Influence of Surface Texture on the Variation of Electrokinetic Streaming Potentials

Li Cheng, Bei Fan, Zichen Zhang, and Prabhakar Bandaru*

ABSTRACT: The electrokinetic streaming potential ($V_s$) obtained through electrolyte flow in a microchannel is shown to be related to the underlying surface pattern. Pillar, mesh, and groove patterns were studied for comparing the relative magnitudes of the $V_s$ with air-/liquid-filled surfaces. A record value of the related figure of merit, in terms of the developed $V_s$ per-unit applied pressure, of $\sim 0.127$ mV/Pa, was observed in a mesh texture liquid-filled surface (LFS) impregnated with an electrolyte-immiscible oil. The study indicated that increasing the solid fraction of the pattern surface decreases the effective slip length while enhancing the overall channel $\zeta$ potential. Consequently, maximizing the obtained $V_s$ implies a balancing of the slip with the surface potential, with plausibly more significance of the latter. The work has implications for higher-efficiency electrical voltage sources.

INTRODUCTION

The generation of electrical voltages through aqueous electrolyte flow on charged surfaces is of both scientific and technological interest for obtaining insights into surface-fluid interactions as well as for new energy sources.3–6 The underlying phenomena involve the attraction of counterions in the bulk electrolyte to the charged surface, forming an electric double layer (EDL). The electrical current from the mobile ions in the EDL and the related separation of the electrical charges are relevant electrokinetic effects. The charge separation is manifested through a streaming potential ($V_s$) proportional to the pressure difference ($\Delta P$) applied to the liquid electrolyte along the channel length, through the Helmholtz–Smoluchowski (H–S) relations,7 i.e., $V_s = \frac{\Delta P}{\eta \varepsilon} \zeta$.

Here, the flowing electrolyte contributions are considered through its dielectric permittivity $\varepsilon = (\varepsilon_r \varepsilon_0)$, where $\varepsilon_r$ is the vacuum permittivity, $\varepsilon_0$ is the relative permittivity, $\eta$ is the dynamic viscosity, and $\sigma$ is the electrical conductivity of the electrolyte, while the substrate interactions of the electrolyte are indicated by the $\zeta$ potential ($\zeta$), defined as the magnitude of the electrical potential at the shear plane.

Two aspects are important for the definition of $\zeta$, i.e., (i) the screening of the electrical field from the charge at the surface (from the Gauss law) in terms of a distance, parameterized through the Debye length ($\lambda_D$) scale, and (ii) the distance away from the surface at which fluid motion first occurs, i.e., the shear plane. With respect to the latter, the H–S relation as stated is strictly applicable for liquid flow over hydrophilic surfaces, corresponding to a no-slip boundary condition (BC).

At the shear plane, there is finite liquid electrolyte velocity, charge motion, and hence potential variation along the channel length, which contributes to the $V_s$. The potential at a particular point in the electrolyte, close to the surface itself, is determined by the field variation perpendicular to the surface and may be increased (/decreased) when the shear plane is close to (/far away from) the solid substrate. Such a modulation of the shear plane is accomplished by tuning the hydrophilicity (/hydrophobicity) of the surface.5,9 For instance, when superhydrophobic (SH) surfaces, where wetting angles are $>135^\circ$, are used,10,11 the electrolyte would have a finite velocity even at the surface, effectively implying that the nonslip plane could be virtually inside the substrate by a distance, termed the slip length ($b$). There is then a finite slip velocity at the surface, $u_s = \partial u_s / \partial y$, where $\partial u_s / \partial y$ is the shear rate.12 Subsequently, there is an enhancement of the effective $\zeta$ potential ($\zeta_{eff}$) to $\zeta \left( 1 + \frac{b}{\lambda_D} \right)$ on hydrophobic surfaces.7,13

While a high $b$ is hence desirable for a large $V_s$, the conventional method through which SH surfaces are synthesized involves air-filled pockets.14–17 As air is nominally uncharged, the related $\zeta$ obtained from electrolyte flows over
such air-filled surfaces (AFS) is negligible and considerably offsets any gains due to $b$. In summary, what is desirable for a high $V_s$ is a hydrophobic surface along with high $\zeta$.

