the titanium nitride side which grows more slowly and couples to the faster-growing region of catalyst directly on silicon dioxide. Scale bars: 100 µm (panel), 20 µm (inset). Reproduced from Ref [3] with permission of Macmillan Publishers Ltd: Nature Communications (Copyright 2014).

2.22 SEM images of several CNT growths to replicate butterfly scales with the growth temperature indicated. The top row provides a top view and the bottom row provides an angled view of the same structures. Scale bars: 100 µm.

2.23 Successive images of a water drop moving against synthetic CNT scales. The scales are coating in DVB. Scale bar: 100 µm.

3.1 Schematics of wetting configurations outside and underneath a drop (column 2). The total interface energies per unit area (column 3) are calculated for each configuration by summing the individual interfacial energy contributions. Equivalent requirements for stability of each configuration are provided in column 4. In this table the lubricant is called ”oil” and the working fluid is called ”water.” Reproduced from Ref [4] with permission from The Royal Society of Chemistry.

3.2 Possible thermodynamic states of a water drop placed on a lubricant impregnated surface. The top two schematics show cases where the drop does and does not get cloaked by the lubricant. For each case, there are six possible states depending on how the lubricant wets the texture in the presence of air (the vertical axis) and the working fluid (horizontal axis). Reproduced from Ref [4] with permission from The Royal Society of Chemistry.
3.3 Cloaking of drops and the liquid-three phase contact line. (top) Confocal images of vertical sections through a water drop placed on lubricant impregnated micropillar array. FC70, decanol, and ionic liquid are used as lubricants. (bottom) Silicone oil cloak around a condensed drop suspended on a lubricant impregnated surface obtained by a Cryo-FIB-SEM process. The film is light grey sandwiched between the dark grey (water) and white (platinum). Reproduced from Ref [5] under the CC BY 3.0 license and from Ref [6] under the CC BY-NC 3.0 license.

3.4 Influence of the filling height. (a-c) Image of a micropillar array infiltrated with decanol before and after a water drop is deposited. The height of the lubricant film is adjusted (a) to be underfilled, (b) to match the height of the posts, and (c) to be overfilled. Color code: water (red), decanol (yellow/green), air or solid (black). Black shadows extended from the pillars result because the sample was imaged from underneath. (d) Contact angle hysteresis of a 5 µL water drop on a lubricant impregnated surface as a function of the lubricant height. Reproduced from Ref [5] under the CC BY 3.0 license and from Ref [7] with permission from Macmillan Publishers Ltd: Nature (Copyright 2011).

3.5 Comparison of condensation of water vapor on superhydrophobic (top row) and lubricant impregnated surfaces (bottom row) with identical textures. (a) Schematic of condensation on superhydrophobic surfaces showing that water can nucleate within the texture and (b-c) timelapse ESEM images. (d) Drops grow and coalesce and eventually form large Wenzel drops that are pinned on the surface. (e) Schematic of condensation on lubricant impregnated surfaces showing condensation on top of the lubricant and (f-g) timelapse ESEM images. (h) Drops that condense and grow on a vertical lubricant impregnated surface are highly mobile. Reproduced with permission from Ref [8] with permission of The American Chemical Society (Copyright 2012).
3.6 (a) Measured heat transfer coefficients for a flat hydrophobic surface, superhydrophobic surface, and Krytox impregnated surface with varying vapor pressures. The Krytox impregnated surface shows roughly twice the heat transfer as compared to the other surfaces. (b) Images of the condensate of three low surface tension fluids on three different surfaces each. Both dropwise condensation (DWC) and filmwise condensation (FWC) is observed. (c) The heat transfer coefficients for the condensation of low surface tension liquids on a flat silicon surface, a flat hydrophobic surface, and a Krytox impregnated surface. Bars are generated from modeling whereas points indicate measured values. Reproduced from [9] and [10] under the CC BY-NC-ND 3.0 license.

3.7 Behavior of water drops on a liquid impregnated surface. (a) Drops meeting at their liquid-air interfaces exhibit coalescence. (b) When the oil menisci of two drops overlap, an oil film forms between the drops that prevents coalescence. (c) Top-down and isometric views of noncoalescing droplets. (d) Multiple drops can be connected into networks which spontaneously rearranged over time. (e) SEM of nanopillar substrate. The oil lubricants are (a, b) Krytox 100 and (c, d) Fomblin 25/6. Reproduced from Ref [11] with permission of The National Academy of Sciences.

3.8 Comparison between an untreated aluminum 1100 sample (top) and lubricant impregnated surface (bottom) comprised of textured alumina and Krytox. The samples were cooled to -10°C at 60% relative humidity and defrosted at room temperature. Both samples are tilted at 75° for the duration of the experiment. Reproduced from Ref [12] with permission of The American Chemical Society (Copyright 2012).
3.9 Cryo-SEM images of a cross-sectioned lubricant impregnated surface with (a) excess lubricant and (b) no excess lubricant. (c) Comparison of the ice adhesion strength on lubricant impregnated surfaces between excess and equilibrium lubricant films. The ice adhesion strength is normalized to that on a smooth, uncoated silicon surface. The lubricant impregnated surface consists of lithographically textured silicon with 10 µm square posts with an edge-to-edge spacing of 50 µm. (d, e) Cross-section SEM images drops before and after freezing. The textured surface of Krytox impregnated surface consists of lithographically textured silicon with 10 µm square posts with an edge-to-edge spacing of 10 µm. In the frozen drop the lubricant has migrated out of the texture and covers icicles. Reproduced Ref [13] and Ref [14] with permission of The American Chemical Society (Copyright 2013).

3.10 A drop of water deposited on a silicone oil impregnated surface tilted to 20° cleans away silica dust particles. b) Evaporated coffee drop on a plastic surface (left) in contrast to a coffee drop that has evaporated on a silicone oil impregnated surface. Reproduced from Ref [15] with permission of IOP Publishing.

3.11 *Staphylococcus aureus* bacteria attachment (a) to a PTFE substrate and (b) to a lubricant impregnated surface. Scale bar is 30 µm. (c) Selective repellency of human cervical tumor cells from the hydrophobic liquid barriers and preferentially attachment to the square hydrophilic areas. The width of each square well is 500 µm. Reproduced from Ref [16] with permission of The National Academy of Sciences and from Ref [17] with permission of Wiley-VCH (Copyright 2013).
3.12 Gypsum scale formation after 80 hours in a salt solution on (a) an untreated smooth silicon surface (b) a silicone oil impregnated surface. Scale bars are 1 mm. (c) The corrosion of low alloy steel after three days of immersion in 3.5 wt% NaCl solution. From left to right: bare steel, hydrophobic steel, lubricant impregnated steel where the volume of lubricant is varied. Reproduced from Ref [18] with permission of Wiley-VCH (Copyright 2014) and Ref [19] with permission of Elsevier (Copyright 2015).

3.13 (a) Measured velocities of water droplets as a function of substrate tilt angle for various lubricant viscosities, textures, and drop sizes. (b) Schematic of a water droplet moving on a lubricant impregnated surface showing the various parameters of consideration. (c) Trajectories of tracer particles measured relative to the water droplet reveal that the drop rolls rather than slides on lubricant impregnated surfaces. (d) Non-dimensional plot collapsing the datasets shown in (a) onto a single curve. Reproduced from Ref [4] with permission from The Royal Society of Chemistry.

3.14 (a) Plot of the drag reduction percentage vs. the ratio of the working fluid to lubricant viscosity for a laminar flow. Mixtures of water and glycerol are used as the working fluid and a laser textured sample impregnated with silicone oil is used as the lubricant impregnated surface. Experiments are conducted in a parallel plate geometry. (b) Plot of drag reduction percentage vs. Reynolds number for a variety of working fluid to lubricant viscosity ratios at higher Reynolds numbers. The least viscous lubricant heptane gives a drag reduction percentage of 14%. Experiments are conducted in a Taylor-Couette geometry. Reproduced from Ref [20] with permission of American Chemical Society (Copyright 2014) and from Ref [21] with permission of Springer.
3.15 (a) Schematic of the analyzed lubricant impregnated surface. Influence of the viscosity ratio on the enhancement factor (given by contours) for longitudinal flow over open grooves with $b/L = 0.98$ where the ratio between the period of the grooves and radius of the channel is (b) 0.02 and (c) 0.1. The enhancement factor is the increased flow rate provided by adding a lubricant impregnated surfaces compared to a no-slip condition. Reproduced from Ref [22] with permission of Springer (Copyright 2014).

3.16 (a) A water droplet on a surface impregnated with a ferrofluid moves in response to a magnet. (b) Images of a water drop electrowetted on a lubricant impregnated surface with an applied voltage of 500 V displaying an apparent CA of $\sim 53^\circ$. The bottom image shows the wetting ridge that forms. The scale bar is 400 $\mu$m on the top image and 200 $\mu$m on the bottom. (c) Simultaneous thermocapillary motion of 10 and 20 $\mu$L droplets on a surface impregnated with silicone oil. Reproduced from Ref [23] with permission of AIP Publishing, from Ref [24] under the CC BY 4.0 license, and from Ref [25] with permission of Wiley-VCH (Copyright 2014).

3.17 Depiction of a microporous silicon filled with a hydrogel. The self-lubricating liquid water layer (SLWL) of the hydrogel surface adheres ice more weakly than superhydrophilic, superhydrophobic, and flat surfaces. Reproduced from Ref [26] with permission of The American Chemical Society (Copyright 2013).
3.18 Experiments in which a water/glycerol mixture flows over grooves filled with a fluorescent green lubricant. The red arrow indicates the flow direction. The grooves are 9 μm wide, 10 μm deep, and 35 mm long. (a-d) Regions with periodicity L that are non-wetting to the lubricant interrupt grooves aligned with the flow and in (a) prevent drainage of the lubricant. For each experiment, the top image shows the initial state and the bottom the steady state. Drained portions of the groove reflect blue light while excess lubricant appears white. The strength of the imposed flow is characterized by a shear stress τ. (e, f) In a separate set of experiments, at a sufficient stress the flow over lubricant filled groups induces overflow of the lubricant at a shear stress of τ = 2.58 Pa. Reproduced from Ref [27] with permission of The Royal Society of Chemistry and from Ref [28] with the permission of AIP Publishing.

4.1 (a) Model for a working fluid flowing over a surface. (b) Details of the velocity profile for the hypothetical case of zero solid fraction in which the lubricant viscosity μ₀ is less than the working fluid viscosity μw and results in an apparent slip length b. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).

4.2 (a) Schematic showing the process to create the lubricant impregnated surface used in this study. (b), (c) SEM images of the laser textured surface showing both microscale and nanoscale features. (d), (e) ESEM images of the lubricant impregnated surface showing the oil lubricant completely filling the texture and protrusion of the tops of the texture. (f) Details of the velocity profile for a liquid-impregnated surface showing a local slip length b. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).
4.3 (a) Schematic of the cone and plate rheometer setup. (b), (c), (d) Images of a water drop resting on a flat OTS-coated silicon wafer, superhydrophobic surface, and lubricant impregnated surface respectively. The inset numbers are static contact angles. (e), (f), (g) Images of the free surface of the working fluid between the cone and substrate for a flat OTS coated silicon wafer, superhydrophobic surface, and lubricant impregnated surface respectively. Despite having drastically different contact angles, the free surfaces are identical. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).

4.4 Measured drag reduction and slip lengths for varying working fluid to lubricant viscosity ratios. Adapted from Ref [20] with permission of The American Chemical Society (Copyright 2014).

4.5 (a) Plot of the drag reduction percentage vs. the ratio of the working fluid to lubricant viscosity. (b) Plot of the computed apparent averaged slip length vs. the ratio of the working fluid to lubricant viscosity. A linear fit is presented alongside the data enclosing a 95% confidence interval. Modified from Ref [20] with permission of The American Chemical Society (Copyright 2014).

4.6 Comparison of drag reduction and slip lengths reported in literature. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).

5.1 Schematic diagrams of (a) a conventional flow cell and (b) a gravity-induced flow cell.

5.2 (a) Schematic of a flow electrode flowing in a channel. (b) The flow electrode can pin on the asperities of a solid surface. (c) A lubricant impregnated surface allows the flow electrode to move freely by eliminating contact with the solid.
5.3 (a) 2nd discharge-charge profiles of 2.5M Li$_2$S$_8$(Catholyte)-Li(Anode) chemistry in a Swagelok cell type configuration with different KB loading cycled galvanostatically at a C-rate of 1/5 hr$^{-1}$. The electrode thickness is 560 µm. (b) Yield stresses for various Li-PS species. (c) Time-lapse comparing a 2.5M Li$_2$S$_8$ suspension with 0.75 vol% KB on flat PTFE and the Krytox LIS. In both cases, supporting salts (0.5M LiTFSI and 1wt% LiNO$_3$) are included in the suspension.

5.4 (a) Schematic of a flow electrode flowing in a channel covered with lubricant impregnated surfaces. The interface between the lubricant impregnated surface and flow electrode can take three distinct morphologies. (a) The encapsulated state is characterized by the lubricant encapsulating the solid including spreading everywhere between the solid and working fluid. (b) In the emerged state lubricant fills the porous solid but does not spread completely between the solid and working fluid. (c) In the impaled state the flow electrode preferentially wets the solid and displaces the lubricant. The encapsulated state is most desirable and the impaled state the least.

5.5 Cyclic voltammogram of the solvent triglyme as well as a variety of candidate lubricants performed at a scan rate of 10 mV/s. Lithium is used as the counter and reference electrodes. A Tonen separator wetted with the electrolyte is used in all the tests.

5.6 Time-lapse of the GIFCell with lubricant impregnated surfaces demonstrating the flow electrode’s mobility even after 25 cycles. Without lubricant impregnated surfaces, the flow electrode does not flow. Here the flow electrode is 2.5M Li$_2$S$_8$ with 0.75vol% of KB.
5.7 (a) Schematic of the GIFCell operating in intermittent flow mode. The GIFCell is horizontal when undergoing electrochemical cycling and tilted to move the next aliquot into the active region. (b) Energy and current density against time during electrochemical cycling for the 1st aliquot. (c) Potentiostatic cycling of the GIFCell-LIS with 2.5M Li$_2$S$_8$ suspension (Catholyte)-Li (Anode). The suspension consists of 0.75vol% of KB, 0.5M LiTFSI and 1wt% LiNO$_3$. The flow-electrode thickness is 1 mm. An intermittent flow mode is used where the 1st aliquot flows into the electroactive region by gravity and remains during cycling. (d) The specific capacity of the GIFCell during discharge and the round-trip efficiency of the GIFCell-LIS for various cycle numbers.

5.8 A blowout schematic of the GIFCell with a lubricant infused surface.

5.9 Shear stress vs. apparent strain rate for the flow of 2.5M lithium polysulfide in triglyme with 0.75vol% KB. The no slip surface is gold sputtered on stainless steel. The stress vs. strain rate is independent of gap for the no slip surface. The variation of measured stress with apparent strain rate with the lubricant impregnated surface is a signature of slip.

5.10 Schematic distinguishing the apparent strain rate $\dot{\gamma}_a$ from the true strain rate in the material $\dot{\gamma}$. The slip velocity is denoted by $u_s$ and the gap by $H$.

5.11 Slip velocity vs. stress for the flow of 2.5M lithium polysulfide in triglyme with 0.75vol% KB on a lubricant impregnated surface, flat Teflon surface, and gold surface with linear fits.

5.12 Parameters for the fits presented in Figure 5.11.

5.13 Photos of the high volume discharged cell as assembled in an inert Argon environment. (a) Closed cell showing. Fiberglass screws secure the cell. (b) Bottom half the cell comprised of stainless steel, lithium metal cathode, Tonen separator, Teflon gasket, and suspension. (c) Top half of the cell after discharge. Even visually the suspension looks thicker.
5.14 a) Galvanostatic discharges performed at a current density of 0.1 mA/cm$^2$ of the 2.5M lithium polysulfide in triglyme with 0.75vol% KB. (b) Yield stress as a function of discharged capacity. Yield stress was determined in a parallel plate rheometer in which three gaps are measured to yield a corrected yield stress.

5.15 Slip velocity vs. stress for the flow of 2.5M lithium polysulfide in triglyme with 0.75vol% KB discharged to 920 mAh/g on a lubricant impregnated surface and gold surface with linear fits.

5.16 Parameters for the fits presented in Figure 5.11.
Chapter 1

Introduction

Recent advances in creating liquid-repellent surfaces have focused on decreasing the interaction between a liquid and a solid surface by modifying the surface’s chemistry and cleverly designing its geometry on nano- and millimetric length scales. Classically, a surface is rendered superhydrophobic by combining a low energy surface chemistry with a roughness. Under the right conditions, a water drop placed on a surface will sit on a composite interface of both solid and air and exhibit high contact angles.

Such a methodology of surface engineering can extend to creating surfaces capable of repelling low surface tension liquids such as oil using reentrent surface textures. Such repulsion of liquids that rely on trapping air in the surface however can fail in a variety of circumstances. The trapped air can collapse under pressure, diffuse into the surrounding liquid, and become damaged. Additionally, the surfaces can fail when liquids condense within the textures.

This thesis explores two advances to control a liquid’s interaction with a surface: 1) deflectable members that enable anisotropic wetting properties and 2) slippery lubricant impregnated surfaces comprised of a porous surface and liquid lubricant. Experimental characterization elucidates the mechanism by which deflectable scales on a butterfly’s wing cause anisotropic drop repellency. Conditions for designing lubricant impregnated surfaces are reviewed, their potential for drag reduction is demonstrated, and they are incorporated...
to enable flow in an electrochemical cell.

The first part of this thesis characterizes how the unique structure of a butterfly’s wings contributes to its anisotropic wetting properties. In particular, a water drop placed on the surface of a butterfly wing will easily roll away from the butterfly’s body, but will roll off at much higher angles toward the body. This phenomenon is observed and quantified using environmental electron microscopy and confocal microscopy. A theory explaining the observed anisotropy that takes into account the deflection of the butterfly’s scales is proposed and validated with wide range of butterfly species. Such deflectable surface structures offer a new way to tune the wetting properties of a surface.

