A Lateral Microfluidic Cell for Imaging Electrodeposited Zinc near the Shorting Condition

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The morphology evolution of zinc electrodeposited from alkaline ZnO/KOH is imaged in situ using a microfluidic cell. Working and counter electrodes are in a lateral configuration, separated by a flow channel with a height of 90 μm, resulting in quasi-two-dimensional zinc layers. At a flow rate of 0.3 cm/s, zinc packing in the channel is highest at a current density just above the transition from porous to dense zinc, i = 170 mA/cm². When deposited, compact zinc is approximately 3 times as dense as porous zinc, as determined by image analysis of the layer. The dense mode invariably leads to ramifications and critical growth, causing cell shorting. Greater zinc packing is possible at a flow rate of 3.1 cm/s, although flow rates of this order are impractical for flow-assisted zinc batteries. Ramified zinc tips approach a kinetically limited rate, independent of electrolyte flow rate. Therefore, increased flow rate cannot control critical growth once it begins. Increased flow rate results in a higher density of ramified tips at equivalent cell potential. The zinc deposition reaction has a Tafel slope of 130 mV below 10 mA/cm² and 50 mV in the second Tafel region > 10 mA/cm². The second Tafel region is relevant to zinc secondary batteries.

The prospect of energy storage on the grid scale, sometimes termed grid-level or massive electricity storage, has reinvigorated interest in secondary battery chemistries not based on lithium. Zinc alkaline systems avoid drawbacks of lithium such as resource limitation and catastrophic reactivity, while providing substantially higher energy density than lead-acid batteries. In addition to being water-compatible, stable, and non-toxic, zinc alkaline cells have a low formal potential, low cost, and high energy density, all of which recommend it as an excellent energy storage medium. However, widespread use of plated zinc metal in secondary batteries has not been achieved. Zinc alkaline batteries face challenges of lifetime stability, with zinc and the formation of dendritic morphologies, causing material loss, shorting, and failure of the cell.

One configuration of zinc alkaline secondary batteries is a flow cell with parallel plate current collectors. Correspondingly, shorting and redistribution issues are questions of zinc morphology and current distribution in such a parallel plate design. Naybour studied the effect of electrolyte flow and current density on electrodeposited zinc morphology. In flow electroplating, three distinct morphological phases were identified: flat, bulbous, and dendritic, with high Reynolds number (Re) and low current density resulting in a flat growth. At high deposition rates, dendrites resulted. The bulbous to dendritic transition current was proportional to (Re)^0.7 for laminar flow and (Re)^1.1 for turbulent, indicating that a zinc mass transport limitation induced the dendritic phase. Naybour also established that growth morphologies and the formation of dendritic morphologies in quiescent solutions differed from those with flow.

In situ analyses that allow tracking of morphological development during electrodeposition of metal films have been reported for various purposes. Barkey and co-workers directly observed the evolution of the concentration boundary layer in radial, thin-layer cells with both copper and zinc dense branching morphologies. Szpak et al. studied the evolution of zinc dendrites in situ in a nonflowing zincate electrolyte, focusing on the fragmentation of zinc tips upon anodic dissolution. Lopez-Tomas et al. reviewed quasi-two-dimensional electrodeposition from zinc sulfate solutions in a parallel plate film cell, providing a phase diagram of morphologies. Oren and Landau studied zinc deposition in a microscopy-enabled flow cell imaging dendrite precursors of 80–300 μm tall, growing upward toward the microscope objective. They determined that tip velocity transitioned from exponential to linear with time upon achieving the diffusion layer thickness.

In a recent work, Wang et al. investigated the micromorphology of zinc electrodeposited from zincate electrolyte in a modified bulk cell, separating morphologies into categories of single- and multiple-factor control. They defined heavy spongy and boulder morphologies as forming under mixed control conditions. Although most of their experiments were conducted in quiescent solution, they also reported that the regime of compact morphologies was greatly enhanced by stirring. Hsu et al. reported in situ X-ray microradiography experiments confirming that in ZnCl₂ electrolyte, hydrogen bubble formation can direct the formation of zinc morphology.

Microfluidic electrochemical systems have been used in recent metallization studies due to several inherent advantages, one of which is low ohmic resistance (some others being small solution volumes, flow control, and rapid chemistry changes). Minimizing ohmic resistance, microelectrodes with small separation make observation of true kinetic current densities possible, whereas in a larger configuration such as a rotating disk electrode (RDE), ohmic overpotential quickly dominates due to high current densities. Crowley and West observed lithium dendrite tip velocities in situ in a microfluidic flow cell made with sandwiched wire electrodes. They observed that lithium dendrites did not initiate under mass transport control but did transition to mass transport control during growth.

The aim of the present work is to report zinc morphology evolution and the density of zinc packing between parallel plate electrodes in a flow channel. The distinct macromorphologies of zinc lead to different capacities for zinc packing and are therefore a factor in energy density. Also, a more thorough understanding of current distribution with zinc depositing in a flow channel is needed, specifically the controlling processes that lead to runaway current distributions and cell shorting. All morphologies of zinc that can become the subject of runaway localized currents, Mossy zinc, which is initially flat, can build to high aspect ratio formation after several cycles, causing efficiency loss in flowing-electrolyte zinc batteries. If such instabilities in the current distribution can be monitored and alleviated with a dynamic control of charging rate, electrolyte flow rate, and electrolyte chemistry, large-scale zinc batteries may prove efficient and cost-effective for grid-scale applications.