Related to this context, liquid-filled surfaces (LFS) were proposed\(^1\)\(^3\)-\(^19\) for optimizing the electrokinetic characteristics. Here, an electrolyte-immiscible oil was infiltrated into patterned surface grooves and the electrolyte flow over the LFS indicated a reduced $b$ as well as an amplified $\zeta$. Indeed, the enclosed oil yields a finite $\zeta$ different from the air, used in conventional AFS, and hence much larger $V_s$ values were measured for flows in the LFS-constituted systems. Earlier work reported streaming potential measurements on liquid-filled grooved surfaces\(^1\)^\(^3\)^\(^16\)\(^20\) with electrolyte flows either parallel or perpendicular to the groove direction. The orientational effects on such patterned surfaces manifested through a tensorial aspect to the developed $V_s$ were considered.

However, many issues related to what would be an ideal patterned surface for a given solid (/liquid) fraction in the LFS are still unclear. One major consideration is the optimization of the $\zeta b$ product evident from the H–S relation. This quantity must consider the dual aspects that (a) the $\zeta$ may be obtained from the oil in the LFS could be smaller than that could be obtained from the solid surface, implying the necessity for a large solid fraction ($\phi_s$), in addition to the aspect (b) that a large $b$ necessitates a small $\phi_s$ or equivalently a large oil fraction ($\phi_s = 1 - \phi_f$). Consequently, the interplay of the $\zeta$ and $b$ with respect to the underlying patterned surface must be considered and understood. In this work, we tackle these issues through detailed experimental studies of the $V_s$ obtained through electrokinetic flows over two categories of surfaces, i.e., (i) the AFS and (ii) the LFS, and four related patterns, i.e., (1) transverse grooves (stripes perpendicular to flow), (2) longitudinal grooves (stripes parallel to flow), (3) pillars (isolated solid patches), and (4) meshes (isolated fluid patches) (Figure 1). Through such studies, we aim to elucidate the influence of trapped (/free) lubricant fluid, e.g., in the mesh and the pillar LFS categories, as well as the parallel (/perpendicular) electrolyte flow, e.g., through the flow-aligned (/orthogonal) groove categories, on the $V_s$. We have obtained fascinating insights into electrolyte flow on such patchy surfaces and have succeeded in further increasing the figure of merit (related to the obtained voltage for a given pressure gradient along the channel) to a record 0.1271 mV/Pa, 3-fold larger compared to that previously obtained,\(^1\)\(^3\) through such experiments.

**EXPERIMENTAL SECTION**

Fabrication of Microchannels and Patterns. The related microchannels, for the experiments, consist of three layers. The upper wall (upper layer) and the side wall (spacing layer) were poly(dimethyl siloxane) (PDMS); the bottom wall (lower layer) of the channel was the specific patterned surfaces, as related to the groove, pillar, and mesh geometries, as depicted in Figure 1a–d, and fabricated through lithographic processes\(^1\)\(^9\). In this work, we conducted measurements with a microchannel of length 12 cm, width 0.9 cm, and height 340 $\mu$m. The base of the microchannel was configured with a template for placing the various patterned surface samples (Figure 1e). The photolithography was carried out on a Si wafer (n-type, (110), thickness 500 $\mu$m, from University Wafer) cleaned with acetone, IPA, and rinsed by DI water, and then baked at 180 °C for 5 min. Photoresist (NR9-3000) was coated on the wafer at 3000 rpm for 40 s and subsequently baked at 120 °C for 60 s. The specific pattern geometry was defined through a laser writer (Heidelberg MLA150) and developed (using RD6) for 1 min. Subsequently, the resist patterned wafer was subject to dry etching (using Oxford Plasmalab 100 RIE/ICP) to yield a trench depth ($d$) of $\sim$30 $\mu$m. A related definition is $\phi_f = w_s/L$, where $L = w_s + w_g$ is the period of the pattern, $w_s$ is the width of the solid, and $w_g$ is the width of the groove in the pattern. Alternately, for a square pillar or mesh pattern, $\phi_f = \frac{w_s}{(w_s + w_g)}$. The etched Si wafer was then put in an RR2 photoresist remover over $\sim$12 h. Finally, the patterned surface was...
coated with parylene-C (using a PDS 2010 Parylene Coater) to a thickness of \( \sim 500 \) nm.