The second part of this thesis reviews and expands on lubricant impregnated surfaces. It explains how to achieve a stable lubricant impregnated surface and discusses its basic features including the wetting ridge and lubricant cloak. Motivated by the slippery nature of these surfaces, the potential of lubricant impregnated surfaces to reduce drag is detailed. A scaling model that incorporates the viscosity of the lubricant and elucidates the dependence of drag reduction on the ratio of the viscosity of the working fluid to that of the lubricant is presented. The model is validated by experiments conducted in a cone and plate rheometer where a drag reduction of 16% is measured.

Finally, lubricant impregnated surfaces are applied to electrochemical systems. Measurements quantify how lubricant impregnated surfaces improve the flowability of a non-Newtonian lithium polysulfide flow electrode in which electronic conductivity is imparted by carbon particles. A framework for the design of such surfaces for a wide range of flow electrode solvents is used to incorporate lubricant impregnated surfaces into a Gravity Induced Flow Cell (GIFCell) prototype to enable the flow of highly conductive suspension.
Chapter 2

Deflection of Butterfly Scales and Anisotropic Roll-off

2.1 Introduction

Surface textures that are deflectable offer potential to control wetting behavior. In this chapter, the observation that the scales on a butterfly can deflect and influence the motion of water drops is investigated. An explanation based on the pinning force resulting from the deflection of scales and their contact with the water drop is offered that is well correlated with many butterfly species.

2.2 Literature Review

In the past, the wings of butterflies have been explored for many remarkable properties. Iridescence, for example is prevalent in butterflies of the genus Lepidoptera[^43] and has been attributed to nanoscale structures on the wings.[^44]

In particular, butterfly wings are decorated with scales as depicted in Figure 2.1. In general these scales are on the order of 150 $\mu$m long and 70 $\mu$m wide. Originally, Zheng et al. reported that drops placed on the wing of a *Morpho aega* display directional roll-off.
Figure 2.1: (a) Image of a male *Morpho aega* butterfly. (b) SEM image of scales on the wing of *Morpho aega*. (c) Image of a male *Papilio cresphontes* butterfly. (d) SEM image of scales on the wing of *Papilio cresphontes*. The red arrows denotes the direction of scales. Scale bars: (a, c) 1 cm (b, d) 100 µm.

The authors observe that a 3 µL drop placed on the surface will roll-off from the wing when the wing is tilted 9° away from the body. Remarkably, the drop will stay attached to the surface when the wing is tilted 90° toward the body.\[1\]

To explain this anisotropic roll-off, the authors investigate the micro- and nanostructure of the wings as shown in Figure 2.2.\[1\] The authors find that the scales of *M. aega* are covered with ridges that are ~184 nm wide and separated by ~586 nm.

In addition, surfaces with similar directional roll-off properties have been fabricated.
Figure 2.3: The proposed model by Zheng et al. to explain roll-off anisotropy on the wings of *Morpho aega*. (a) When the wing is tilted away from the butterfly’s the morphology of the contact line is different than when the wing is tilted against the scales. Reproduced from Ref [1] with permission of The Royal Society of Chemistry.

Notably, Malvadkar et al. engineered a surface using a vapor-phase oblique angle polymerization technique. The resulting surface comprised slanted poly(p-xylylene) nanorods.\(^{[45]}\) The anisotropic nanorods thus gave rise to anisotropic roll-off.

### 2.3 Experimental Observations

#### 2.3.1 Roll-off Anisotropy

Figure 2.4 shows two butterfly species in which the roll-off behavior of a water drop has been tested. In all cases, the top side of the butterfly wings are tested. Figure 2.4(a, b) show the top side of a male *Morpho aega* and SEM image of the scales decorating its wing.

As depicted in Figure 2.4(c, d) a water drop placed on the surface will roll-off at 42.4° ± 5.2° when moving against the scales and 15.6° ± 1.2° when moving with the scales. Conversely, on the male *Papilio cresphontes* wing shows a different behavior in which the
Figure 2.4: (a) A *Morpho aega* butterfly in which scales on the surface of the wings are directed radially outward. (b) SEM image of the scales. A drop placed on the wing rolls of at (c) 42.4° against the scales or (d) 15.6° with the scales. (e) A *Papilio cresphontes* butterfly also decorated with scaled. (f) SEM of *Papilio cresphontes* scales. (g) A water drop placed on the surface of *Papilio cresphontes* rolls off at 0° in all directions. Scale bars: (a, e) 1 cm (b, f) 100 µm (c, d, g) 1 mm.

roll-off of the water drop is 0° in all directions. For these experiments, the water drop was 3.2 ± µL which corresponds to a radius of 0.93 ± 0.04 mm.

The anistropic roll-off is consistent with the observation of Zheng et al.\[1\] The results suggest that the anisotropy of the scales cause the directional roll-off. However, the observation of roll-off on *Papilio cresphontes* is inconsistent with this qualitative theory. *P. cresphontes* has scales and thus an anisotropic texture, yet the roll-off is 0° in all directions.
Figure 2.5: Depiction of a drop of a tilted surface when capillary pinning forces balance gravity. The front edge makes an angle $\theta_a$, and the back edge angle and angle $\theta_r$.

### 2.3.2 Hysteresis

A drop placed on a surface that is tilted will roll-off provided gravity forces overcome capillary pinning forces which can be written as:

$$\pi r \gamma (\cos \theta_r - \cos \theta_a) = \rho \Omega g \sin \alpha$$  \hspace{1cm} (2.1)

Here $r$ is the radius of the drop, $\rho$ in the density of the drop, $\Omega$ is the volume of the drop, $\gamma$ is the liquid’s surface tension, and $g$ is the gravitational constant.\[^{46}\] As depicted in Figure 2.5, at the point in which gravity overcomes the pinning forces, the front edge of the drop will make contact at a greater angle than the back edge. The front edge angle is called the advancing angle $\theta_a$, and the back edge angle is called the receding angle $\theta_r$.

It is common to measure an advancing angle of a liquid drop on a surface by placing a drop on a surface and adding volume. As the contact line advances, a constant angle is typically measured. Similarly, the receding angle can be measured as the contact line recedes when volume is withdrawn.

For seven species of butterflies advancing and receding angles were measured by volume addition and withdrawal. The results are summarized in Figures 2.6 and 2.7. For one experiment, a $3 \mu L$ drop is placed on the surface of the wing. Next $5 \mu L$ is added to the drop at a rate of $1200 \mu L/s$. The experiment is measured in a direction perpendicular to the direction of the scales so two measurements of the advancing angle can be made. One
Figure 2.6: Advancing and receding angles in the direction with the scales measured for seven butterfly species.

<table>
<thead>
<tr>
<th>species</th>
<th>advancing angle with scales (°)</th>
<th>receding angle with scales (°)</th>
<th>hysteresis with scales (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. aega</td>
<td>145.0 ± 7.4</td>
<td>142.0 ± 2.8</td>
<td>3.0 ± 7.9</td>
</tr>
<tr>
<td>L. virgaureae</td>
<td>140.8 ± 5.3</td>
<td>140.7 ± 4.1</td>
<td>0 ± 6.7</td>
</tr>
<tr>
<td>C. bipunctatus</td>
<td>148.3 ± 5.2</td>
<td>145.2 ± 6.6</td>
<td>3.0 ± 8.4</td>
</tr>
<tr>
<td>A. io</td>
<td>152.3 ± 6.7</td>
<td>145.8 ± 2.8</td>
<td>4.6 ± 7.3</td>
</tr>
<tr>
<td>B. aurota</td>
<td>145.7 ± 0.5</td>
<td>145.0 ± 0.9</td>
<td>0.7 ± 1.1</td>
</tr>
<tr>
<td>D. plexippus</td>
<td>143.2 ± 5.6</td>
<td>147.0 ± 2.9</td>
<td>-3.8 ± 6.3</td>
</tr>
<tr>
<td>P. crespontes</td>
<td>144.7 ± 4.7</td>
<td>144.7 ± 3.0</td>
<td>0 ± 5.6</td>
</tr>
</tbody>
</table>

Figure 2.7: Advancing and receding angles in the direction against the scales measured for seven butterfly species.

<table>
<thead>
<tr>
<th>species</th>
<th>advancing angle against scales (°)</th>
<th>receding angle against scales (°)</th>
<th>hysteresis against scales (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M. alga</td>
<td>141.3 ± 4.3</td>
<td>140.7 ± 3.8</td>
<td>0.7 ± 5.8</td>
</tr>
<tr>
<td>L. virgaureae</td>
<td>143.5 ± 3.9</td>
<td>142.5 ± 3.8</td>
<td>1.0 ± 5.5</td>
</tr>
<tr>
<td>C. bipunctatus</td>
<td>150.3 ± 8.5</td>
<td>147.0 ± 11.6</td>
<td>3.3 ± 14.3</td>
</tr>
<tr>
<td>A. io</td>
<td>153.7 ± 3.6</td>
<td>151.3 ± 3.8</td>
<td>2.4 ± 5.2</td>
</tr>
<tr>
<td>B. aurota</td>
<td>146.0 ± 6.6</td>
<td>146.0 ± 4.9</td>
<td>0 ± 8.2</td>
</tr>
<tr>
<td>D. plexippus</td>
<td>143.0 ± 4.7</td>
<td>145.2 ± 5.3</td>
<td>-2.2 ± 7.1</td>
</tr>
<tr>
<td>P. crespontes</td>
<td>145.3 ± 5.2</td>
<td>144.3 ± 3.1</td>
<td>1.0 ± 6.1</td>
</tr>
</tbody>
</table>

Interestingly, both contact angles measured at all times are the same for all species of butterflies. One might expect when the drop is receding that the contact line moving against the scales exhibits a lower angle. In fact, for a drop placed on a flat surface the pressure inside is constant and given by the Laplace pressure $2\gamma/r$ where $\gamma$ is the surface tension and $r$ the radius of the drop.\[47\] Accordingly, because the pressure is constant everywhere in the drop the curvature $1/r$ is constant everywhere. Thus both contact angles are constrained to be identical.

When the drop recedes the contact line that moves against the scales stays pinned while only the contact line that moves with the scales moves. Motivated by this observation, optical microscopy was used to deduce what is going on at the microscale.
Figure 2.8: Roll-off angles of seven butterfly species with scales and against scales. In all cases, the roll-off against scales is as least as large as the roll-off with scales. The two species Danaus plexippus and Papilio cresphontes both show 0° roll-off in all directions. Scale bars: 1 cm.

2.3.3 Roll-off of Many Species

Seven butterflies have been received from around the world to investigate if they show similar roll-off properties. The results are presented in Figure 2.8. While Morpho aega shows the greatest roll-off against the scales, Lycaena virgaureae shows the greatest difference in roll-off. The two species Danaus plexippus and Papilio cresphontes both show 0° roll-off in all directions.

2.3.4 Optical Microscopy

In an effort to elucidate what is pinning the drop at the microscale optical microscopy is used. Figure 2.9 shows two experiments in which a water drop is moved against the wing of the Morpho aega. Images are collected using a Nikon D800 digital SLR camera body connected to a Navitar 6.5x zoom body with 2.0x F-mount adapter tube and 2.0x lens attachment.

Figure 2.9 clearly depicts the Morpho aega butterfly scales deflecting as the drop moves.
Figure 2.9: (a) Schematic for the images shown in (c) showing the drop moving into the page against the scales. b) Schematic for (d) showing the drop moving to the left against the scales. (c, d) Orthogonal views of a drop moving against scales where scale deflection is clearly visible. Scale bar: 200 µm.

The *Morpho aega* is easy to image optically due to its iridescence. On the other hand, the details of what is going on at the moving contact line cannot be sufficiently resolved with *Papilio cresphontes*. In addition, the resolution of the images in Figure 2.9 are not high enough to accurately deduce the mechanics.

### 2.3.5 Environmental Scanning Electron Microscopy

As mentioned, optical microscopy cannot provide sufficient resolution to resolve the details of the contact line. Scanning Electron Microscopy provides a high resolution images method, but does not allow for easy drop manipulation. In order to get around this, a custom fixture is built as depicted in Figure 2.10.\(^2\)

The setup shown in Figure 2.10 leverages the rotation of the stage to rotate a water drop across a sample’s surface. Both the rotating stage and sample are moved using the x, y, z
controls of the stage, but the sample is mounted in such a way that rotation does not affect it. As depicted, a wire affixed to the rotating stage allows the drop to be translated. This setup has previously been used by Paxson & Varanasi to image capillary bridges on superhydrophobic surfaces.\cite{2} The drop used is around 10 µL but evaporates over the course of an experiment.

In order to image liquid water, an environmental scanning electron microscope (Zeiss EVO-55 ESEM) is used. The ESEM is capable of operating at low vacuums up to 1000 Pa. As seen in Figure 2.11, the triple point of water is around 600 Pa and 0.05 °C.

Accordingly, it is possible to image liquid water in the environmental SEM if pressures are maintained between 600 and 1000 Pa and the stage is cooled. Figure 2.12 shows the
Figure 2.12: Environmental scanning electron microscopy setup viewed from the direction that the electron beam travels and the backscatter detector. A chilled water line provides cooling to the chamber. The wing sample is fixed to a copper plate that is held in place by a custom fixture screwed into the stage.

setup viewed from the direction that the electron beam travels and the backscatter detector. A chilled water line provides cooling to the chamber. Also, the wing sample is fixed to a copper plate that is held in place by a custom fixture screwed into the stage.

Videos are taken for drops translated across the butterfly wing. The water drop is translated at around 2 $\mu$m/s. Typically images are collected a chamber pressure of 1000 Pa and stage temperature of 0.5$^\circ$. An accelerating voltage around 15 kV and working distance of 8 mm are found to give the most favorable imaging conditions.

Figure 2.13 shows frames from videos collected at one frame per second as a drop is translated against the direction of scales. In both the case of *Morpho aega* and *Papilio cresphontes* deflection of scales can be seen. In addition, the drop makes less contact with *Papilio cresphontes* scales than it does *Morpho aega* scales.

### 2.3.6 Confocal Microscopy

As evidenced by Figure 2.13, a water drop shows significantly less contact with *Papilio cresphontes* scales as compared to *Morpho aega* scales. In order to deduce the contact, a
Figure 2.13: Frames from ESEM videos collected at one frame per second as a drop translates against the direction of scales. Scale bars: 100 µm.

confocal microscope is used to image the air-water interface of a water drop sitting on a butterfly wing. Figure 2.14 is a schematic of the setup in which water is put between the butterfly wing and a coverslip held up by a 1 mm spacer.

Microscopy is done on a Zeiss LSM 780 NLO using a LD Plan-Neofluar 20x/0.4 Corr objective. Light with a wavelength of 405 nm is used to image the air-water interface. Figure 2.15 shows SEM images (top row) and confocal microscopy images (bottom row) for several butterfly species. In the confocal microscopy images, the air-water interface strongly reflects light and can easily be distinguished.
Comparing the species shown in Figure 2.15 several observations can be made. To start, *Papilio cresphontes* shows the lowest amount of contact among the four species shown in Figure 2.15. Conversely, both *Lycaena virgaureae* and *Morpho aega* show a large amount of contact. Finally, *Aglais io* shows a moderate amount of contact. Later on in this chapter, the amount of contact will be quantified and incorporated into a model.

## 2.4 Discussion

### 2.4.1 Deflection of *Morpho aega* Scales

First, to rationalize the observed difference in roll-off anisotropy of *Morpho aega* ESEM imaging is used to deduce the dynamics of the contact line. Figure 2.16 shows both the case where the drop is translating with the scales and against the scales.

Figure 2.16(a, b) shows the receding water drop over the scales. In the case where the drop is moving with the scales, the total receding angle \( \tilde{\theta}_r \) is measured to be \(102^\circ\) whereas in the case where the drop is moving against the scales the total receding angle \( \tilde{\theta}_r \) is measured to be \(16^\circ\). The pinning force resisting the motion of the drop scales with \( \cos \theta_r \), so in
Figure 2.16: Frames from ESEM videos collected at one frame per second as a drop translates (a) with the direction and scales and (b) against the direction of scales. The total receding angle $\tilde{\theta}_r$ is the angle the water drop makes with the horizontal. (c, d) Schematics showing the total angle $\tilde{\theta}_r$ decomposed into a scale deflection angle $\alpha$ and intrinsic receding angle $\theta_r$. Scale bar: 100 $\mu$m.

In this case the pinning for is greater in the case where the drop moves against the scales as shown in Figure 2.16b. This is consistent with the higher observed roll-off in the against scale direction.

In addition, Figure 2.16(c, d) shows that the total receding angle $\tilde{\theta}_r$ can be decomposed such that $\tilde{\theta}_r = \alpha + \theta_r$. Here $\alpha$ is the angle that the scale deflects and $\theta_r$ the intrinsic receding angle of the water drop on the scale.

In both cases, calculating the intrinsic angle from the equation $\tilde{\theta}_r = \alpha + \theta_r$ results in $\theta_r = 90^\circ$. This consistency demonstrates that the total receding angle $\tilde{\theta}_r$ can be thought of as arising from two decoupled effects being the scale angle $\alpha$ and the intrinsic receding angle $\theta_r$ of the scales.

### 2.4.2 Modeling Pinning Force

Figure 2.17 shows the important parameters in pinning. To start, as shown earlier the total receding angle that the water drop makes with the horizontal is important. Figure 2.17(a, b) depict a drop moving against the scales of *Morpho aega* and *Papilio cresphontes* respec-
Figure 2.17: (a, b) ESEM images of a drop moving against the scales of *Morpho aega* and *Papilio cresphontes* respectively. (c, d) SEM images showing the density of scales of *Morpho aega* and *Papilio cresphontes* respectively. (e, f) Confocal microscopy images of *Morpho aega* and *Papilio cresphontes* respectively. The air-water interface strongly reflects light.

Figure 2.17(c, d) show the density of scales on the wings of *Morpho aega* and *Papilio cresphontes*. In this case when the contact line recedes against the scales the relevant linear density is in the perpendicular direction indicated. The scale spacing is denoted $L$.

Lastly, confocal microscopy reveals the contact between the scales and water drop. The perimeter of contact is denoted by $P$. A parameter $\Phi = P/L$ is defined. Essentially the contact line of the water droplet is amplified by $\Phi$. Using these parameters, the pinning force can be written as:

$$F_p \sim r\Phi \gamma \cos(\theta_r + \alpha) \quad (2.2)$$

The terms in Equation 2.2 can be understood as follows. When a drop makes contact with a butterfly wing, the length of contact is proportional to the radius $r$ of the drop. It
depends on the contact angle of the drop as well, but as shown in Figures 2.6 and 2.7 the contact angles are very close for all species tested. Next $\Phi = \frac{P}{L}$ represents the amplification to the contact line as a result of the scale density and the perimeter of contact of each scale. The pinning force is a direct result of the surface tension $\gamma$ and linearly depends on it. Finally, the cosine of the total receding angle $\tilde{\theta}_r = \theta_r + \alpha$ gives the component of the force that opposes the action of gravity.

To confirm this model, the properties above are measured for all species and presented in Figure 2.18 where the pinning force is calculated according to $F_p \sim r \Phi \gamma \cos(\theta_r + \alpha)$. The resulting estimated pinning force $F_p$ is plotted against the difference in roll-off originally presented in Figure 2.8. The plot shown in Figure 2.19 demonstrates that the observe roll-off difference among species is correlated with the estimated pinning $F_p$ given by the model of Equation 2.2.
2.5 Synthetic Replication

Naturally, for any commercial use of such surface it is desirable to be able to synthetically replicate a surface. Namely, the surface should have deflectable structures that give rise to anisotropic roll-off.

A fabrication approach has been developed based on a technique developed by De Volder et al. to grow carbon nanotube (CNT) forests.\[3\] As depicted in Figure 2.20, first underlayers of titanium nitride and silicon dioxide that are 80 nm in thickness are applied via lithography. Next, an Fe/Al$_2$O$_3$ catalyst is patterned. Finally, carbon nanotubes are grown, and the rate of growth depends on the underlying substrate. The SEM image confirms that carbon nanotube forests with a silicon dioxide underlayer growth faster than those with a titanium nitride underlayer.

Volder et al. also showed that by patterning the two underlayer materials side by side, the carbon nanotube forces curves as it grows as a result of faster growth on the outside compared to the inside. This is shown in Figure 2.21.

Using this methodology, synthetic carbon nanotube scales are grown to replicate butterfly scales. Figure 2.22 shows SEM images of several CNT growths to replicate butterfly scales. Figure 2.19: Roll-off difference vs. estimated pinning force. The roll-off data is also presented in Figure 2.8 and the estimated pinning force presented in Equation 2.2.
Figure 2.20: Fabrication method in which first underlayers of titanium nitride and silicon dioxide that are 80 nm in thickness are applied via lithography. Next, an Fe/Al$_2$O$_3$ catalyst is patterned. Finally, carbon nanotubes are grown, and the rate of growth depends on the underlying substrate. The SEM image confirms that carbon nanotube forests with a silicon dioxide underlayer grows faster than those with a titanium nitride underlayer. Scale bar: 40 µm. Reproduced from Ref [3] with permission of Macmillan Publishers Ltd: Nature Communications (Copyright 2014).

Figure 2.21: Micropillars are grown from catalyst rectangles partially overlapping titanium nitride (shown as green layer in the inset) and bend towards the titanium nitride side which grows more slowly and couples to the faster-growing region of catalyst directly on silicon dioxide. Scale bars: 100 µm (panel), 20 µm (inset). Reproduced from Ref [3] with permission of Macmillan Publishers Ltd: Nature Communications (Copyright 2014).

scales. The temperature indicates the growth temperature which is held for five minutes. The top row provides a top view and the bottom row provides an angled view of the same structures. As evident, the growth is highly dependent on temperature and achieving repeatable structures is difficult.
Each synthetic scale is comprised of a forest of carbon nanotubes. Carbon nanotubes are inherently hydrophilic and will wick water and densify.\cite{48} To prevent this, the polymer divinylbenzene (DVB) is deposited conformally by initiated chemical vapor deposition (iCVD).\cite{49} Figure 2.23 depicts successive images of a water drop moving against synthetic CNT scales coated with DVB. Similar to the butterfly scales, the CNT scales are seen to deflect.

The roll-off of a water drop on the CNT scales pictured in Figure 2.23 is $6.7^\circ \pm 1.9^\circ$ against the scales and $4.4^\circ \pm 0.5^\circ$ with the scales. The *Morpho aega* by comparison showed a greater difference in roll-off between the two directions with $42.4^\circ \pm 5.2^\circ$ when moving against the scales and $15.6^\circ \pm 1.2^\circ$ when moving against the scales.
2.6 Outlook

While the anisotropic properties of butterfly wings have been described in literature, this chapter discusses for the first time how the deflection of the wing’s scales play a roll in pinning drops. In pinning the deflection of scales, their density, and the amount of contact they make are all important in determining the roll-off anisotropy.

A model taking into account these factors is expressed in Equation 2.2, and the observed roll-off anisotropy (the roll-off angle in the against scales direction minus the roll-off angle in the with scales direction) is shown to correlate with the pinning force predicted by this model.

Finally, a method to fabricate synthetic butterfly scales is proposed whereby carbon nanotube forests are grown to resemble scales and coated in a DVB polymer. Although they do deflect and show anisotropic roll-off, many butterfly species including *Morpho aega* show a greater difference in roll-off between against scale and with scale directions.
Chapter 3

Lubricant Impregnated Surfaces

3.1 Introduction

Lubricant impregnated surfaces are composed of a porous or textured solid and a liquid lubricant that is stabilized by capillary forces. The lubricant provides remarkably low contact angle hysteresis (<1°) and many other exceptional properties. Many research groups have taken interest in this technology and have expanded their use to many applications.

The following section outlines how to achieve a stable lubricant impregnated surface and discusses its basic features including the wetting ridge and lubricant cloak. Next, applications of lubricant impregnated surfaces are detailed including condensation, anti-icing, anti-fouling, fluid mobility, optics, and active surfaces. In each application, the design of a lubricant impregnated surface has particularly relevant criteria. For example, cloaking of condensed water drops can adversely affect condensation heat transfer, and ice adheres more weakly to surfaces with more densely packed textures.

3.2 Fundamentals

A lubricant impregnated surface is composed of a porous or textured solid and a liquid lubricant that is stabilized by capillary forces. The interface between a lubricant impregnated
surface and an immiscible liquid which it comes into contact (the working fluid) gives rise to many novel properties. If the system is properly designed, the working fluid will not displace the lubricant. This section discusses how to achieve stability and later discusses the cloak a lubricant can form over a working fluid drop and the lubricant ridge around the drop.

Whereas a water drop on a solid surface forms a single three-phase contact line between water, air, and solid, the boundary between a working fluid drop and a lubricant impregnated surface is more complex. Consider the morphology of a lubricant impregnated surface beneath a working fluid drop depicted in Figure 3.1. Based on the energetics of the materials involved (working fluid, lubricant, solid) three distinctly different morphologies are observed.\[^{[4]}\] In the impaled state, the working fluid displaces the lubricant and makes direct contact with the solid everywhere under the drop. In the impregnated, emerged state the lubricant remains contained in the solid and the working fluid contacts only the exposed features. In the encapsulated state, the working fluid makes no contact anywhere with the solid. The encapsulated state exhibits the most slipperiness (as quantified by the roll-off angle) whereas the impaled state, similar to the Wenzel state on a superhydrophobic surface, has poor slipperiness.\[^{[4]}\]

These three states can be quantified in terms of their total interfacial energy (Figure 3.1). The state with the lowest total energy will be the one observed in steady state. The total surface energy per area is $E_{w1} = r\gamma_{sw}$ for the impaled state, $E_{w2} = (r - \phi)\gamma_{os} + \phi\gamma_{ws} + (1 - \phi)\gamma_{ow}$ for the impregnated, emerged state, and $E_{w3} = \gamma_{ow} + r\gamma_{os}$ for the encapsulated state. Here $r$ denotes the total surface area of the solid normalized by the projected area and $\phi$ denotes the fraction of the solid that makes contact with the working fluid in the impregnated, emerged state. $\gamma_{ij}$ denotes the interfacial tension between component “$i$” and component “$j$” (“$w$” for working fluid, “$o$” for lubricant, and “$s$” for solid).

Equivalently, the encapsulated state is favored over the emerged state ($E_{w3} < E_{w2}$) when $S_{os(w)} = \gamma_{ws} - \gamma_{ow} - \gamma_{os} > 0$. Here $S_{os(w)}$ is the spreading coefficient of the lubricant ”$o$”
on the solid ”s” in the presence of the working fluid ”w”. Spreading coefficients can be experimentally deduced by observing if a drop of lubricant spreads on a flat solid when in an environment of the working fluid. The drop size $R$ should be small relative to the capillary length $\ell_c = (\gamma/\rho g)^{1/2}$ to ensure the spreading is not driven by gravity. Here, $\gamma$ is the surface tension of the spreading liquid, $\rho$ its density, and $g$ is the gravitational acceleration.\[52\] Observing spreading of a lubricant indicates that $S_{os(w)} > 0$ and the encapsulated state will exist for a textured solid of the same chemistry. These conclusions are summarized in Figure 3.1.

As described by the above equations, lubricants and solids with low surface energies tend to form the most stable lubricant impregnated surfaces. Oftentimes fluorocarbons (e.g. Krytox, FC-70), fatty alcohols (e.g. decanol), hydrocarbons, and silicone oils are used. Because evaporation of the lubricant causes a lubricant impregnated surface to lose its properties,\[53\] ionic liquids (e.g. BMIIm) have been proposed due to their extremely low vapor pressures but tend to exist in the impregnated, emerged state rather than the encapsulated state.\[4\] They are also acutely toxic to the nervous system.
Porous or textured solids can either be inherently low energy materials (e.g. PTFE membranes) or other materials (e.g. silicon, SU-8, aluminum) treated to be hydrophobic. Fabricating a texture for creating a lubricant impregnated surface is identical to fabricating a texture to make a superhydrophobic surface. See Li et al.\cite{54} and Roach et al.\cite{55} for comprehensive reviews of superhydrophobic surfaces that include techniques to create textured surfaces. Researchers have successfully demonstrated lubricant impregnated surfaces created by photolithography,\cite{4,5}, wet etching\cite{56–58}, sol-gel synthesis\cite{59–63}, layer-by-layer assembly,\cite{64–67} and other techniques.\cite{58,68–72}

A convenient way of filling a texture is to withdraw the textured or porous solid from a bath of lubricant. A lubricant will spontaneously wick into a texture provided its contact angle $\theta_{os(a)}$ on a smooth substrate of the same chemistry is below a critical angle. The critical angle $\theta_c$ is defined by $\cos \theta_c = (1 - \phi)(r - \phi)$ where $\phi$ is the solid fraction and $r$ the total area divided by the projected area of a texture (Figure 3.1).\cite{50,73}

In withdrawing a substrate from a bath of lubricant, Seiwert et al. showed that a solid with well-defined micropillars entrains no excess lubricant provided the capillary number $Ca = \mu_o U / \gamma < 10^{-4}$ where $\mu_o$ is the viscosity of the lubricant, $U$ is the withdrawal speed, and $\gamma$ is the surface tension of the lubricant.\cite{74} Such a dipcoating method is a popular technique to ensure the lubricant impregnated surface has no excess film.

### 3.2.1 The Cloak

The lubricant can spread over the top of a working fluid drop and form a cloak (Figure 3.2). A cloak will form provided the spreading parameter $S_{ow(a)}$ of the lubricant ”o” on the working fluid ”w” in the presence of air ”a” is greater than zero. Consideration of the cloak extends the possible morphologies of a drop on lubricant impregnated surfaces to twelve possible states as shown in Figure 3.2.
Figure 3.2: Possible thermodynamic states of a water drop placed on a lubricant impregnated surface. The top two schematics show cases where the drop does and does not get cloaked by the lubricant. For each case, there are six possible states depending on how the lubricant wets the texture in the presence of air (the vertical axis) and the working fluid (horizontal axis). Reproduced from Ref [4] with permission from The Royal Society of Chemistry.

The thickness of the lubricant cloak is set by a balance between the repulsive disjoining pressure and the Laplace pressure due to curvature. The Laplace pressure writes as $2\gamma/R$ where $\gamma$ is the surface tension of the lubricant and $R$ is the drop radius. The disjoining pressure $A_H/6\pi h^3$ is a function of the film thickness $h$ and the Hamaker constant $A_H$ which quantifies the interaction between air and working fluid molecules across the lubricant film. By balancing the Laplace pressure and disjoining pressure, Schellenberger et al. estimate that a cloak of the fluorocarbon FC-70 on a 1 mm drop of water is on the order of 20 nm thick.[5] Both Schellenberger et al. and Anand et al. have confirmed cloaks over water drops by confocal microscopy and SEM respectively (Figure 3.3).[5,6,75] Cheng et al. have also demonstrated high resolution X-ray tomography to visualize the water-lubricant interface.[76]
Anand et al. suggest that the formation of the cloak occurs in two steps.\textsuperscript{[6]} First, a monolayer front spreads and its position follows \( R = \left( \frac{4S_{ow(a)}}{3(\mu_o \rho_o)^{1/2}} \right)^{1/2} t^{3/4} \) which is deduced from a balance between surface tension gradients and shear stress of the lubricant monolayer spreading on the liquid drop.\textsuperscript{[6,77]} Next, a thicker film spreads. The relative scale of surface tension, viscous, and inertial forces in the spreading film is captured by the Ohnesorge number \( Oh = \frac{\mu_o}{(\rho_o R \gamma_{oa})^{1/2}} \) where \( \mu_o \) is the lubricant viscosity, \( \rho_o \) the lubricant density, \( R \) the working fluid drop radius, and \( \gamma_{oa} \) the lubricant surface tension. Carlson et. al observe that the time it takes a drop to detach from a needle when brought into contact with an oil film is \( \tau_p = \frac{\rho_o R^3}{\gamma_{oa}} \) and \( \tau_{\mu} = \frac{\mu_o R}{\gamma_{oa}} \) for \( Oh > 1 \). These timescales give an estimate for the time it takes for the thicker film to completely cover the drop presuming detaching from the needle is a result of the complete spreading. Further work is needed to understand the dynamics of the spreading of liquids on liquids.

### 3.2.2 The Wetting Ridge

When a drop of working fluid contacts a lubricant impregnated surface, a ridge of lubricant forms around the drop that is similar to ridges that can develop on soft solids.\textsuperscript{[78,79]} Schellenberger et al. analyze the wetting ridge of several lubricant impregnated surfaces (Figure 3.3).\textsuperscript{[5]} They find that the height \( z \) of the wetting ridge follows from a balance between Laplace pressure and hydrostatic pressure, and its solution is a modified Bessel function of the second kind approximated by \( z = \exp(-r/\ell_c) \) where \( r \) is the radial position and \( \ell_c \) the capillary length. The wetting ridge is important because the majority of viscous dissipation in a mobile drop occurs in the wetting ridge as discussed later in this chapter.\textsuperscript{[4]} Neeson et al. present a useful analysis on the morphology of drops with immiscible fluids that is relevant to drops on lubricant impregnated surfaces.\textsuperscript{[80]}
3.2.3 Excess Films and Steady-State

In equilibrium, a lubricant impregnated surface contains a lubricant perfectly filling the textures such that capillary forces retain the lubricant in the presence of gravity. The texture however can be also overfilled as depicted in Figure 3.4. In addition, Schellenberger et al. demonstrated that overfilling a texture leads to different wetting ridge morphology,\cite{5} and researchers have shown that the contact angle hysteresis and sliding speed of a water drop on a lubricant impregnated surface are is significantly improved if an excess film is present.\cite{57,81} While excess oil films may be beneficial (and also better in ice adhesion)\cite{13}, the excess fluid is not stabilized by capillary forces and can readily drain by gravity and
Figure 3.4: Influence of the filling height. (a-c) Image of a micropillar array infiltrated with decanol before and after a water drop is deposited. The height of the lubricant film is adjusted (a) to be underfilled, (b) to match the height of the posts, and (c) to be overfilled. Color code: water (red), decanol (yellow/green), air or solid (black). Black shadows extended from the pillars result because the sample was imaged from underneath. (d) Contact angle hysteresis of a 5 µL water drop on a lubricant impregnated surface as a function of the lubricant height. Reproduced from Ref [5] under the CC BY 3.0 license and from Ref [7] with permission from Macmillan Publishers Ltd: Nature (Copyright 2011).

Carlston et al. demonstrate that when film drainage is favored a water drop can sit atop a thin oil film on a substrate for a finite amount of time draining.[82] Similarly, drops on lubricant impregnated surfaces may be mobile in transient states but behave differently once the lubricant impregnated surface reaches its equilibrium state. The dipcoating method studied by Seiwert et al, and mentioned earlier in this chapter,[74] is a convenient way to achieve a lubricant impregnated surface with no excess lubricant.

3.3 Applications

3.3.1 Condensation

Approximately 40% of water usage worldwide is related to energy generation;[83] this demand primarily from power plants most of which use steam cycles in their operation. A steam cycle comprises many components, but the condenser consumes the most water and most greatly contributes to the overall steam cycle efficiency.[84] On a typical surface, steam
condenses as a film that acts as a substantial thermal barrier to subsequent condensation
(filmwise condensation). Alternatively, steam can condense as drops that roll off under
gravity (dropwise condensation) and can provide up to a tenfold increases in heat transfer
when compared to surfaces that condense filmwise.\textsuperscript{[84,85]} Efforts to promote drop roll-off
have focused on superhydrophobic surfaces that exhibit extremely low droplet adhesion.
However, these useful properties are lost during condensation because droplets nucleating
randomly within textures of the solid can grow to large sized drop that may remain en-
trained within the textures in a Wenzel state (Figure 3.5(a-c)).