**Fabrication and Characterization of LFS.** The LFS constituting the patchy surfaces was fabricated by infiltrating oil into the grooves of lithographically patterned surfaces mentioned above. The oil used (Dupont Krytox GPL 101 of viscosity 30 mPa·s at 25 °C) was found to be immiscible with the NaCl electrolyte. The general purpose lubricant (GPL) represents a family of widely used perfluorinated oils known to be inert and stable over a wide temperature range. The oil spillage out of the structures was taken to be negligible due to the enhanced surface tension forces and was also verified through an environmental scanning electron microscope (ESEM). Experiments were performed with the flow direction perpendicular to the grooves considering the stability of the LFS, i.e., whether the filling oil would experience shear-induced drainage under external flow or maintain an intact surface with pressure stability. The liquid filling the LFS could be contained indefinitely inside the grooves in such a configuration, for instance, if the groove period was smaller compared to the critical length scale \( L_w \) inversely proportional to the \( \sqrt{h/w} \) ratio. For the given experimental conditions, \( L_w \) was at the mm scale, and it was assumed from such a consideration as well as from ESEM observations that the LFS are stable.

**Streaming Potential \((V_f)\) Measurement.** The \( V_f \) was monitored, on related pattern geometries in the microfluidics setup, using saltwater (with NaCl dissolved in water at a concentration of 0.1 mM) as an electrolyte. Electrodes (Ag/AgCl) at either end were used to measure the potential difference \( V_f \) (Figure 1e). A syringe pump (Cavro S/NxP) was used for electrolyte flow, and the pressure drop \( \Delta P \) along the channel length was monitored (UEI EM152 manometer) and checked to be in correspondence with Poiseuille characteristics over the chosen pressure range \((150−800 \) Pa). The \( V_f \) was monitored six times for each particular pressure for estimating the reported mean and the standard deviation.

### RESULTS AND DISCUSSION

**Comparison of the Obtained \( V_f \) on Air-Filled Surfaces (AFS) and Liquid-Filled Surfaces (LFS).** A validation of the H−S relation, indicating a linear \( V_f − \Delta P \) relation, was generally noted (Figure 2).

A small offset on the pressure axis, of \( \sim 50 \) Pa, was ascribed to the channel inlet resistances. At the very outset, higher values of the \( V_f \) were obtained through the use of the LFS for all of the tested patterns, i.e., the longitudinal and transverse grooves, as well as the mesh and the pillar structures, in comparison to when AFS were used (Figure 2). However, the individual magnitudes, as well as the enhancement, were dependent on the specific patterned surface. Such observations are in line with that previously determined and were ascribed to a higher effective \( \zeta \) arising from the combined influence of a higher charge density as well as the slip at the electrolyte−LFS interface. The slope of the \( V_f − \Delta P \) plot may be considered a figure of merit (FOM), in terms of the developed voltage for a given increment in pressure, for the obtained streaming potential and is plotted for the various patterns in Figure 3.

The superiority of the LFS (marked in red) is again evident. Moreover, an increase of \( \sim 15\% \) was obtained through the use of mesh patterns in comparison to that of groove patterns, with such an increase especially marked for the LFS. The relatively high FOM value of \( \sim 0.1271 \) mV/Pa is significantly larger than on AFS.

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**Figure 2.** Streaming potential \((V_f)\) as a function of pressure drop \((\Delta P)\) on air-filled surfaces (AFS) and liquid-filled surfaces (LFS) for (a) pillar, (b) mesh, (c) longitudinal groove \((G_0)\), and (d) transverse groove \((G_90)\), all with a \( \phi_s \) of \( \sim 0.5 \).