Lubricant impregnated surfaces promote dropwise condensation. With a lubricant im-
pregnated surface, the lubricant contained in the surface prevents water from condensing
within the texture (Figure 3.5(e-f)). In addition, the presence of the lubricant imparts ex-
ceptional mobility to condensed drops. On a conventional superhydrophobic surface, the
critical size for drops to shed from the surface is on the order of a few millimeters (Fig-
ure 3.5(g)). On a lubricant impregnated surface, Anand et al. observe drops as small as
20 \( \mu \text{m} \) are mobile (speeds around 1 mm/s) on the surface (Figure 3.5(g)).\textsuperscript{[8]} In addition,
researchers have observed that under identical conditions, the onset of water condensation
on lubricant impregnated surfaces is faster than on superhydrophobic surfaces which sugg-
ests that the lubricant impregnated surfaces have a lower energy barrier for nucleation.\textsuperscript{[8,9]}

The enhanced shedding and nucleation of drops indicates the potential of lubricant
impregnated surfaces for high condensation heat transfer. Xiao et. al. quantify the con-
densation heat transfer of lubricant impregnated surfaces as twice that of conventional hy-
drophobic and superhydrophobic surfaces when exposed to conditions comparable to those
of industrial condenser operation (Figure 3.6(a)).\textsuperscript{[9]} A lubricant impregnated surface main-
tained dropwise condensation of steam up to the highest supersaturation tested whereas a
superhydrophobic surface transitioned to filmwise condensation at high supersaturation.

Initially, Anand et al. had postulated that the nucleation of steam into water on lubricant
impregnated surfaces occurs at the lubricant-air interface,\textsuperscript{[8]} whereas Xiao et al. had sug-
Figure 3.5: Comparison of condensation of water vapor on superhydrophobic (top row) and lubricant impregnated surfaces (bottom row) with identical textures. (a) Schematic of condensation on superhydrophobic surfaces showing that water can nucleate within the texture and (b-c) timelapse ESEM images. (d) Drops grow and coalesce and eventually form large Wenzel drops that are pinned on the surface. (e) Schematic of condensation on lubricant impregnated surfaces showing condensation on top of the lubricant and (f-g) timelapse ESEM images. (h) Drops that condense and grow on a vertical lubricant impregnated surface are highly mobile. Reproduced with permission from Ref [8] with permission of The American Chemical Society (Copyright 2012).

Figure 3.6: (a) Measured heat transfer coefficients for a flat hydrophobic surface, superhydrophobic surface, and Krytox impregnated surface with varying vapor pressures. The Krytox impregnated surface shows roughly twice the heat transfer as compared to the other surfaces. (b) Images of the condensate of three low surface tension fluids on three different surfaces each. Both dropwise condensation (DWC) and filmwise condensation (FWC) is observed. (c) The heat transfer coefficients for the condensation of low surface tension liquids on a flat silicon surface, a flat hydrophobic surface, and a Krytox impregnated surface. Bars are generated from modeling whereas points indicate measured values. Reproduced from [9] and [10] under the CC BY-NC-ND 3.0 license.
gested that nucleation occurs at the solid surface beneath the lubricant.\(^9\) In a later work, Anand et al. rationalize that water vapor has limited absorption into the lubricant and cannot achieve the required supersaturation to allow for nucleation within the lubricant. This suggest nucleation should occur only at the lubricant-air interface.\(^6\) They show that depending on the lubricant’s surface tension and interfacial tension with water nucleation on a lubricant can have a significantly lower energy barrier compared to that on solids. Based on such an analysis, they construct a regime map to aid in the selection of lubricants that may lead to enhanced nucleation.\(^6\)

Because condensers operate at low pressures, lubricants used for condensation applications must have low vapor pressure so that they are not rapidly lost. For condensation the existence of a lubricant cloak plays a special role. As discussed previously, a lubricant can cloak over the top of a working fluid drop deposited on a lubricant impregnated surface (Figure 3.3). The lubricant will cloak provided the spreading coefficient of the lubricant on the working fluid in the presence of air is positive \(S_{ow(a)} > 0\). Anand et al. show that the rate of condensed water drop growth on lubricant impregnated surfaces is significantly reduced on lubricants that form a cloak over the condensed water drops as compared to those that do not. In a later work, Anand et. al. show that a lubricant cloak forms almost immediately after water drops nucleate at the lubricant-air interface.\(^6\) As a consequence, the capillary forces of the lubricant tend to submerge the drop after its formation. This prediction is confirmed by observing submerged microscopic droplets after condensation on a thin film of lubricant using a cryogenic FIB-SEM technique.

Figure 3.7 shows the non-coalescence of drops on a lubricant impregnated surface. Boreyko et al. find that the non-coalescence is due to the lubricant wetting ridge.\(^{11}\) Surprisingly, the time for two water drops to coalesce on a lubricant impregnated surface is greater than for two waters drops in a bath of the same lubricant by more than an order of magnitude.\(^{11}\) This time increases with the lubricant viscosity.\(^{11}\) For example, the time for two 5 \(\mu\)L water drops to coalesce is roughly one day when the lubricant is 500 cSt silicone oil but only one second when the lubricant is 10 cSt silicone oil. Furthermore,
Figure 3.7: Behavior of water drops on a liquid impregnated surface. (a) Drops meeting at their liquid-air interfaces exhibit coalescence. (b) When the oil menisci of two drops overlap, an oil film forms between the drops that prevents coalescence. (c) Top-down and isometric views of noncoalescing droplets. (d) Multiple drops can be connected into networks which spontaneously rearranged over time. (e) SEM of nanopillar substrate. The oil lubricants are (a, b) Krytox 100 and (c, d) Fomblin 25/6. Reproduced from Ref [11] with permission of The National Academy of Sciences.

they show that mixing phospholipids into the water drops creates lipid bilayers that prevent coalescence indefinitely. Barman et al. demonstrate that the coalescence process can be rapidly accelerated by applying a voltage between the two drops.\[86\]

Drops that condense and grow on a surface impregnated with 1000 cSt silicone oil tend to grow in a narrow size distribution whereas drops that condense on a surface impregnated with 10 cSt oil tend to be more polydisperse.\[6\] While preventing coalescence can create controlled formation of condensed drops, which may find use in breath figure templating,\[87\] cloaking of water droplets by the lubricant affects the longevity of lubricant impregnated surfaces. Drops smaller than the solid texture features can submerge and displace lubricant. In addition, shedding of cloaked drops further depletes the lubricant. As a result, non-cloaking lubricants are more robust for condensation applications.
Rykaczewski et al. extend the body of literature on condensation on lubricant impregnated surfaces to demonstrate the condensation of low surface tension liquids such as pentane and toluene (Figure 3.6(b, c)). A variety of low surface tension liquids with surface tension ranging from 12 - 28 mN/m are tested on a surface impregnated with Krytox and are compared with flat and re-entrant textured oleophobic surfaces. Some liquids displaced the Krytox as liquid condensed and thus exhibited filmwise, but most liquids exhibited sustained dropwise condensation. Up to an eight times increase in heat transfer resulted from promoting dropwise condensation of the low surface tension liquids.

The condensation heat transfer discussed up until this point involves a vapor transitioning to a liquid when it cools. A related problem is the generation of water from fog comprised of liquid water drops (rather than water vapor) where phase change doesn’t occur. The efficiency of fog collection is greatly dependent on the mobility of collected water drops on the collecting surface which can be improved by using lubricant impregnated surfaces. However, experiments of fog collection by Park et al. using Krytox impregnated surfaces have shown the gradual loss of lubricant with time. Later, Boor et al. studied fog collection using superhydrophobic electrospun surfaces and compared fog collection with and without impregnated liquids. Their results showed that a lubricant impregnated surface with Krytox increased the water collection rate from fog as compared to a superhydrophobic surface by about 130%. Furthermore, they also investigated the leeching of oil from the surfaces and showed that the under their experimental conditions 3-5 µL of lubricant was detected per liter of collected water.

### 3.3.2 Anti-icing

Lubricant impregnated surfaces have been demonstrated as a passive means of reducing ice adhesion which is a significant issue spanning multiple industries including transportation, agriculture, energy, and construction. While superhydrophobic surfaces have been explored
Figure 3.8: Comparison between an untreated aluminum 1100 sample (top) and lubricant impregnated surface (bottom) comprised of textured alumina and Krytox. The samples were cooled to -10°C at 60% relative humidity and defrosted at room temperature. Both samples are tilted at 75° for the duration of the experiment. Reproduced from Ref [12] with permission of The American Chemical Society (Copyright 2012).

for anti-icing,[91,92] Varanasi et al. showed that frost that forms on superhydrophobic surfaces leads to strong ice adhesion.[40]

Kim et. al. demonstrate reduced ice and frost adhesion and accumulation on a Krytox impregnated surface with excess lubricant.[12] As shown in Figure 3.8, during frost tests the impregnated aluminum sample tilted at 75° shows no frost formation and no residual water after defrosting when compared to untreated samples. The lubricant impregnated surface has less ice accumulation because condensed water can roll-off easily at the 75° tilt angle before it freezes, and any accumulated ice easily rolls off the surface when defrosted. Additionally, measurements of ice adhesion strength show a reduction in adhesion strength of almost two orders of magnitude on surfaces with an excess lubricant film.

Subramanyam et. al. extend these results by comparing a lubricant impregnated surface
with an excess film to one with an equilibrium film obtained by a controlled dip-coating process.\textsuperscript{[13]} Compared to a lubricant impregnated surface with excess lubricant, a lubricant impregnated surface with the same texture and no excess lubricant shows higher ice adhesion (Figure 3.9). Optimizing the texture density of the lubricant impregnated surface with no excess film results in lower ice adhesion than one of the lowest surface energy materials (80/20 PEMA-FluoroPOSS). Surprisingly, ice adhesion is lower on lubricant impregnated surfaces that have higher texture densities. The researchers suggest that ice fractures more easily from surfaces with higher texture densities because there is higher density of stress concentration sites.

Even with a lubricant in thermodynamic equilibrium, the lubricant can be depleted due
to cloaking, solubility, evaporation, and other effects. In particular during ice and frost formation, Rykaczewski et. al. show using cryogenic FIB-SEM that the lubricant can wick into icicles that accumulate on frozen water on lubricant impregnated surfaces (Figure 3.9(d, e)).\textsuperscript{[14]} When the ice is removed from the surface it takes some lubricant with it. Depending on the selection of lubricant and texture, significant depletion can occur in just a single frost-defrost cycle. Once the lubricant is depleted the ice adhesion will closely mirror the performance of the underlying superhydrophobic surface which can be worse than an untreated surface.\textsuperscript{[40]}

Accordingly, active research focuses on developing lubricant impregnated surfaces for anti-icing with enhanced durability.\textsuperscript{[56,64,93,94]} In one approach, Yin et. al. introduce nanoparticles into the lubricant layer to selectively heat the lubricant impregnated surface under near-infrared irradiation.\textsuperscript{[95]} This allows for thermal deicing while still maintaining many of the benefits inherent to a lubricant impregnated surface.

### 3.3.3 Self-Cleaning

A surface from which contaminants such as dust can easily be removed by a liquid is referred to as a self-cleaning surface. Self-cleaning has been achieved using superhydrophilic surfaces that rely on film flow or using superhydrophobic surfaces with low contact angle hysteresis on which drops can easily roll-off taking contaminants with them.\textsuperscript{[96]} Unfortunately, the limited durability of such surfaces to a wide range of contaminants and fluids has constrained their widespread use.

Lubricant impregnated surfaces are well-suited for self-cleaning applications because of their extremely low contact angle hysteresis and ability to repel a wide variety of liquids.\textsuperscript{[7,15,88,94]} Additionally, the angle at which a drop of a given size rolls off a lubricant impregnated surface is much smaller compared to that on smooth, low surface energy solid materials. Furthermore, identically sized drops will have a larger area of contact on a
The slippery nature of lubricant impregnated surfaces also alters the drying pattern of droplets containing particles. Figure 3.10(b) shows a typical deposition pattern observed on a surface often called the "coffee ring effect." When an evaporating drop becomes pinned, particles migrate to the contact line and deposit forming a ring pattern. This behavior is compared with the drying pattern of the same drop on a lubricant impregnated surface. The lack of pinning during evaporation on liquid impregnated surfaces allows for a more uniform and localized deposition of particles.\textsuperscript{[15,88,97]} Yang et al. have taken advantage of this effect to concentrate analytes in an evaporating liquid drop to improve Raman characterization.\textsuperscript{[98]}

### 3.3.4 Preventing Biofilm Formation

Biofouling is widely prevalent in numerous industrial and medical applications. The formation of biofilms hampers the operation of marine vessels and desalination plants and
can be catastrophic in catheter tubes and implants. Bacteria can also evolve to resist anti-
microbial agents and hence other solutions are needed. The design of non-fouling surfaces
has primarily focused on preventing protein adsorption and bacterial adhesion using func-
tional groups including poly(ethylene glycol), zwitterions, and other hydrophilic groups
that only remain free from biofilm formation for a limited time. Initial experiments show-
ing that lubricant impregnated surfaces can repel blood and prevent bacteria attachment
have prompted further investigation into biofilm prevention.\cite{7,99}

Epstein et al. have shown the slippery nature of lubricant impregnated surfaces re-
duces the bacterial accumulation and the overall adhesion of films under mild flow condi-
tions.\cite{16} Figure 3.11(a) compares the accumulation of \textit{Staphylococcus aureus} bacteria on
a PTFE substrate with a lubricant impregnated surface. The lubricant impregnated surface
has 97.2\% less bacteria after 48 hours under flow. Similar reduction is observed for \textit{Es-
cherichia coli},\cite{16} \textit{Pseudomonas aeruginosa},\cite{16,100} and \textit{Chlorella vulgaris}\cite{101} as well as
bacteria of the genus \textit{Desulfovibrio}.\cite{102}

Selective cell-repellency, which is important in biosensing and microfluidics, has also
benefitted from liquid impregnated surfaces. Ueda and Levkin have repelled cells into well-
defined regions by patterning liquid impregnated regions of a substrate.\cite{17} Figure 3.11(b)
shows fluorescent human cervical tumor cells separated by lubricant impregnated regions
in which cells cannot attach.

In marine vessels fouling can also occur from plants and animals that adhere the hull. Xiao et al. investigate the attachment and adhesion of motile spores of the seaweed *Ulva linza*.\[^{100}\] After two hours, the number of *U. linza* spores that had attached on a Krytox impregnated surface is significantly lower than on a control glass surface. However the spores that do attach have comparable adhesion strength to those that have attached to the glass surface as indicated by their ability to remain attached under a shear water flow. In separate assays, they also demonstrate that the coverage of the larvae of the barnacle *Balanus amphitrite* is up to an order of magnitude less on Krytox impregnated surfaces when compared to glass and polystyrene.

### 3.3.5 Preventing Scale Fouling

Fouling and corrosion of heat exchangers, oil and gas pipelines, and turbine systems lead to increased maintenance and losses in production. The cost associated with heat exchanger scaling alone when considering operational losses, energy costs, and maintenance costs is on the order of one quarter percent of the GDP of industrialized countries.\[^{103}\] Mechanical and chemical cleaning methods are expensive economically or environmentally unfriendly. Low surface energy coatings have been shown to provide a passive route for limiting the fouling of surfaces but lack robustness in harsh conditions.

Liquid impregnated surfaces are promising as a robust alternative to other low surface energy coatings. Reducing the nucleation rate of scale requires a lower density of nucleation sites and a high activation barrier. A low surface tension liquid entrained within the solid texture offers a molecularly smooth surface with a large activation barrier that can be used to lower the nucleation rate. Figure 3.12(a, b) show a comparison between an untreated surface and a silicone oil impregnated surface immersed in a gypsum (calcium sulfate) solution for over three days.\[^{18}\] Subramanyam et al. showed that an optimal design
with respect to the liquid surface tension and spreading coefficient can result in up to ten times lower scale formation on the impregnated surface when compared to an untreated surface.\cite{18} They also show that lubricant impregnated surfaces can be fabricated on steel which is used in industrial applications. Charpentier et al. extended this work to show a ten times decrease in scale deposits of calcium carbonate on liquid impregnated surfaces.\cite{104}

The corrosion of a material can also be slowed down with a liquid impregnated surface. The use of superhydrophobic surfaces in marine environments to lower corrosion rates has limited success because over time the trapped air is lost. Figure 3.12(c) compares the corrosion of bare steel, hydrophobic steel, and a liquid impregnated steel with varying amounts of infused liquid after three days of immersion in 3.5% NaCl solution.\cite{19} On the liquid impregnated surface, the perfluoropolyether lubricant acts as a protective layer and lowers the corrosion rate. Song et al. further quantify this corrosion resistance using electrochemical impedance spectroscopy to show that lubricant impregnated surfaces do not corrode even after 76 days immersed in 3.5 wt% NaCl.\cite{105,106}
3.3.6 Fluid Mobility

A drop placed on a lubricant impregnated surface is mobile at very low angles. Smith et al. conclude that drops roll on lubricant impregnated surfaces rather than slide by balancing shear forces in the lubricant film beneath a drop and those within a drop.[4] Looking at the lubricant-working fluid interface beneath a drop on a lubricant impregnated surface, the shear forces on the lubricant side scale as $\mu_o V_i / t$ where $\mu_o$ is the lubricant viscosity, $V_i$ is the interface velocity, and $t$ is the lubricant film thickness beneath the drop. The shear stress on the working fluid side scales as $\mu_w (V - V_i) / h_{cm}$ where $\mu_w$ is the working fluid viscosity, $V$ is the velocity of the center of mass of the drop, and $h_{cm}$ is the height of the center of mass. At the interface the shear stresses must balance giving the $V_i \sim V (1 + \mu_o h_{cm} / \mu_w t) - 1$. For the experiments of Smith et al. $V_i \ll V$ which indicates that the drop rolls. They confirm the rolling motion of the drop using tracer particles (Figure 3.13(c)).

Next, the speed of a drop in steady state on an inclined lubricant impregnated surface is determined by balancing gravitational, pinning, and viscous forces. There are three possible regions of viscous dissipation resisting a drop’s motion: in the rolling drop, in the
lubricant beneath the drop, and in the wetting ridge. For a water drop on a silicone oil impregnated surface with no excess film, Smith et al. show that dissipation in the wetting ridge is the most dominant term and explains observed velocities for a wide range of lubricants, tilt angles, and drop sizes (Figure 3.13d).\textsuperscript{[4]}

Abstracting away from drop level experiments, introducing a slippery interface has many applications in established industries. Slip in the walls of a pipe for example will increase the flow rate or decrease the power required to pump a fluid.

At a fluid-solid interface the most universally accepted boundary condition is no-slip meaning the velocity of the fluid and solid must be matched. The no-slip condition has been experimentally validated under most normal flow conditions.\textsuperscript{[107]} The interface between a lubricant impregnated surface and working fluid however takes special consideration because the working fluid interfaces with either only the lubricant or a combination of lubricant and solid. In such a situation an apparent slip can arise although no-slip can still hold microscopically.

Such drag reduction has been studied for superhydrophobic surfaces by modeling the air-working fluid interface as shear free. Several studies have extended such work to incorporate the viscosity of air into models.\textsuperscript{[108–110]} While lubricant impregnated surfaces are more stable than superhydrophobic surfaces and can repel a wider variety of liquids, lubricant impregnated surfaces should provide less drag reduction than superhydrophobic surfaces since the viscosity of the lubricant is greater than that of air. Solomon et al. use a rheometer to measure the drag reduction on lubricant impregnated surfaces in laminar flow with varying working fluid viscosities and attained a drag reduction of 16% in a 1 mm geometry when the working fluid was 260 times more viscous than the lubricant (Figure 3.14(a)).\textsuperscript{[20]} Jacobi et al. point out that such measurements involving two immiscible fluids in a rheometer can be subject to an interfacial distortion that can contribute to the torque measurement.\textsuperscript{[111]}
Figure 3.14: (a) Plot of the drag reduction percentage vs. the ratio of the working fluid to lubricant viscosity for a laminar flow. Mixtures of water and glycerol are used as the working fluid and a laser textured sample impregnated with silicone oil is used as the lubricant impregnated surface. Experiments are conducted in a parallel plate geometry. (b) Plot of drag reduction percentage vs. Reynolds number for a variety of working fluid to lubricant viscosity ratios at higher Reynolds numbers. The least viscous lubricant heptane gives a drag reduction percentage of 14%. Experiments are conducted in a Taylor-Couette geometry. Reproduced from Ref [20] with permission of American Chemical Society (Copyright 2014) and from Ref [21] with permission of Springer.

Schönecker et al. analytically investigated the drag reduction of lubricant impregnated surfaces in laminar flow and found that a working fluid to lubricant viscosity ratio of 56 (consistent with water on a superhydrophobic surface) can attain a 20% flow increase on an optimized lubricant impregnated surface (Figure 3.15). In comparing the flow enhancement when using lubricant impregnated surfaces, the reference plane must be carefully chosen. For example, adding a lubricant impregnated surface to the inner surface of a pipe reduces the radius. The advantages of a lubricant impregnated surface would have to be greater than the added resistance of a decreased pipe radius.

Rosenberg et al. extended findings on drag reduction to higher Reynolds numbers.[21] Using a Taylor-Couette geometry they measure 10% drag reduction on superhydrophobic surfaces and 14% drag reduction on a heptane impregnated surface which was constant over the Reynolds numbers 7,000 - 9,000 (Figure 3.14(b)). Other works suggest that drag reduction can also be achieved in turbulent flows on lubricant impregnated surfaces[112] as has been measured and rationalized on superhydrophobic surfaces.[113] Jackson points
Figure 3.15: (a) Schematic of the analyzed lubricant impregnated surface. Influence of the viscosity ratio on the enhancement factor (given by contours) for longitudinal flow over open grooves with \( b/L = 0.98 \) where the ratio between the period of the grooves and radius of the channel is (b) 0.02 and (c) 0.1. The enhancement factor is the increased flow rate provided by adding a lubricant impregnated surfaces compared to a no-slip condition. Reproduced from Ref [22] with permission of Springer (Copyright 2014).

out using simulations that confining lubricants on small scales may lead to additional drag reduction benefits.\textsuperscript{[114]} Wang et al. established up an alternate way of measuring drag by spraying surfaces with a controlled flow to measure up to a 7\% decrease in drag force on a lubricant impregnated surfaces.\textsuperscript{[94]}

Drag reduction experiments in Taylor-Couette flows should be extended to Reynolds numbers in excess of \( 1 \times 10^4 \). Below this critical Reynolds number, flow instabilities are present in Taylor-Couette flows that prevent the results from being generalized to other geometries.\textsuperscript{[113,115]}

\section*{3.3.7 Active Surfaces}

Previously discussed motion of drops on lubricant impregnated surfaces has relied on passive methods, namely the action of gravity. An under-explored area for future work is utilizing active force fields (i.e. magnetic, electric, thermal) to manipulate drops. Chen et al. have demonstrated that the low hysteresis of lubricant impregnated surfaces enables drops with magnetic particles to be moved with a magnetic field.\textsuperscript{[116]} More recently, Khalil et al. (Figure 3.16(a)) have created a lubricant impregnated surface where the lubricant is a super-paramagnetic ferrofluid.\textsuperscript{[23]} The lubricant is designed to cloak over drops deposited
Electrowetting, which modifies wetting properties by applying a voltage bias, has emerged as a versatile tool to manipulate droplets of various sizes in a controlled fashion and has been applied to electronic displays, energy generation, and microfluidic systems. In a typical system, a voltage between a conducting drop and substrate covered with a dielectric film is applied. Upon application of the voltage, the contact angle of a water drop decreases. When the voltage is removed, contact angle hysteresis can prevent the drop from recovering. Also, severe and uncontrollable droplet oscillations are often encountered. Lubricant impregnated surfaces have been shown to reduce these undesirable effects as well as reduce any contact angle hysteresis to minimize the reversibility issues as shown in Figure 3.16(b). Barman et al. have also demonstrated that electrowetting two adjacent water drops on lubricant impregnated surfaces decreases the time it takes them to coalesce by an order of magnitude.
Because liquid surfaces provide extremely low contact angle hysteresis, thermocapillary can drive the drop along surfaces as shown in Figure 3.16(c).\textsuperscript{25} Eifert et al. remark that the motion can have contributions from thermocapillary forces in the working fluid drop as well as bulk motion of the lubricant but deduce that the motion must be due to thermocapillary forces within the working fluid drop by varying the drop size. Drops on lubricant impregnated surfaces have also been controlled by changing the local wettability of lubricant impregnated surfaces.\textsuperscript{66,122} The techniques mentioned promise useful for the fabrication of microfluidic designs where a pre-existing microchannel design is not needed.

3.3.8 Optics

Coupling transparency and slipperiness is important for applications ranging from solar modules to commercial eyewear. Superhydrophobic surfaces comprising sub-wavelength features in transparent materials have shown high transparency while being non-wetting.\textsuperscript{123} Lubricant impregnated surfaces also enable highly transparent and slippery surfaces by reducing the refractive index contrast at the lubricant air interface in comparison to the original solid-air interface. Several researchers have reported enhancement in broadband optical transmission compared to textured surfaces.\textsuperscript{68,71,81,94,116,124,125} Vogel et al. demonstrate that the optical transmission through lubricant impregnated surfaces can surpass that through a glass slide.\textsuperscript{68}

Manabe et al. point out that even for surfaces with nanoscale features where total transmittance is similar with and without impregnation, lubricant impregnated surfaces significantly reduce the amount of light scattered.\textsuperscript{93} Yao et al. impregnated an elastic matrix with a lubricant and showed that the optical transmission can be tuned by deforming the lubricant impregnated surface.\textsuperscript{126}
3.3.9 Infused Gels

A related technology is achieved when for example silicone oil is absorbed by cross-linked solid PDMS. The resulting organogel shows slippery properties similar to liquid impregnated surfaces owing to the absorbed silicone oil, but unlike a lubricant impregnated surface the solid texture does not stabilize the silicone oil. Such an infused gel has confusingly been called a lubricant impregnated surface, but its principle of construction and operation is different from lubricant impregnated surfaces as described earlier in this chapter.

Surfaces where an organic liquid (e.g. silicone oil or Krytox) is infused into a polymer are referred to as organogels. Analogously, water can be absorbed by hygroscopic polymers to form a hydrogel. It is also possible to create ionic liquid infused polymer gels.

Liquid infused gels exhibit many similar properties to lubricant impregnated surfaces including low roll-off of drops, anti-icing, enhanced condensation, and anti-biofouling. For example MacCallum et al. prevent biofilm accumulation by infusing silicone oil into silicone tubing. They demonstrate by flowing a cultured bacteria solution that the infused silicone tube is devoid of *P. aeruginosa* cells while the control has a large amount of accumulation. Leslie et al. also report an infused organogel that prevents thrombosis. Chen et al. have also created a hydrogel gel surface on which adheres ice more weakly than on superhydrophilic, superhydrophobic, and flat surfaces (Figure 3.17).

3.3.10 Durability

Lubricant impregnated surfaces show promise in a wide range of applications, but their durability and robustness remains an open question. In shear flow, Howell et al. report that Krytox impregnated surfaces remain stable under shear flow. However, the work of Wexler, Jacobi, and Stone undercover two mechanisms by which lubricant impregnated
Figure 3.17: Depiction of a microporous silicon filled with a hydrogel. The self-lubricating liquid water layer (SLWL) of the hydrogel surface adheres ice more weakly than superhydrophilic, superhydrophobic, and flat surfaces. Reproduced from Ref [26] with permission of The American Chemical Society (Copyright 2013).

surfaces can fail. In the first, shear forces by an imposed flow can overcome the capillary forces holding the lubricant in place, but cleverly placing non-wetting regions prevents this phenomena from occurring (Figure 3.18(a)).[27,27] Also, a flow can cause the lubricant to overflow and eventually leave the surface (Figure 3.18(b)).[28]

In addition, Boor et al. measured that water drops condensing and rolling off a surface remove 3-5 µL of lubricant per liter of collected condensed water. As with superhydrophobic surfaces, lubricant impregnated surfaces are also vulnerable to mechanical failure. Shellingford et al. observe mechanical damage to lubricant impregnated surfaces when mechanically abraded that compromises their repellancy.[61] While drop impact has been investigated on lubricant impregnated surfaces,[142,143] under sufficiently high impact conditions an impinging water drop should displace the lubricant and cause the surface to fail.
Figure 3.18: Experiments in which a water/glycerol mixture flows over grooves filled with a fluorescent green lubricant. The red arrow indicates the flow direction. The grooves are 9 µm wide, 10 µm deep, and 35 mm long. (a-d) Regions with periodicity $L$ that are non-wetting to the lubricant interrupt grooves aligned with the flow and in (a) prevent drainage of the lubricant. For each experiment, the top image shows the initial state and the bottom the steady state. Drained portions of the groove reflect blue light while excess lubricant appears white. The strength of the imposed flow is characterized by a shear stress $\tau$. (e, f) In a separate set of experiments, at a sufficient stress the flow over lubricant filled groups induces overflow of the lubricant at a shear stress of $\tau = 2.58$ Pa. Reproduced from Ref [27] with permission of The Royal Society of Chemistry and from Ref [28] with the permission of AIP Publishing.

3.4 Outlook

Researchers have also begun creating systems iterating on lubricant impregnated surface technologies to extend their use in new ways. Hou et al. have created a liquid impregnated surface that functions as a membrane to selectively pass gases and liquids,\cite{144} while Sun et al. have created a surface that secretes antifreeze upon contact with ice.\cite{145} Dai et al. report on a slippery surface comprised of a thin layer of oil trapped in nanoscale textures on a surface of microscale textures. A water drop placed on the surface impales into the texture in a Wenzel-like state but is surprisingly still highly mobile.\cite{146} Similar to liquid marbles, McHale and Newton hypothesize that it should be possible to fabricate a liquid impregnated surface around a liquid drop that would serve microfluidic applications.\cite{147}

Lubricant impregnated surfaces are a versatile platform that show promise in condensation, anti-icing, anti-fouling, fluid mobility, optics, and drop control. In each application, the design of a lubricant impregnated surface has particularly relevant criteria of which some are not intuitive. In time further development will allow lubricant impregnated sur-
faces to reach commercial applications where superhydrophobic surfaces have fallen short and also promise to benefit a multitude of yet undiscovered applications.
Chapter 4

Lubricant Impregnated Surfaces for Drag Reduction in Laminar Flow

4.1 Introduction

Surface modifications that reduce drag in fluid flows would benefit a multitude of industries. For example, maritime shipping is the world’s most carbon-efficient form of transporting goods yet still accounts for 10% of global carbon emissions produced in transportation.\(^{[148]}\) The reduction of the drag on ship hulls would benefit both the environment and provide cost savings. Additionally, the United States has over two million kilometers of pipelines for transporting oil and natural gas that would also benefit from such a technology.\(^{[149]}\)

To date, the most successful method of drag reduction in internal flows is the use of polymers in turbulent flows. The addition of only ten parts per million of certain polymers is sufficient to produce drag reductions of up to 80% and is used in the oil industry, fire fighting equipment, irrigation, and sewage transport.\(^{[150–152]}\) Such additives work only in turbulent flow, and furthermore they must be continuously supplied. Alternatively, superhydrophobic surfaces that rely on trapped air pockets have been explored as a passive method of drag reduction.

Another application is microfluidics where superhydrophobic grooves,\(^{[153–155]}\) carbon
nanotubes,[156,157] nanoscale spikes,[158] pillars,[154,159] and meshes[160] have been shown experimentally to reduce drag in laminar internal flows and in some cases produce slip lengths on the order of hundreds of microns.[154,159,160] Superhydrophobic surfaces however lack robustness as air pockets can collapse and thus have limited practical applicability in the case of drag reduction.[38] Surface defects, air dissolution,[36] external forces, and phase transitions such as condensation and desublimation[40] cause the desirable Cassie state to transition to an undesirable Wenzel state[33] and erase any potential drag reduction benefits. Moreover surfaces that rely on trapped air pockets and are phobic to low surface tension liquids require intricate surface textures.[29]

Whereas a superhydrophobic surface is a composite surface composed of a solid and air, a lubricant impregnated surface is composed of a solid and liquid lubricant. As discussed extensively in Chapter 3, lubricant impregnated surfaces have been shown to display low contact angle hysteresis,[4,7,15,25,50,65,82,161] be self-cleaning,[15,126,127] and promote dropwise condensation,[8–10] anti-icing,[12,13,68,116] and anti-fouling.[16–18,100,162] These robust, slippery composite surfaces have great potential for drag reduction.

A drop on a lubricant impregnated surface can exist in several thermodynamically stable states which are dependent on the relative spreading coefficients of the lubricant and the drop as well as the surface texture.[4] A lubricant will spontaneously impregnate a texture given its contact angle on a chemically identical smooth surface is below a critical contact angle. The lubricant will impregnate a textured surface in vapor/air $\theta_{os(v)} \leq \theta_c$ where $\theta_{os(v)}$ is the contact angle of lubricant (subscript “o”) on the smooth solid (subscript “s”) in the presence of vapor/air (subscript “v”) and $\theta_c$ is the critical contact angle for impregnation given by:[4,50]

$$\theta_c = \cos^{-1}\left[\frac{1 - \phi_s}{r \phi_s}\right]$$

(4.1)

Here $\phi_s$ is the fraction of the projected area of the textured surface that is occupied by a solid (the solid fraction) and $r$ is the ratio of total surface area of the textured surface
to its projected area. Analogously, the impregnation criterion for a surface under water is \( \theta_{os(w)} \leq \theta_c \) where \( \theta_{os(w)} \) is the contact angle of lubricant on the smooth solid in the presence of water ("w").

For these experiments a surface must be chosen that can be textured and easily chemically functionalized to alter its surface energy. Silicon wafers are readily available and are often functionalized with silane chemistries. A lubricant must be chosen that spontaneously impregnates the texture in air. Furthermore, the lubricant should also impregnate in the presence of water and glycerol. Silicone oil readily spreads on flat silicon functionalized with octadecyltrichlorosilane (OTS) both in air (\( \theta_{os(v)} = 0^\circ \)) and in the presence of water. In addition, since the contact angle of silicone oil on the smooth solid in the presence of either water or glycerol is zero (\( \theta_{os(w)} = 0^\circ \)) silicone oil will fully spread over the textures beneath the working fluid and lead to virtually no drop pinning. Thereby silicon functionalized with OTS and silicone oil are chosen to form the lubricant impregnated surface. A water drop on this surface has an advancing contact angle of 108°, extremely low contact angle hysteresis (<1°), and high drop mobility and thus anticipates potential drag reduction.

Theoretically, maximum drag reduction is achieved in the case where the solid fraction \( \phi_S \) of the texture is zero as depicted in Figure 4.1(b). Consider the laminar pressure driven flow of a working fluid of viscosity \( \mu_w \) through of pipe of radius \( R \) with a layer of lubricant of viscosity \( \mu_o \) and thickness \( \delta \) separating the working fluid from the pipe wall. For a given flow rate, the drag reduction \( DR \) is taken to be one minus the ratio of the pressure drop required to pump the working fluid \( \Delta P \) to the case without a lubricant layer \( \Delta P_0 \). By matching the velocity and shear stress at the working fluid/lubricant interface and assuming that the thickness of the lubricating layer is sufficiently small (\( \delta \ll R \)), the drag reduction \( DR \) can be solved analytically as:

\[
(1 - DR)^{-1} = \frac{\Delta P_0}{\Delta P} = 1 + \frac{4\delta}{R} \left( \frac{\mu_w}{\mu_o} - 1 \right) - \frac{2\delta^2}{R^2} \left( \frac{2\mu_w}{2\mu_o} - 1 \right) \tag{4.2}
\]
In the above derivation, it is assumed that the velocity profile is quadratic in the working fluid and approximately linear in the lubricating layer. Note that to first order $DR \sim \mu_w / \mu_o$. Thus it is only beneficial to use a lubricant that is less viscous than the working fluid, and more viscous working fluids experience greater drag reduction.