**Figure 3.** Figure of merit (FOM), related to the streaming potential \((V_f)\) − pressure ratio on air-filled surfaces (AFS, black circles) and liquid-filled surfaces (LFS, red circles) for four different surface geometries. For all textures, the \( V_f \) generated on LFS is larger than that on AFS.
Assessment of the Measured \( V_s \) on Surfaces with Different Solid Fractions. We have indicated that the \( V_s \) enhancement in the LFS would essentially arise from a modified \( \eta_{\text{eff}} \) incorporating both (i) \( \eta \) and (ii) the \( \zeta \). With respect to the slip length, the dynamic viscosity of GPL 101 (~33 mPa·s) is orders of magnitude larger than that of air (~18 μPa·s). The shear stress between the electrolyte and the LFS-infiltrated oil would be expected to be much greater than that between the electrolyte and air in the AFS. Consequently, \( b \) would be significantly reduced from the AFS to the LFS. However, the results in Figures 2 and 3 clearly indicate an overall \( V_s \) enhancement for the LFS over the AFS, most plausibly due to the nonzero \( \zeta \) at the electrolyte–oil interface. Such a notion is remarkable, in which orders of magnitude increase in the \( \zeta \) potential are not typically encountered. To probe whether the oil in the LFS does contribute to such \( \zeta \) increase, we sought to investigate the influence of different solid–air (oil) ratios, particularly for the pillar- and mesh-patterned structures, where the largest LFS was observed (see Figure 3). Three particular ratios of solid to nonsolid fractions, i.e., \( \phi_s = 0.25, 0.5, \) and 0.75, were investigated, through detailed streaming potential measurements (Figure 4). Interestingly, it was determined that \( \phi_s = 0.5 \), i.e., with a balanced lubricant-oil-to-solid ratio of 1:1, yielded the largest \( V_s \). It does not seem then that a higher oil fraction magnitude, or equivalently a smaller \( \phi_s \) alone, was responsible for the larger \( V_s \). Further understanding and exploring the mutual interaction between \( \zeta \) and \( b \), for parameterizing the influences of electrostatics and fluid dynamics, would help in the design of devices for higher \( V_s \).

**Table 1. Comparison of the Obtained Figure of Merit (FOM)—the Ratio of the Obtained Streaming Potential Generation to Applied Pressure Difference \( \frac{V_s}{\Delta P} \), to the Reported Literature**

<table>
<thead>
<tr>
<th>report</th>
<th>surface</th>
<th>electrolyte</th>
<th>( \frac{V_s}{\Delta P} ) (mV/Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olthuis et al.</td>
<td>glass with pore sizes of 1.0–1.6 μm</td>
<td>1 mM KCl</td>
<td>0.0004</td>
</tr>
<tr>
<td>van der Heyden et al.</td>
<td>silica surface</td>
<td>1 mM KCl</td>
<td>0.003</td>
</tr>
<tr>
<td>Fan et al.</td>
<td>patterned parylene/PDMS</td>
<td>0.1 mM NaCl</td>
<td>0.044</td>
</tr>
<tr>
<td>Mandal et al.</td>
<td>gold-nanoparticle-embedded PDMS</td>
<td>40% H2O2</td>
<td>0.025</td>
</tr>
<tr>
<td>this work</td>
<td>patterned parylene/PDMS</td>
<td>0.1 mM NaCl</td>
<td>0.012</td>
</tr>
</tbody>
</table>

**Figure 4.** Streaming potential \( (V_s) \) as a function of pressure drop \( (\Delta P) \) for different solid fractions \( (\phi_s) \) on a (a) pillar AFS, (b) mesh AFS, (c) pillar LFS, and (d) mesh LFS.
$q_1$ and $q_2$ characterize the surface charge density at the no-slip and slip regions, respectively. Broadly, $\zeta$ could be replaced by $\zeta_{\text{air}}$, invoking the Gauss-law-related relationship $\zeta_{\text{air}} = \frac{\phi_{\text{air}}}{\varepsilon}$. In the microchannel, we considered the $\zeta$ potential of the upper PDMS surface as $\zeta_{\text{PDMS}}$, while for the bottom surface, a weighted summation of $\zeta_{\text{parylene}}$ (coating the solid) and $\zeta_{\text{oil}}$ (/$\zeta_{\text{air}}$) for LFS (/AFS) is assumed. Then, the effective $\zeta$ of the channel with the textured surface would be

$$\zeta_{\text{channel}} = \frac{1}{2} \zeta_{\text{PDMS}} + \frac{1}{2} \left( \phi_{\text{parylene}} + (1 - \phi_{\text{oil}}) \zeta_{\text{oil}} \right) \left[ 1 + \frac{b_{\text{eff}}}{b} \frac{q_{\text{oil}}}{q_{\text{parylene}}} \left( 1 + \frac{b}{h_o} \right) - 1 \right]$$

(2)