In order to demonstrate drag reduction by lubricant impregnated surfaces and confirm the dependence on $\mu_w / \mu_o$, lubricant impregnated samples are fabricated and compared to flat samples using a cone and plate rheometer. This dependence is studied while taking steps to overcome the typical errors associated with rheometry.

### 4.2 Experimental Methods

#### 4.2.1 Surface Fabrication

To construct a lubricant impregnated surface it is necessary that the lubricant be immiscible with the working fluid and that the system be thermodynamically stable. When a water drop is placed on a lubricant impregnated surface, the portion of the solid covered by a thin layer of lubricant in contact with the working fluid is referred to as the “tops of the texture.” The resulting surface behaves as depicted in Figure 4.2(f) where the lubricant is held in the textures and the working fluid flows above it. For this study water-glycerol mixtures are
used as the working fluid and oils of varying viscosities as the lubricant. This allows a span of several orders of magnitude in the viscosity ratio.

Figure 4.2(a) shows a schematic of the sample preparation method. As received 2” diameter polished silicon wafers (University Wafer) are subjected to a laser ablation process. A 1064 nm Nd:YAG laser (Electrox) is rastered across the surface in a controlled pattern. The resulting texture is well-ordered and reproducible with post-like features spaced approximately 50 µm apart and 50 µm deep that are covered with nanoscale features (Figure 4.2(b, c)). The wafers are then coated with a hydrophobic monomer octadecyltrichlorosilane (OTS, Sigma-Aldrich). A circle approximately 20 mm in radius is then laser ablated into the coated sample (seen in Figure 4.3(h, i)). This step ablates the hydrophobic material to reveal the underlying hydrophilic silicon. The utility of this step in pinning the free surface of the working fluid is described later.

Finally, samples are dip-coated in lubricant oils to create lubricant impregnated surfaces. To create a thermodynamically stable film the dip-coating withdrawal velocity must be below a critical speed $V_{crit} = 0.121 \mu_0 \gamma (\delta / \ell_c)^{2/3}$ where $\mu_0$ is the viscosity of the lubricant, $\gamma$ is its surface tension, $\ell$ is its capillary length, and $\delta$ is the depth of the texture. Accordingly, samples are dip-coated at a maximum withdrawal speed of 1 mm/s. Flat control samples are coated with OTS and then a 20 mm circle is ablated in similar fashion, but flat control samples did not undergo the first laser texturing step or subsequent dip-coating.

An environmental scanning microscope (Philips XL30 FEG ESEM) is used to image the final lubricant impregnated surface. A typical image is taken at an accelerating voltage of 10 kV at a pressure of 100 Pa. Figure 4.2(e) reveals lubricant inside the textures while the tops of the textures are visible. Although not visible, a thin lubricant film spreads over the tops of the textures.

A water drop on the flat silicon samples coated with OTS has advancing and receding contact angles of 110° and 98° respectively (Figure 4.2(b)). Prior to impregnation of
the lubricant, the surface is superhydrophobic and has an advancing and receding contact angle of 164° and 162° (Figure 4.3(c)). The lubricant impregnated surface has an advancing contact angle of 108° ± 2° and a receding contact angle 107° ± 2° (Figure 4.3(d)). While these are considerably lower angles than that of the superhydrophobic surface, its contact angle hysteresis was extremely low (<1°). Cassie-Baxter theory relates the contact angle on a superhydrophobic surface to that on a chemically identical smooth surface by \( \cos \theta_{SHo} = \phi_S (\theta_{flat} - 1) + 1.44 \). Taking the static contact angles \( \theta_{SHo} = 163° \) and \( \theta_{flat} = 105° \) (shown in Figure 4.3) gives the solid fraction \( \phi_S \approx 0.06 \). Alternatively, the solid fraction can be estimated as the area of visible solid in SEM micrographs (Figure 4.3(e)) per unit area to yield \( \phi_S \approx 0.08 \).

### 4.2.2 Rheometry

To probe the drag reduction capabilities of lubricant impregnated surfaces, a rheometer (AR-G2, TA Instruments) is used. A cone and plate geometry (depicted in Figure 4.3(a)) with a 40 mm diameter cone (2°, 1° cone angle, 54 μm truncation gap) is used. Because generally a fluid becomes less viscous at higher temperatures, a fluid undergoing shear heating in this setup would incorrectly imply higher drag reduction. The degree of shear heating is characterized by the Brinkman number which for this flow geometry is \( Br = \mu_w R^2 \Omega^2 / k T \) where \( \mu_w \) is the viscosity of the working fluid, \( R \) is the cone radius, \( \Omega \) is the angular velocity, \( k \) is the working fluid’s thermal conductivity, and \( T \) is its temperature. The deviation in torque is approximately \( b_0 Br / 12 \) where \( b_0 \) characterizes the dependence of viscosity on temperature\[^{164}\] (roughly 0.1 for glycerol solutions). With the most viscous working fluid at the highest shear rates, it is estimated that the torque will deviate by less than 0.4% as a result of shear heating. Conversely, inertial effects would tend to increase dissipation and thus would imply higher drag. The characteristic Reynolds number is \( Re = \rho \Omega \beta^2 R^2 / \mu_w \) where \( \beta \) is the cone angle and is low for all experiments. In trial experiments at very high shear rates, the measured viscosity for Newtonian fluid samples is lower as compared to at lower shear rates. This suggests that shear heating effects influence the data before inertial
At low shear rates, noise associated with ambient vibration is dominant. Accordingly, the shear rate $\dot{\gamma} = \Omega/\beta$ is kept in the range of 10-100 s$^{-1}$ to avoid noise on the low end and shear heating on the high end. All samples are tested on a Peltier stage controlled to 25°C.

For varying the viscosity ratio, pure glycerol (Sigma-Aldrich) is diluted with 18 MΩ deionized water (Millipore) and used as a working fluid. The lubricant oil is either 10 cSt or 100 cSt silicone oil (Sigma-Aldrich). In addition, viscosity standard N1000 calibration fluid (Cannon Instrument Company) is used as a working fluid as received. Its viscosity is

Figure 4.2: (a) Schematic showing the process to create the lubricant impregnated surface used in this study. (b), (c) SEM images of the laser textured surface showing both microscale and nanoscale features. (d), (e) ESEM images of the lubricant impregnated surface showing the oil lubricant completely filling the texture and protrusion of the tops of the texture. (f) Details of the velocity profile for a liquid-impregnated surface showing a local slip length $b$. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).
Figure 4.3: (a) Schematic of the cone and plate rheometer setup. (b), (c), (d) Images of a water drop resting on a flat OTS-coated silicon wafer, superhydrophobic surface, and lubricant impregnated surface respectively. The inset numbers are static contact angles. (e), (f), (g) Images of the free surface of the working fluid between the cone and substrate for a flat OTS coated silicon wafer, superhydrophobic surface, and lubricant impregnated surface respectively. Despite having drastically different contact angles, the free surfaces are identical. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).

Over the course of an experiment water can absorb/desorb from the working fluid. Separate experiments measuring the absorption/desorption of water from glycerol/water solutions show the weight change to be less than 0.5%.

Each experiment is conducted at least three times. Between experiments the working fluid is replaced, and the sample is realigned. The truncation gap is also reset and standard calibration on the rheometer performed. A typical experiment lasts fifteen minutes.

4.2.3 Pinning of the Free Surface

Edge effects are the largest source of error in rheometry experiments.\textsuperscript{165,166} In calculations in this paper, it is assumed that the free surface is a spherical cap and that a consistent
velocity field is maintained up to the boundary. Careful precautions are taken to ensure this.

Owing to different wettabilities of the control surfaces compared to the lubricant impregnated surface, a significant difference in measured torques would arise if this discrepancy is not controlled.\cite{167} As depicted in Figure 4.3(b-d), a substrate with a higher contact angle has less working fluid in contact with it. As a result, the measured torque will be lower and result erroneously in measured drag reduction. To control this, a hydrophilic pinning line is introduced to force the contact line of the working fluid to be reproducible across all samples. The volume of working fluid is controlled by a precision micropipette (BrandTech Scientific). The shape of the free surface is monitored by camera. For each experiment, the shape of the free surface is visually matched to a reference image to ensure the edge condition consistent. The surfaces of Figure 4.3(b-d) all produce the same free surface when pinning lines are present as shown in Figure 4.3(e-g).

After loading the working fluid onto the substrate, the cone is lowered to the truncation gap height. Because lubricant impregnated surfaces exhibit such low contact angle hysteresis and are extremely slippery, the working fluid is easily pushed out from the cone and outer pinning ring even when the cone is slowly lowered. As a result four concentric pinning circles are fabricated into each sample to control the spreading of the working fluid as the cone is lowered. These pinning circles are also used with the flat control samples for consistency. The pinning circles occupy less than 0.6% of the surface area and do not significantly impact measurements.

4.3 Results and Discussion

A convenient way to model drag reduction is to introduce the apparent slip length. Contrary to the traditional no-slip condition, the Navier slip condition posits a velocity $u_s$ at the
boundary interface proportional to the shear stress $\tau_{xy}$ by the slip length $b$ (Figure 4.1(a)).

$$u_s = \frac{b}{\mu} \tau_{xy}|_{\text{interface}} \quad (4.3)$$

Thus the slip velocity and slip length are inherently taken to be area-averaged quantities because the slip velocity varies spatially on the boundary. For example it is smallest at the tops of texture features. It should be noted in this work the slip length $b$ is taken from the top of the lubricant impregnated surface (Figure 4.1(a)).

On a superhydrophobic surface, stress-free interfaces between the working fluid and the trapped air within the composite solid results in an apparent slip length.$^{[168]}$ For post-like arrays this slip length can be described by $b_{r=0}/L = A/\phi_s^{1/2}$ where the constants $A$ and $B$ have been deduced both computationally and analytically.$^{[108,169,170]}$ As the viscosity of the trapped fluid increases, its contribution to shear is increasingly more relevant. A heuristic formula incorporating viscous dissipation within the trapped air or lubricant is:$^{[108]}

$$\frac{1}{b} = \frac{\mu_0 q}{(1 - \phi_S) \mu_w \tanh(q \delta)} + \frac{1}{b_{r=0}} \quad (4.4)$$

where $\delta$ is the thickness of the lubricant and $q$ describes the hydrodynamic interactions between post-like structures.$^{[108,171]}$ Clearly for negligible lubricant viscosity $\mu_0$ the shear-free case is recovered in which the slip length $b$ is independent of the viscosity ratio $\mu_w/\mu_o$. At some point the slip length becomes dependent on $\mu_w/\mu_o$ and in general depends on the lubricant viscosity, periodicity, texture geometry, solid fraction, and thickness of the lubricant. By simplification of Equation 4.4 in this viscosity dependent regime the slip length scales as:

$$b \sim \frac{\mu_w}{\mu_o} (1 - \phi_S) \delta \quad (4.5)$$

Assuming a no-slip boundary condition and laminar flow, the apparent viscosity measured for a given configuration and working fluid is $\mu_{w,app} = 3\beta M/2\pi \Omega R^3$.$^{[164]}$ For a lubricant impregnated surface that reduces drag, the ratio of apparent viscosity to actual
viscosity $\mu_{w,\text{app}}/\mu_w$ is less than one. An experimental plot of this ratio $\mu_{w,\text{app}}/\mu_w$ versus the ratio of working fluid to lubricant viscosity $\mu_w/\mu_o$ is shown in Figure 4.5(a). Consistent with the aforementioned theory, drag reduction is greater for more viscous working fluids.

It is instructive to extract a space-averaged apparent slip length from the torque measurements in order extend results to practical flows (like the pipe flow solved by Equation 4.2). Solving the Navier-Stokes equations in spherical coordinates and applying the Navier slip boundary condition gives the relationship between the measured torque $M$ and the average slip length $b$ as:[154]

$$M = \frac{2\pi}{3} \frac{\mu_u \Omega R^3}{\beta} \left( 1 - \frac{3b}{2R\beta} + \frac{3b^2}{R^2\beta^2} \right) - 2\pi\Omega \mu_u \frac{b^3}{\beta^4} \log \frac{R\beta + b}{b}$$

(4.6)

This equation is numerically solved for the slip length. The results are presented in Figure 4.5(b). A linear fit of $y = cx$ consistent with the scaling of Equation 4.5 yields an $R^2$ value of 0.7874. Instead, a linear fit of the form $y = ax + y_0$ is presented in Figure 4.5(b) alongside lines enclosing 95% confidence intervals for the fit. The fitting parameters are $a = 1.3 \times 10^{-3} \pm 5.2 \times 10^{-4}$ and $y_0 = 0.068 \pm 0.066$ where the error is expressed as 95% confidence intervals ($R^2 = 0.9536$).

The poor fit ($R^2 = 0.7874$) of Equation 4.5 to the data presented in Figure 4.5(b) raises several questions. Physically, one would expect the slip length to converge to zero as the viscosity $\mu_o$ of the lubricant approaches infinity and the surface resembles a solid. Rather, the data tend to a finite value of slip. Slip on solid surfaces has been observed but can only amount to at most tens of nanometers,[153,172] whereas here $y_0 = 0.068$ corresponds to a slip length of 3.3 $\mu$m. The observed intercept and deviation from the expected physics prompts further study and confirmation using different experimental techniques. For example, particle image velocimetry (PIV) can be used to directly measure the slip length on lubricant impregnated surfaces and has been shown as a viable method for measuring slip on superhydrophobic surfaces.[173]
Figure 4.4: Measured drag reduction and slip lengths for varying working fluid to lubricant viscosity ratios. Adapted from Ref [20] with permission of The American Chemical Society (Copyright 2014).

For working fluids with a viscosity around that of the lubricant ($\mu_w < 30 \mu_o$) little or no drag reduction is observed. Experiments at the highest value of $\mu_w/\mu_o$ have characteristic torques three magnitudes greater than those at the lowest (Figure 4.4). Measurements at low $\mu_w/\mu_o$ are thus less sensitive which explains the slight drag reduction seen for the lowest viscosity ratios. As the working fluid becomes more viscous ($\mu_w > 100 \mu_o$) drag reduction is observed. With the most viscous working fluid ($\mu_w = 210 \mu_o$) a drag reduction of 16% is observed which correlates to a slip length of 18 $\mu$m.

As previously mentioned, in this work the slip length $b$ is measured from the top of the lubricant impregnated surface. To understand the implications of this convention, consider the case where a lubricant impregnated surface of thickness $\delta$ is added to the inside of a pipe of radius $R_p$. In this case, the effective pipe radius will be $R_p + b - \delta$. Accordingly, adding a lubricant impregnated surface with $b < \delta$ increases drag and is not advantageous if drag reduction is the main criterion. Schönecker et al. build on this idea and extensively study the implications of such a convention.[22]

Figure 4.6 presents the reported slip lengths of other researchers along with relevant parameters where available. Note that $b/L$ is roughly consistent indicating that in these experiments the effect of viscous dissipation in trapped air or lubricant is negligible. As shown in our experiment (Figure 4.5) at lower viscosity ratios viscous dissipation within the lubricant is important. For a given surface, the regime in which the viscosity ratio af-
Figure 4.5: (a) Plot of the drag reduction percentage vs. the ratio of the working fluid to lubricant viscosity. (b) Plot of the computed apparent averaged slip length vs. the ratio of the working fluid to lubricant viscosity. A linear fit is presented alongside the data enclosing a 95% confidence interval. Modified from Ref [20] with permission of The American Chemical Society (Copyright 2014).

<table>
<thead>
<tr>
<th>Flow geometry</th>
<th>Surface</th>
<th>Viscosity ratio</th>
<th>Solid fraction $\phi_0$</th>
<th>Periodicity $L$ (μm)</th>
<th>Drag reduction DR%</th>
<th>Slip length $b$ (μm)</th>
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<td>400</td>
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<td>Hydrophobized sand</td>
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<td>2100/32*</td>
<td>213</td>
<td>0.36</td>
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<tr>
<td>Cone-plate rheometer</td>
<td>Laser ablated posts</td>
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<td>50</td>
<td>16</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

*Surface comprised a dual-scale texture

Figure 4.6: Comparison of drag reduction and slip lengths reported in literature. Reproduced from Ref [20] with permission of The American Chemical Society (Copyright 2014).

Effects the slip length is dependent on the parameters of the texture following from Equation 4.4.

To date, the highest slip length of 400 μm has been achieved on a superhydrophobic surface (essentially a lubricant impregnated surface with air as a lubricant) by designing robust, high periodicity structures with low solid fraction. In this case the working fluid to lubricant viscosity ratio is 45. One would expect a high slip length could be achieved for
a lubricant impregnated surface by designing a similar texture and impregnating it with a
lubricant.

These results demonstrate that similar to superhydrophobic surfaces, lubricant impregnated surfaces reduce drag in laminar internal flows but have the additional advantage of increased pressure-stability.[7] Consistent with Equation 4.2, significant drag reduction in pipe flow is only expected when the diameter of the pipe is of the order of the slip length. Accordingly, drag reduction using lubricant impregnated surfaces shows immediate promise for application in microfluidics. These results prompt similar studies for turbulent flows in which drag reduction may be achieved by effecting the dynamics of the viscous sublayer.[174] In addition to future studies in the turbulent regime, the dependence on solid fraction should also be confirmed.

Modifying the structure and periodicity of the texture can optimize lubricant impregnated surfaces for drag reduction. For example, grooves that are longitudinal to the flow should offer better drag reduction than those transverse as shown analogously for superhydrophobic surfaces.[175,176] Although lubricant impregnated surfaces show promise for drag reduction, the lubricant can deplete over time due to its solubility in the working fluid[8] and can also drain over time. A lubricant reservoir to replenish the lubricant can overcome these issues.

4.4 Conclusions

We systematically demonstrate drag reduction using lubricant impregnated surfaces for a variety of lubricant to working fluid viscosity ratios using cone and plate rheometry. The free surface of the working fluid in the rheometer is carefully controlled to prevent error. Consistent with theory, the drag reduction is highest for the most viscous working fluid ($\mu_w = 210\mu_o$), and its measured slip length is $18 \mu\text{m}$. Performance can be improved by optimizing the texture design and longevity issues associated with solubility and drainage
can be overcome by designing a replenishing lubricant reservoir.
Chapter 5

Lubricant Impregnated Surfaces in Electrochemical Systems

A Gravity Induced Flow Cell (GIFCell) is a new flow battery architecture which has the potential to provide low-cost energy storage to enable widespread integration of renewable energy sources into the power grid. A key challenge is to achieve uniform flow with energy dense non-Newtonian flowing electrodes in the GIFCell. In addition, high carbon black loading in the suspension is desired to increase electronic conductivity and discharge power; however, high carbon loadings impart a significant increase in yield stress of the suspension which prevents the suspension from flowing. Lubricant impregnated surfaces are demonstrated as a highly slippery surface to provide adequate slip for yield-stress suspensions (yield stress, $\sigma_y > 3$ Pa). In particular, a lithium polysulfide (Li-PS) suspension with 0.75v% carbon black ($\sigma_y > 4$ Pa) moves freely on a lubricant impregnated surface while the same suspension does not flow on commercial PTFE. A half-flow GIFCell based on lithium as the anode and Li-PS as the catholyte operated in an intermittent flow mode was demonstrated. Energy efficiencies of $> 75\%$ was achieved.
5.1 Introduction

Integrating renewable power sources such as solar and wind to the electric grid\textsuperscript{[177]} can reduce the reliance on fossil fuel, a diminishing natural resource.\textsuperscript{[178]} However, large-scale energy storage is required to overcome the intermittency of these sources to ensure reliability in providing electricity to meet demand.\textsuperscript{[179–181]} It is predicted that such an electric system can provide 90-99.9\% of the energy required by grid by 2030 at today’s cost through optimization of generation and storage technologies.\textsuperscript{[182]} Redox flow batteries (RFBs) are a promising technology for large-scale energy storage due to their potential to meet the cost target of $100 per kWh at a system level and their ease of scalability.\textsuperscript{[183]} Today, most RFBs are based on flowable electrodes comprising dissolved redox molecules (i.e. vanadium ions) in an aqueous solution. However, the need of expensive ion-selective membranes, the low solubility of active materials (<2 M), and the low cell voltage of <1.2 V (limited by the electrolysis of water) offset any advantages of RFB.

Flow electrodes based on semi-solid suspensions,\textsuperscript{[184–186]} on the other hand, can increase the energy density of RFBs by an order of magnitude and allows the use of high voltage insoluble materials such as lithium iron phosphate. The principle is to suspend a continuous percolating network of nano-sized carbon to provide electronic conductivity to the suspended active materials in the electrolyte. Such continuous conducting networks increase the overall change-transfer area and reduces the molecular diffusion length between

Figure 5.1: Schematic diagrams of (a) a conventional flow cell and (b) a gravity-induced flow cell.
electroactive regions. However, these suspensions have high yield-stresses (often $> 3$ Pa) and non-Newtonian properties and can be damaged by the shearing action of a pump. To minimize the shearing of these suspensions during flow an architecture based on a gravity-induced flow mechanism (gravity-induced-flow-cell, GIFCell) is utilized to move the active materials across the active region. The GIFCell requires just one mechanical actuator as opposed to two pumps (Figure 5.1). This eliminates the contact between the solvent and the pump and increases the pump’s durability. Another advantage of the GIFCell is that shearing of the suspension caused by a pump is avoided. Pumping can induce significant shearing on the flow electrode, resulting in the decrease in electrochemical energy efficiency and pumping energy losses. Finally, there is no mixing between the charged and discharged material as seen in conventional RFBs which can result in a drop of the cell voltage.\cite{187}

Using higher loadings of carbon black (KB) in the suspension is favorable to extract energy at a faster current density (or C-rate) and lower polarization. The increase in KB concentration increases the electronic conductivity of the suspension resulting in a higher rate-capability or a higher capacity at the same rate for the suspension during electrochemical cycling. In Figure 5.3(a), $\sim 250$ mAh/g of specific capacity is achieved for a 0.5vol% KB loading while $\sim 750$ mAh/g was achieved for a 0.75vol% KB loading. In addition, lower KB loadings have higher polarization thus lowering the energetic efficiency of the cell. While higher KB loadings offer electrochemical advantages, higher loadings of KB contribute to higher yield-stresses for the suspension. Currently, the most repellant commercially available surfaces (e.g. PTFE) are not able to provide high enough slip for semi-solid suspensions with yield stresses in excess of 2 Pa ($\sigma_y > 2$ Pa). For instance, a 0.5vol% of KB in a lithium polysulfide (Li-PS) suspension ($\sigma_y = 1.33$ Pa) can move freely on a PTFE surface but a 0.75vol% of KB ($\sigma_y = 4$ Pa) gets pinned to the same surface (Figure 5.3(c)). The pinning of the suspension prevents a stable flow of the suspension and reduces the active material available in the cell since active material is left stuck to the cell walls.

In this chapter the design and implementation of lubricant impregnated surfaces to
reduce drag and adhesion for high yield-stress suspensions in a flow cell (in particular the GIFCell) is detailed. Lubricant impregnated surfaces have been shown to exhibit low contact angle hysteresis,\cite{4,7,15,25,50,65,66,82,161,188} be self-cleaning,\cite{15,126,127} and promote dropwise condensation,\cite{8–10} anti-icing,\cite{12,13,68,116,164} and anti-fouling.\cite{16–18,100,144,162} More recently, lubricant impregnated surfaces have been shown to provide drag reduction for internal flows of Newtonian liquids.\cite{20,22} Two criteria must be satisfied: (1) the impregnating liquid lubricant must remain in the texture surfaces during operation, (2) the lubricant must be electrochemically inactive. The combination of Krytox as the lubricant and a nanoporous PTFE membrane as the texture surface is suitable as a lubricant impregnated surface. Figure 15.3(c) shows a 0.75vol% KB suspension able to freely move on the lubricant impregnated surface.
Figure 5.3: (a) 2nd discharge-charge profiles of 2.5M Li$_2$S$_8$(Catholyte)-Li(Anode) chemistry in a Swagelok cell type configuration with different KB loading cycled galvanostatically at a C-rate of 1/5 hr$^{-1}$. The electrode thickness is 560 µm. (b) Yield stresses for various Li-PS species. (c) Time-lapse comparing a 2.5M Li$_2$S$_8$ suspension with 0.75 vol% KB on flat PTFE and the Krytox LIS. In both cases, supporting salts (0.5M LiTFSI and 1wt% LiNO$_3$) are included in the suspension.

5.2 Experimental Procedure

Handling and storage of suspension components, GIFCell assembly, rheological testing, and electrochemical testing were all conducted in an Argon-filled glove box (MBRAUN, Newburyport, MA, US) with oxygen and moisture levels maintained below 5 and 1 ppm, respectively.
5.2.1 Preparation of Electrolyte and Catholyte

An electrolyte solution was formulated by adding a 1 wt% of lithium nitrate (LiNO$_3$, Sigma-Aldrich) and 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich) to triglyme (Sigma-Aldrich). The addition of LiNO$_3$ improves the passivation of lithium metal by forming a non-reactive surface to dissolved polysulfides on the lithium, which reduces capacity fading.[189]

The catholyte was then prepared in the following steps. Lithium sulfide (Li$_2$S, Alfa) and sulfur (Sigma-Aldrich) was added to the electrolyte solution to prepare a sulfur concentration of 2.5 M in the solution. The mixture was stirred mechanically in an argon gas-filled glove box at a temperature of 60°C for 12 hours to obtain a dark brown lithium polysulfide (Li$_2$S$_8$) solution. Conductive carbon black (KB, Ketjen, ECP600JD, specific surface area of 800-1200 m$^2$/g, Azko Nobel Polymer Chemicals LLC, Chicago, Illinois, US) was used to provide an electronic conducting network to the otherwise insulating sulfur species. KB was weighed and mixed in a 20 ml glass vial. Half of the Li$_2$S$_8$ solution was added to the vial. KB was then added after which the remaining Li$_2$S$_8$ solution was added. This method of mixing was found to yield a more uniform suspension than by adding the solution directly to KB. The former exhibits a lower yield stress under the same viscometric testing conditions. The resulting suspension was then sealed in a vial by black insulating tape and removed from the glove box. The vial was subjected to sonication in an ultrasonic bath for 60 minutes to obtain a homogenous suspension of the catholyte.

5.2.2 Preparation of Lubricant Impregnated Surfaces

A PTFE membrane (Sterlitech Corporation, United States) with 200 nm pores is lowered into a bath of Krytox 1506 (DuPont) at 10 mm/min. When withdrawing the membrane above a critical capillary number $Ca_c$ an excess film is viscously entrained. During battery operation, such an excess film will be dragged by the electrolyte and compromise conductivity. For capillary numbers $Ca_c = \mu_o V_{crit} \gamma < 10^{-4}$ no excess film is viscously
entrained. Here, $\mu_o$ is the viscosity of the lubricant, $\gamma$ its surface tension, and $V_{crit}$ the critical withdrawal speeds. Accordingly the PTFE membrane is withdrawn at a rate of 2 mm/min.

The viscometric behavior of the different solutions and semi-solid suspensions was measured using a Malvern Kinexus Pro torsional rheometer enclosed in a glove box. Steady shear viscometry tests were performed using a smooth parallel plate geometry ($D = 40$ mm; mean roughness $R_q = 0.36 \mu$m). All tests were performed at $25^\circ$C and the temperature was regulated with a Peltier plate system. All samples were pre-sheared at $100 \text{s}^{-1}$ prior to measurement and left to equilibrate until the normal force had relaxed ($\sim 15$ min). Steady shear tests were performed with decreasing applied shear rates as described by Ovarlez et al. to insure the existence of a simple yield stress for the material and to avoid possible transient shear banding. In addition, following the protocol proposed by Yoshimura and Prud’homme, the same sample is tested at four different gaps (1, 0.66, 0.5 and 0.4 mm respectively) to probe and correct for slip effects. If the flow curves at different gap distances are approximately equivalent, the material does not slip. If gap-dependent rheology is observed, a correction needs to be applied to extract the true shear rate applied on the sample at each value of the applied stress.

5.2.3 Cyclic Voltammetry Experiments for Measuring Electrochemical Stability of Lubricant

Swagelok type cells with 0.56 mm deep and 0.55 mm diameter circular wells were used. Lithium was used as the counter and reference electrode. A Tonen separator soaked with the electrolyte (0.5 M LiTFSI, 1wt% LiNO$_3$ in triglyme) separated the lithium from the cathode. The cathode consisted of 5 $\mu$L of solution of interest with and without carbon fabric (AvCarb, 1071 HCB). In some tests, the cathode was a mixture of the lubricant (3 $\mu$L) and electrolyte (1 $\mu$L) in a volumetric ratio of 3:1. The voltage was swept between 1.6 and 2.8 V with respect to Li/Li$^+$, at a sweep rate of 10 mV/s. All cell assembly was
5.2.4 Cycling Experiments in Non-flowing Half-cells

Swagelok type cells with 0.56 mm deep wells were used. A Tonen separator soaked with electrolyte was used. All cell assembly was performed inside an argon-filled glovebox. The cells were tested on a Solartron potentiostat operating a 1400 Cell Test System.

5.2.5 Assembly of GIFCell with Lubricant Impregnated Surfaces

Prior to assembly of the GIFCell, the following procedures were carried out. The stainless steel current collector that would be in contact with the cathode material was sputtered with gold to reduce interfacial impedance. The lubricant impregnated surface was placed on the flow channels as indicated on Figure 5.8.

The GIFCell parts were then assembled in the glove box. A thin foil of lithium was placed on a current collector and then wrapped with a micro-porous polymer separator (Tonen, Tonen Chemical Corporation, average pore size of <100 nm). The wrapped current collector was then secured onto one plate of the GIFCell. A drop of electrolyte was introduced to wet the separator. The two plates of the GIFCell were secured using bolts and nuts. The catholyte (Li$_2$S$_8$ suspension) was introduced into one side of the channel by injection with a syringe through the port. Finally, the tubing was attached to the ports to create the fully sealed GIFCell.
Figure 5.4: (a) Schematic of a flow electrode flowing in a channel covered with lubricant impregnated surfaces. The interface between the lubricant impregnated surface and flow electrode can take three distinct morphologies. (a) The encapsulated state is characterized by the lubricant encapsulating the solid including spreading everywhere between the solid and working fluid. (b) In the emerged state lubricant fills the porous solid but does not spread completely between the solid and working fluid. (c) In the impaled state the flow electrode preferentially wets the solid and displaces the lubricant. The encapsulated state is most desirable and the impaled state the least.

5.3 Design of Lubricant Impregnated Surfaces for Electrochemical Devices

In this section, the theory behind designing a lubricant impregnated surface for this application is discussed. A lubricant impregnated surface is composed of a porous or textured solid and a liquid lubricant that is stabilized by capillary forces as depicted in Figure 5.4. On a typical surface, for example a flat PTFE surface, even a small amount of roughness causes pinning especially with thick suspensions as depicted in Figure 5.4. Lubricant impregnated surfaces however provide a smooth interface over which the suspension can slide.

In order to function as designed, the lubricant and working fluid should be immiscible otherwise no interface exists. Second as depicted in Figure 5.4, a working fluid in contact with a porous solid and lubricant can form three distinct morphologies. The encapsulated state is characterized by the lubricant encapsulating the solid including spreading...
everywhere between the solid and working fluid. This state maximizes the working fluid’s mobility.\[4\] In contrast, the working fluid may preferentially wet the solid and displace the lubricant to form the impaled state that does not offer any advantages. In the emerged state, lubricant fills the porous solid but does not spread completely between the solid and working fluid. Interfacial energies of the system determine which of these three states are favored thermodynamically. In the following discussion:

- interfacial tensions are denoted by $\gamma_{ow}$, $\gamma_{os}$, and $\gamma_{ws}$ for the lubricant-working fluid, lubricant-solid, and working fluid-solid interfaces respectively

- surface tensions are denoted by $\gamma_o$ and $\gamma_w$ for lubricant and working fluid interfaces respectively

- the fraction of solid that is not covered by the lubricant is denoted by $\phi$

- the total surface area of the solid divided by its projected area is the Wenzel roughness $r$

The total interfacial energy of each state can be written in terms of the interfacial energies and geometric parameters:

- $E_1 = \gamma_{ow} + r\gamma_{os}$ for the encapsulated state

- $E_2 = (1 - \phi)\gamma_{ow} + (r - \phi)\gamma_{os} + \phi\gamma_{ws}$ for the emerged state

- $E_3 = r\gamma_{ws}$ for the impaled state

To achieve the desirable encapsulated state, the lubricant impregnated surface must be designed such that the encapsulated state is favored thermodynamically ($E_1 < E_2$ and $E_1 < E_3$). To start, the impaled state is avoided if both $E_1 < E_3$ and $E_1 < E_2$. In the special case of a porous solid, the Wenzel roughness $r$ is infinite\[50\] and these two conditions reduce simply to $\gamma_{os} < \gamma_{ws}$. Next, two versions of Young’s equation for both a drop of lubricant and a drop of working fluid on the solid are written:
\[ \gamma_s - \gamma_{os} - \gamma_i \cos \theta_{os} = 0 \]
\[ \gamma_s - \gamma_{w3} - \gamma_w \cos \theta_{w3} = 0 \]

where \( \theta_{os}, \theta_{ws} \) are the equilibrium contact angles of a lubricant drop and a water droplet on the solid respectively. Using the equation above the condition \( \gamma_{os} < \gamma_{ws} \) can be rewritten \( \gamma_o \cos \theta_{os} > \gamma_w \cos \theta_{ws} \). This condition is more tractable as \( \gamma_o \) and \( \gamma_w \) can be found in literature for most liquids and \( \theta_{ws}, \theta_{os} \) readily measured.

In our system, the lubricant is Krytox 1506 (\( \gamma_o = 17 \) mN/m) into porous PTFE (\( \gamma_s = 20 \) mN/m). The system is demonstrated for nine common solvents (\( \gamma_w = 25 - 72 \) mN/m): acetonitrile, dichloromethane, diglyme, dimethyl sulfoxide (DMSO), polypropylene carbonate (PC), tetraethylene glycol dimethyl ether (TEG-DME), tetrahydrofuran (THF), triglyme, and water. All solvents used as well as Krytox wet PTFE (\( \theta_{os} < \pi/2 \) and \( \theta_{ws} < \pi/2 \)) and the condition \( \gamma_o < \gamma_s < \gamma_w \) meaning that the impaled state will be avoided.

The roll-off angle of a 5 \( \mu \)L drop of solvent on the Krytox/PTFE lubricant impregnated surface is \(< 5^\circ\) for all nine tested solvents which strongly suggests the encapsulated state whereas a higher roll-off angle is indicative of the emerged or impaled states.\[^4\] It is possible that such a roll-off test doesn’t allow the system to achieve a steady-state thermodynamic equilibrium. Accordingly, the Krytox/PTFE lubricant impregnated surface is submerged in each solvent for 5 days. The Krytox impregnated surface is then removed and a droplet of the test solvent placed on the lubricant impregnated surface. In all cases, the lubricant impregnated surface retained its slippery characteristics (\(< 5^\circ\) roll-off) and indicates that the test solvent doesn’t displace Krytox. In addition, Krytox remains impregnated in the porous PTFE demonstrating its immiscibility with all solvents. Silicone oil, a common lubricant, on the other hand is miscible with many of the solvents.