Knowing that $\zeta_{\text{PDMS}} \sim 26.9$ mV and $\zeta_{\text{parylene}} \sim 62.1$ mV from earlier work, $\zeta_{\text{air}}$ is $\zeta_{\text{oil}}$ at AFS and $\zeta_{\text{slip}}$ for the LFS. Since the charge density of the air may be considered close to zero, i.e., $\zeta_{\text{air}} \sim 0$ mV, the air phase does not contribute to the $\zeta$ potential. Following the reported surface charge density of oils in the range of 0.6–1.5 mC/m², our estimate of $\zeta_{\text{oil}}$ at $\sim 15$ mV yields a good fit to our experimental observations.

For obtaining the effective $\zeta$ potential ($\zeta_{\text{channel}}$) as related to eq 2, both the $b$ and the $b_{\text{eff}}$ must be known. References to the literature indicate estimates of $b$ from numerical analysis, computational simulations, as well as empirical formulae from experiments on superhydrophobic (SH) surfaces. It was also discussed how dissipation in the gas phase of textured surfaces modifies liquid flow friction with respect to a gas cushion model for one- and two-dimensional SH textures in the Cassie state or rough surfaces impregnated by a low-viscosity lubricant. The related models were deployed for estimating the local $b$ for a patterned surface as

$$b_{\text{eff}}^\zeta = \frac{\eta_o}{\eta} b_{\text{eff}}^\zeta_{\zeta}$$

(3)

$$b_{\text{eff}}^\zeta = \frac{\eta_o}{\eta} b_{\text{eff}}^\zeta_{\zeta}$$

(4)

Here, $w_o$ is the characteristic size of the air phase, $\eta$ is the dynamic viscosity of fluid (air, oil), and $b$ is a dimensionless local slip length, with respect to two orthogonal directions, say $x$ and $y$, on the patterned surface; $\beta_x \approx 0.32$, and $\beta_y \approx 0.12$ was estimated numerically.

For rectangular groove surfaces with patterns extending parallel (perpendicular) to the fluid flow direction, the following relations are commonly used for the $b_{\text{eff}}$. For longitudinal groove-based surfaces

$$b_{\text{eff}} = \frac{L}{\pi} \ln \left[ \tan \left( \frac{\pi w_o}{2T} \right) \right]$$

(5)

Alternately, for a transversely oriented groove surface

$$b_{\text{eff}} = \frac{L}{\pi} \ln \left[ \tan \left( \frac{\pi w_o}{2T} \right) \right]$$

(6)

These approximate relations for the $b_{\text{eff}}$ were found to be in good agreement with the exact numerical solution for any surface slip fraction and imply that the flow past stripes is controlled by the ratio of the local slip length to texture size. In this work, we extrapolated from such relations for the pillar and mesh geometries. The pillar manifold may be considered as a superposition of transverse and longitudinal groove geometries, while the mesh arrangement arises mainly from the transverse groove attribute. Therefore, we assume for a pillar-patterned surface

$$b_{\text{eff}} = b_{\text{eff}}^{\parallel} + b_{\text{eff}}^{\perp} - b_{\text{eff}}^{\parallel} b_{\text{eff}}^{\perp} \approx b_{\text{eff}}^{\parallel} + b_{\text{eff}}^{\perp}$$

(7)

The $b_{\text{eff}}$ of the mesh-patterned surface could be modeled, with eq 6 as the basis and with $L = w_o + w_o$ (Figure 1d) as the characteristic mesh length. The $b_{\text{eff}}$ is mainly contributed by the gaps in the mesh. However, the fluid in the mesh is...
constrained akin to the situation for the transverse groove. Indeed, such a correspondence of the \( b_{\text{eff}} \) between a mesh surface and a transverse stripe surface has been previously acknowledged.\(^{66} \) The above relations, i.e., eqs 3–7, were then used to determine the \( b \) and the \( b_{\text{eff}} \) of the patterned (groove, pillar, mesh) surfaces. Subsequently, these quantities were substituted into eqs 1 and 2 for determining the effective \( \zeta \) potential, \( \zeta_{\text{channel}} \), for pillar- and mesh-related channel patterns, which is then plotted in Figure S5a–d. The figures also indicate the computed \( b_{\text{eff}} \) for the various patterns.

It is apparent, from Figure S5, that the calculated \( \zeta_{\text{channel}} \) (\( /b_{\text{eff}} \)) on pillar and mesh samples increases (\( /b_{\text{eff}} \)) with increasing \( \phi_i \). While the reduction of the \( b_{\text{eff}} \) accords with the expectation from a reduced electrolyte–groove lubricant contact interface, it is important to note that the \( b_{\text{eff}} \) values of the LFS were much smaller in comparison to those of the AFS. For instance, in the pillar pattern, with \( \phi_i = 0.5 \), the \( b_{\text{eff}} \) was estimated to be \(~29 \text{ nm} (/\sim 1.7 \mu m)\) for the LFS (/AFS) configurations. Correspondingly, for the mesh pattern, with \( \phi_i = 0.5 \), the \( b_{\text{eff}} \) was \(~50 \text{ nm} (/\sim 4.4 \mu m)\) for the LFS (/AFS) configurations. On the other hand, the contrast of the \( \zeta_{\text{channel}} \) is less marked between the mesh and pillar patterns as well as between the AFS and the LFS.

However, the \( \zeta_{\text{channel}} \) yet increases with increasing \( \phi_i \), broadly indicating the greater influence of the charge density of the solid with respect to that of the groove lubricant. It was also interesting to note that the \( \zeta_{\text{channel}} \) was only estimated to be slightly larger, at \(~20\%\), for the LFS compared to that of the AFS. It is then reinforced that replacing an AFS with an LFS contributes to an increased \( \zeta_{\text{channel}} \) as indicated in Figure 4, mainly through an increased \( \zeta \) potential.

**Influence of the Pattern Geometry and Orientation on Obtained Electrokinetic Streaming Potentials.** The aspect of the oppositely varying \( \zeta_{\text{channel}} \) (\( /b_{\text{eff}} \)) with increasing \( \phi_i \) naturally suggests an optimal value of the \( \phi_i \) for obtaining a large \( V_s \) in line with the experimental data of Figure 4. The aim of an optimal \( \phi_i \) was to obtain the largest figure of merit (FOM) in terms of the \( V_s \) for a given pressure drop. With such an aim, we fabricated the four geometries as instances of composite surfaces (Figure 1a–d) and subsequently examined the flow characteristics over the surfaces. The composite surfaces embody the attributes of combining solid and fluid regions, with varying electrokinetic \( \zeta \) potentials and slips depending on the fluid. The optimality of the chosen \( \phi_i \) of \(~0.5\), with respect to all of the studied composite surfaces, is indicated in Figure S5. In addition to the solid and lubricant fractions, there also seems to be a dependence on the specific pattern geometry as may be inferred through a comparison of the higher obtained \( V_s \) for (a) the grooves parallel to the flow compared to flow over grooves perpendicular to the flow, of \(~50\%\), as well as in the case of (b) mesh geometry compared to the pillar geometry with an LFS of \(~10\%\) (see Figure 3). We focus on the effect of the grooves, considering the larger magnitude of the effect. The \( \zeta_{\text{channel}} \) as well as the \( b_{\text{eff}} \) for both the AFS and the LFS, are indicated for the grooves in Table 2. The largest FOM was obtained for electrolyte flows parallel to the grooves, both for the AFS and for the LFS. It is likely that the connectivity of the electrolyte flow on the solid surface, as in the mesh structure, may be more relevant to a higher figure of merit (FOM), as indicated in Figure 3. While both the pillar- and mesh-segmented surfaces show higher FOM values compared to the nonsegmented surfaces, the FOM in the longitudinal grooves (G0) is comparable. It was seen that the

<table>
<thead>
<tr>
<th>texture</th>
<th>( V_s ) (mV/Pa)</th>
<th>( b_{\text{eff}} ) (( \mu \text{m}))</th>
<th>( \zeta_{\text{channel}} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>perpendicular (AFS)</td>
<td>0.0531</td>
<td>1.90</td>
<td>28.70</td>
</tr>
<tr>
<td>parallel (AFS)</td>
<td>0.0886</td>
<td>3.84</td>
<td>28.77</td>
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<tr>
<td>perpendicular (LFS)</td>
<td>0.0732</td>
<td>25.20</td>
<td>30.95</td>
</tr>
<tr>
<td>parallel (LFS)</td>
<td>0.1112</td>
<td>66.80</td>
<td>37.35</td>
</tr>
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</table>