The encapsulated state exists over the emerged state provided \( E_1 < E_2 \). This condition can be rewritten as \( S_{ow(s)} = \gamma_{ws} - \gamma_{ow} - \gamma_{os} \). Here \( S_{ow(s)} \) denotes the spreading coefficient of the lubricant on the solid in the presence of the working fluid. In particular, the
spreading coefficient $S_{ow(s)}$ contains no geometrical parameters and is a function of only the three materials involved. Again, Young’s equation can be used to write $S_{ow(s)} > 0$ as

$$\gamma_o \cos \theta_{os} - \theta_{ow} > \gamma_w \cos \theta_{ws}.$$ 

The contact angle of a drop on a flat surface can take a range of values bounded by the advancing and receding angle so that in measuring the equilibrium contact angles $\theta_{os}$, $\theta_{ws}$ isn’t straightforward.

Instead, $S_{ow(s)} > 0$ is demonstrated by observing that a drop of Krytox spreads on a flat PTFE surface in a background of solvent. In this experiment 2 µL drop of Krytox is deposited on flat PTFE, and the substrate is submerged in a sealed container containing a test solvent. After 24 hours, the substrate is removed and in all cases the Krytox drop has spread indicating that $S_{ow(s)}$ for all solvents is positive.

Now that the thermodynamic stability from a wetting perspective has been demonstrated, electrochemical stability is required. Although the lubricant and the working fluid are designed to be immiscible, there is always slight miscibility that can possibly instigate unwanted side reactions. For example, although water and hexadecane are considered insoluble, it is well established that 0.9 ppb of hexadecane dissolves in water at 25°C.\textsuperscript{192} To ensure against this, lubricants should be screened for electrochemical activity in the voltage window of the cell’s operation. In the case of the Li-PS GIFCell, the lubricant should be electrochemically inactive over a voltage window of 1.6 to 2.8 V with respect to Li/Li$^+$. Hence, performing a cyclic voltammetry examination on the lubricant and the mixture can show presence of parasitic current flow. Figure 5.5 shows the cyclic voltammograms of the lubricant Krytox and mixtures of Krytox and the working electrode. The negligible current densities ($<1.5 \mu A/cm^2$) over the voltage window are significantly less than the desired electrochemical reactions ($>0.1 mA/cm^2$); hence the lubricant Krytox is not significantly electrochemically active.

Finally, an excess of lubricant should not exist on the lubricant impregnated surface during any part of its operation. An excess film will drain over time and disturb the efficiency of the cell. To prevent this, the lubricant impregnated surface is prepared via a
Figure 5.5: Cyclic voltammogram of the solvent triglyme as well as a variety of candidate lubricants performed at a scan rate of 10 mV/s. Lithium is used as the counter and reference electrodes. A Tonen separator wetted with the electrolyte is used in all the tests.

dipcoating process whereby no excess film is viscously entrained.

5.4 Application of Lubricant Impregnated Surfaces to the GIFCell

Lithium-sulfur (Li-S) chemistry is used due to its high theoretical energy density (2567 Wh/kg and 2199 Wh/L for elemental Li and S as reactants) and low material costs\textsuperscript{193} to demonstrate operation of the GIFCell with lubricant impregnated surfaces. In particular, employing lubricant impregnated surfaces on the flow channels of the flow cell is relevant for Li-S chemistry as higher energy density can be obtained by utilizing the full regime from S to Li\textsubscript{2}S. The solubility of Li\textsubscript{2}S\textsubscript{x} (1 < x < 8) in ether-based solvents changes during the electrochemical cycling of S to Li\textsubscript{2}S. For instance, high order Li-PS species (Li\textsubscript{2}S\textsubscript{8} to Li\textsubscript{2}S\textsubscript{4}) are soluble in ether-based solvent while low order Li-PS species (Li\textsubscript{2}S\textsubscript{2} and Li\textsubscript{2}S) are not. This affects the rheology of the suspension as suspensions with more dissolved Li-PS species have higher viscosities compared to the those with less. However, lubricant impregnated surfaces are able to accommodate to these differences and provide a slippery surface for all the species throughout the full cycling range.
Figure 5.6: Time-lapse of the GIFCell with lubricant impregnated surfaces demonstrating the flow electrode’s mobility even after 25 cycles. Without lubricant impregnated surfaces, the flow electrode does not flow. Here the flow electrode is 2.5M Li$_2$S$_8$ with 0.75vol% of KB.

In this test system, intermittent-flow mode is used rather than a continuous flow mode for the GIFCell to enable higher energy efficiency.[194] In the intermittent-flow mode shown in Figure 5.7(a) the aliquot remains stationary during electrochemical cycling. Upon completion of the cycle, the next aliquot flows into the electrochemical active region by tilting the GIFCell. Figure 5.7(b-d) shows the potentiostatic cycling performance of the Li-PS in the GIFCell. Energy efficiency of ∼ 93% is achieved for the first cycle, which shows that energy can be effectively transferred in and out of the GIFCell. The current density of 0.65-0.7 mA/cm$^2$ for the first 6 minutes corresponds to a theoretical C-rate of 1/20 h$^{-1}$ for the sulfur cathode. The current density then decays to ∼ 0.2 mA/cm$^2$ eventually, giving a discharge specific density of 777 mAh/g over the duration of 20 hrs. This lower current density indicates low order Li-PS (Li$_2$S$_2$ and Li$_2$S). In the second cycle, a higher current density of 1.1 mA/cm$^2$ is obtained corresponding to a theoretical C-rate of 1/12 h$^{-1}$. This may be due to presence of sulfur species at the start of the discharge, Li$_2$S$_8$ vs. Li in the first cycle and S$_8$ vs Li in the second cycle. The second aliquot is then moved into the active region by tilting the GIFCell. Successful electrochemical cycling shows that the lubricant does not spread onto the separator and current collector in the electroactive region. Otherwise, an insulating layer would prevent the operation of the GIFCell. The overall specific capacity degrades over the course of operation and is limited by the shuttle mechanism and the unstable solid-electrolyte interface at the lithium.
Figure 5.7: (a) Schematic of the GIFCell operating in intermittent flow mode. The GIFCell is horizontal when undergoing electrochemical cycling and tilted to move the next aliquot into the active region. (b) Energy and current density against time during electrochemical cycling for the 1st aliquot. (c) Potentiostatic cycling of the GIFCell-LIS with 2.5M Li$_2$S$_8$ suspension (Catholyte)-Li (Anode). The suspension consists of 0.75vol% of KB, 0.5M LiTFSI and 1wt% LiNO$_3$. The flow-electrode thickness is 1 mm. An intermittent flow mode is used where the 1st aliquot flows into the electroactive region by gravity and remains during cycling. (d) The specific capacity of the GIFCell during discharge and the round-trip efficiency of the GIFCell-LIS for various cycle numbers.
Figure 5.8: A blowout schematic of the GIFCell with a lubricant infused surface.

5.5 Characterizing Slip

5.5.1 As-Mixed Suspension

In an effort to accurately characterize the effect of lubricant impregnated surfaces, rheometry can be used to deduce the effect of slip. The lithium polysulfide suspension exhibits a yield stress. To quantify this, the as-mixed suspension is tested in a Malvern Kinexus Pro torsional rheometer enclosed in an inert Argon environment. The parallel plate geometry had a 40 mm diameter and the bottom surface is maintained at 25 °C at all times.

Figure 5.9 shows a plot of stress vs. strain rate for the 0.75vol% KB suspension. Data is collected at gaps of 660 µm, 500 µm, and 400 µm. In this experiment steel surfaces sputtered with gold are used because previously they have been reported to exhibit no slip with similar suspensions. The stress vs. strain dependence is found to not vary.

A Herschel-Bulkley model is used to fit the relationship between the stress \( \tau \) and strain...
Figure 5.9: Shear stress vs. apparent strain rate for the flow of 2.5M lithium polysulfide in triglyme with 0.75vol% KB. The no slip surface is gold sputtered on stainless steel. The stress vs. strain rate is independent of gap for the no slip surface. The variation of measured stress with apparent strain rate with the lubricant impregnated surface is a signature of slip.

The gap dependence of the flow data in Figure 5.9 is indicative of slip. The effect of slip can be accounted for by following the analysis of Yoshimura and Prud’homme.\cite{[191]} Figure 5.10 shows a schematic that decouples the apparent strain rate \( \dot{\gamma}_a R \) into a contribution due to the real strain rate of the material \( \dot{\gamma}_R \) and the slip velocity \( u_s \). It is straightforward to write a kinematic condition that holds for a given stress \( \tau \):

\[
\dot{\gamma}_a R(\tau_R) = \dot{\gamma}_R(\tau) + \frac{2u_s}{H} 
\]  

(5.2)

Here \( \tau \) is the yield stress and \( k \) is referred to as the consistency index. A shear thinning fluid has \( n < 1 \) whereas a shear thickening fluid has \( n > 1 \).

In this case, the model returns \( \tau_0 = 3.58 \pm 0.20 \) Pa, \( k = 2.05 \pm 0.22 \) Pa·s\(^n\), and \( n = 0.39 \pm 0.022 \) with an \( R^2 \) value of 0.9973. Here the errors represent a 95% confidence interval. In this case \( n < 1 \) indicates that the suspension is shear thinning.

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Figure 5.10: Schematic distinguishing the apparent strain rate $\dot{\gamma}_a$ from the true strain rate in the material $\dot{\gamma}$. The slip velocity is denoted by $u_s$ and the gap by $H$.

where $H$ is the gap height and the subscript ‘$R$’ denotes a parameter evaluated at the cones radius. For each gap Equation 5.5.1 shows that the apparent strain rate $\dot{\gamma}_aR$ can be plotted against $2/H$ and the slip velocity $u_s$ can be readily deduced from the slope.

However, in order to use Equation the corrected shear stress $\tau_R$ must be calculated for each apparent strain rate $\dot{\gamma}_aR(\tau)$ and gap $H$. By integrating the torque experienced and use of a clever change of variable (see Ref [191] for details):

$$\tau_r = \frac{T}{2\pi R^3} \left( 3 + \frac{d\log T}{d\log \dot{\gamma}_aR(\tau)} \right) \quad (5.3)$$

By deducing the corrected stress $\tau_r$ for each apparent strain rate $\dot{\gamma}_aR$, Equation 5.5.1 can then be applied to get the relationship between slip velocity $u_s$ and stress $\tau$ by plotting the apparent strain rate $\dot{\gamma}_aR$ against against $2/H$. The slip velocity $u_s$ can be readily deduced from the slope.

Figure 5.11 shows the relationship of slip velocity as a function of stress for the lubricant impregnated surface, a flat Teflon surface, and the no-slip gold surface. A linear model predicts a minimum stress $\tau_c$ which must be overcome to slip to occur on lubricant impregnated surfaces. The fits are presented in Figure 5.12. The critical stress require for slip on the lubricant impregnated surface is 0.57 Pa which is lower than for the tested Teflon surface at 1.26 Pa.
5.5.2 Discharged Suspension

It has been noted that discharging into the precipitation regime causes a drastic increase in the viscosity and yield stress of the flow electrode. In order to understand this phenomena, rheometry is used to deduce the yield stress as a function of state of charge. Rheology requires high volumes of material, so to this end a high volume discharge cell is built. The cell is machined from stainless steel and uses a teflon spacing to maintain a 1.6 mm gap. The cell is capable of discharging 10 mL of material and is shown in Figure 5.13.

Figure 5.14(a) shows discharge curves for several samples in the high volume discharge cell. At most the suspension is discharged to 920 mAh/g. For all tests discharges are performed galvanostatically at 0.1 mA/cm$^2$. All curves except the 920 mAh/g curve are shifted vertically down for clarity.

Figure 5.14 plots the yield stress as a function of state of discharged capacity. Yield stress is determined using a parallel plate Malvern Kinexus Pro in which three gaps are
Figure 5.13: Photos of the high volume discharged cell as assembled in an inert Argon environment. (a) Closed cell showing. Fiberglass screws secure the cell. (b) Bottom half the cell comprised of stainless steel, lithium metal cathode, Tonen separator, Teflon gasket, and suspension. (c) Top half of the cell after discharge. Even visually the suspension looks thicker.

Figure 5.14: a) Galvanostatic discharges performed at a current density of 0.1 mA/cm\(^2\) of the 2.5M lithium polysulfide in triglyme with 0.75 vol% KB. (b) Yield stress as a function of discharged capacity. Yield stress was determined in a parallel plate rheometer in which three gaps are measured to yield a corrected yield stress. The as-mixed sample exhibits a yield stress around 4 Pa. Throughout the soluble regime the yield stress seems to be unchanged. In the insoluble regime the yield stress increases.
Figure 5.15: Slip velocity vs. stress for the flow of 2.5M lithium polysulfide in triglyme with 0.75vol% KB discharged to 920 mAh/g on a lubricant impregnated surface and gold surface with linear fits.

![Slip Velocity vs. Stress](image)

<table>
<thead>
<tr>
<th></th>
<th>(\beta) (mm(\cdot)s/kg)</th>
<th>(\tau_c) (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIS</td>
<td>0.1801</td>
<td>1.16</td>
</tr>
<tr>
<td>Gold</td>
<td>0.0768</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 5.16: Parameters for the fits presented in Figure 5.11.

to around 12 Pa. The precise functional dependence of yield stress on state of charge is unclear, and further experimentation needs to be carried out to delineate the change in rheology with discharge.

In addition, the rheology of a suspension discharged to 920 mAh/r is measured on gold and a lubricant impregnated surface to yield a plot of slip velocity vs. stress by the analysis mentioned above. The results are presented in Figure 5.15. As compared to the data of the as-mixed sample presented in Figure 5.12, the critical stress \(\tau_c\) is higher for the discharged sample on the lubricant impregnated surface. In addition, the discharged sample slips on gold whereas the as-mixed sample did not.

It should be noted that the discharged suspension is extremely heterogeneous. After the discharge in the high volume cell, a hard, thick layer can be observed on the stainless steel cathode. There is also a liquid phase present. In these experiments, all of the material is
collected and mixed by preshearing before starting the rheology tests.

In addition, the observed rheology should depend on the state of stress during discharge. In this case, a static cell is used, but in the case of a flow cell the suspension undergoes shear while being discharged. That should alter its rheology and needs to be investigated further.

5.6 Outlook

Flow electrodes based on semi-solid suspensions expand the material space for flow batteries beyond traditional dissolved redox molecules. The inevitable yield stress of semi-solid flow electrodes can be addressed by employing lubricant impregnated surfaces. Introducing slip at the interface between a flow battery electrode and the internal surface of a flow channel by using lubricant impregnated surfaces enables flow in the GIFCell and in addition prevents the loss of material by contact-line pinning. Even for pump driven flow electrodes, lubricant impregnated surface should decrease the pumping power required and increase the robustness of the cell and enable new chemistries involving more viscous and higher-yield stress flow electrodes.

In addition, the rheology of the flow electrode has been shown to change as it is discharged. The mechanism for this is quite complex and likely depends on the rate of shear the suspension undergoes while it is being discharged. The most accurate way to characterize this phenomenon is to build a setup in which rheology can be measured while the suspension is discharged. For example, a parallel plate rheometer can be modified whereby the bottom surface is an ion separator and lithium anode. A practical way to maintain a closed circuit to discharge the suspension may be difficult to achieve but would yield detailed and useful results.
Chapter 6

Conclusions and Future Work

This thesis has departed from typical approaches to altering the wettability of surfaces. It has explored two advances to control a liquid’s interaction with a surface: 1) deflectable members that enable anisotropic wetting properties and 2) lubricant impregnated surfaces comprised of a porous surface and liquid lubricant.

The first part of this thesis considered anisotropic wetting resulting from deflectable members and the observation that butterfly scales deflect as a water drop moves on the wing of the butterfly. A model has been proposed that incorporates scale deflection, the intrinsic wettability of the scales, and the amount of contact the water drop makes with the butterfly. The roll-off behavior of seven butterfly species from around the world was shown to correlate well with the proposed mechanism of pinning.

Deflectable structures provide a new route to control wettability. A method for fabricating synthetic scales based on carbon nanotube forests was presented. Like the scales of a butterfly, the CNT scales deflected as a water drop moved across their surface. The CNT scales showed roll-off anisotropy ($6.7^\circ \pm 1.9^\circ$ against the scales and $4.4^\circ \pm 0.5^\circ$ with the scales) but did not achieve as high roll-off anisotropy as the *Morpho aega* butterfly ($42.4^\circ \pm 5.2^\circ$ against the scales and $15.6^\circ \pm 1.2^\circ$ with the scales). Further investigation is needed to optimize these structures to match and exceed the performance of the butterflies.
The second part of this thesis reviewed and expanded on lubricant impregnated surfaces. It explained how to achieve a stable lubricant impregnated surface and discussed its basic features including the wetting ridge and lubricant cloak. A broad range of applications of lubricant impregnated surfaces was proposed, with potentially wide-reaching benefits in fields such as transportation, agriculture, energy, construction, and medical devices.

The specific use of lubricant impregnated surfaces for Newtonian drag reduction was investigated. A scaling model that incorporates the viscosity of the lubricant and elucidates the dependence of drag reduction on the ratio of the viscosity of the working fluid to that of the lubricant was presented. The model was validated by experiments conducted in a cone and plate rheometer where a drag reduction of 16% is measured.

Finally, lubricant impregnated surfaces were applied to electrochemical systems. Measurements quantified how lubricant impregnated surfaces improve the flowability of a non-Newtonian lithium polysulfide flow electrode in which electronic conductivity is imparted by carbon particles. A framework for the design of such surfaces for a wide range of flow electrode solvents was used to incorporate lubricant impregnated surfaces into a Gravity Induced Flow Cell (GIFCell) prototype to enable the flow of highly conductive suspension.

The GIFCell demonstrates a new application for lubricant impregnated surfaces and shows a promising future for the technology. Rheological experiments revealed that the yield stress of lithium polysulfide flow electrodes is approximately unchanged in the soluble regime but increases with further discharge when precipitated species form. The precise functional depends of yield stress and other rheological properties on state of charge remains to be studied. Up until this point, flow battery models have considered that rheology is constant with state of charge, so this finding prompts studies to understand the effects of flow electrode thickening.

This body of work expands the toolbox of surface engineers to design surfaces with
new properties and for new applications where the interaction between a liquid and a solid is important.
References