**Table 2. Measured \( V_s \) and Variation of the Estimated Effective Slip Length (\( b_{\text{eff}} \)) and Effective \( \zeta \) Potential of the Microfluidic Channel (\( \zeta_{\text{channel}} \)) for Groove-Based and LFS Patterns with \( \phi_i = 0.5 \)**

variation in the \( b_{\text{eff}} \) between the parallel and perpendicular orientations, as well as between the AFS and LFS, is much more significant than the related modulations in the \( \zeta_{\text{channel}} \). Indeed, these results seem to indicate that \( b_{\text{eff}} \) may be the dominant factor in the obtained \( V_s \).

However, it must also be noted that the \( b \) values measured in experiments or estimated computationally span a wide range, from a few nanometers to hundreds of micrometers.\(^ {14,47-59} \)

Indeed, the sensitivity of the fluid flow to surface boundary conditions, as well as the difficulty of experimental techniques, such as particle-induced velocimetry (PIV), to determine boundary velocities is a major contributor to the lack of precision in the knowledge of the \( b \). As indicated previously, the \( b / \lambda_{\text{eff}} \) factor was invoked to rationalize the increased \( V_s \). The related modification of the \( H–S \) equation positing a \( \zeta_{\text{eff}} \) in place of \( \zeta \), yields some insight into the influence of the \( b \). We have indicated that the \( \zeta_{\text{channel}} \) from eq 2 is probably a better metric for understanding the integrated surface charge effects in microchannel flow for heterogeneous surfaces.

**CONCLUSIONS**

In summary, we have experimentally determined the influence of various pattern textures on the streaming potential (\( V_s \)) that may be obtained in electrokinetic flows with both AFS and LFS. The clear benefit of using the latter was indicated through a record-obtained FOM value (related to the \( V_s \) per given pressure drop) of \(~0.1271 \text{ mV/Pa}\), which has been ascertained to be orders of magnitude larger compared to values obtained in the literature. The utility of segmented patterns, i.e., mesh or pillar geometry, over nonsegmented patterns, i.e., parallel or perpendicular grooves, for obtaining a larger \( V_s \) was demonstrated. Further technology development using such features may yield voltages much larger, on the order of even 10 V or larger for atmospheric pressure variations, for viable devices and applications.\(^ {5,50,51} \) The competing tendencies of the slip and the surface charge/potential were evaluated with respect to the consideration of an optimal solid fraction for the pattern surface. Considering the AFS and the LFS, the significantly smaller computed \( b \) in the LFS compared to that in the AFS does not reduce \( V_s \) per se. The nominal increase in the \( \zeta \) in the LFS then seems to have an effect much larger than the estimated decrease in the \( b_{\text{eff}} \). A plausible hypothesis for the importance of the \( \zeta \) would be related to the variation of the electrical field lines. The stability of the two-fluid interface due to the differing charge densities (\( \sigma \)) of the solid surface and the oil, i.e., \( \sigma_{\text{solid}} – \sigma_{\text{oil}} \), which is expected to yield a longitudinal electric field (\( E_{\text{z}} \)) as well as a transverse electric field (\( E_{\perp} \)), with respect to the obtained \( V_s \) may be relevant and needs further investigation. In the AFS, there is a more rapid variation of the charge density (and the related potentials) between the solid and the nonsolid/air portions of the underlying pattern. Such a
variation is considerably reduced using an LFS, which involves a solid and dielectric liquid on the pattern. We then suggest that it is the variation that may determine the magnitude and stability of the obtained $V_\alpha$. For instance, in the electrolyte flow parallel to the grooves, such modulations would have less of an effect compared to when the flow is perpendicular to the grooves. Consequently, the $V_\alpha$ is larger in the former case. With respect to the pillar and mesh geometries, the influence of the electric field changes is less obvious. The periodic potentials are expected to influence the distribution of ions and alter the electrokinetic flows.51 Work in progress, from our group, would clarify such aspects through a focus on the influence of the charge density and related potential variations. This could be done through investigating flow on surfaces with variable surface charge, as may be induced through ion irradiation or plasma processing methodologies.

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**Notes**

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