A single-use microfluidic electrochemical cell was used to monitor a metal layer electrodeposited from a flowing electrolyte stream, with the working electrode (WE) and the counter electrode (CE) in a lateral configuration and separated by a flow channel. The cell height was 90 μm, resulting in a quasi-two-dimensional metal layer. This work focused on zinc layers that were grown to thick-
The channel cross section is 0.0009 cm². Current densities are reported with reference to this initial electrode area. Each lateral channel experiment began by passing a low cathodic current ($i = -60$ mA/cm²) to convert the silver CE/RE to silver oxide ($E_{\text{cell}} = -1.25$ V), which occurred under 30 s and was observed by the darkening of the electrode surface near the electrolyte interface.

The three-electrode microfluidic cell (see Fig. 1b) has been discussed in detail elsewhere. Briefly, the microfluidic channels were molded from PDMS over a negative pattern created from SU-8 photolithography. The working channel had a rectangular cross section 500 μm wide and 180 μm tall and a parallel reference channel of identical size contained a Ag/AgCl RE (BASI, model RE-6). Flow rates in the working and reference channels were equal. The WE and CE were produced by curing copper wires with diameters of 100 and 250 μm, respectively, in Spurr low viscosity embedding media (Polysciences, Inc.). The WE–CE distance was 800 μm. The wires were cross-sectioned and polished with silicon carbide sandpaper (Leco) from 320 to 1200 grit and this electrode-epoxy structure formed the floor of the cell. A connection to the electrodes was made by copper alligator clips on the underside of the device.

In both microfluidic cells, the WE interface was imaged in situ using an Omnano microscope. Images were captured with a Flea2 digital camera (Point Grey Research, Inc., Richmond, BC) interfaced with Astro IIDC software (Upperleft Services and Contracting, Calgary, AB). Electrolyte flow was controlled using an NE-500 syringe pump (New Era Pump Systems, Wantagh, NY) interfaced to a personal computer running Syringe Pump Pro (New Era Pump Systems, Wantagh, NY). The cross-sectional area of the channel in both types of microfluidic cells was $9 \times 10^{-4}$ cm², resulting in fluid velocities of 0.3 and 3.1 cm/s for pump settings of 1 and 10 mL/h, respectively. The current or potential of the cell was controlled using a μAutolab III (three-electrode cell) or a VersaSTAT 4 potentiostat (lateral cell). Ex situ images of zinc micromorphology were taken using a Hitachi TM3000 TableTop scanning electron microscope (SEM). Cross-sectioned images were taken using a Zeiss EVO40 XVP SEM after embedding the zinc layer in Spurr resin, cross-sectioning, and polishing.

Image analysis of in situ zinc layers began by processing the images to render zinc in solid black with the flow channel in white. Depending on cell lighting conditions and zinc coloration, one of the two methods was used: (i) black and white threshold followed by inversion or (ii) post-contrast to a three-color image and mapping the zinc color to black. It was important to maintain a consistent color processing, interface distances and deposited zinc areas were calculated using ImageJ software (Wayne Rasband, NIH). Zinc packing densities in the flow channel were calculated from a histogram of pixel hues.

The electrodeposition of zinc was simulated using COMSOL Multiphysics 3.5a (COMSOL, Inc.). The governing equations were the Navier–Stokes and the Nernst–Planck equations using the electroneutrality condition. The boundary of the WE was defined as columns of increasing height to represent different stages of zinc protrusion growth, with Tafel kinetics applied at both WE and CE boundaries (zinc deposition and oxygen generation, respectively).

Current densities and concentration profiles were calculated for a potentiostatic cell voltage of −2.5 V. This method was verified by the agreement of predicted current densities for a flat, parallel plate geometry with those calculated from the analytical solution, i.e., the annulus problem.
At potentials below the formal potential, measured as $E_{\text{face}}$, overpotential, and back. The zinc deposition reaction is given as

$$i = i_0 \exp(-\eta_i F/RT)$$

where $i$ is the exchange current density, $\eta_i = (E - E^0)$ is the surface overpotential, and $i_0$ is the cathodic transfer coefficient. Results for the current range of $10$–$300$ mA were the same as those at $5$ mV/s and $10$ mV/s, which were indicative of steady-state behavior while being rapid enough to minimize the change in WE area during the scan. Return scans displayed a hysteresis with higher cathodic current due to an increase in the electrode area during vigorous deposition at high current densities. Outbound scans were used for determination of kinetic parameters. Galvanostatic deposition experiments were performed to assure that outbound scans were characteristic of the steady-state potential-current relationship, which was the case. Electrolyte flow rate was varied to assess the importance of zincate mass transport.

Kinetic parameters for the zinc electrodeposition reaction were calculated using the cathodic current–potential expression

$$E = E^0 - 0.152 V$$

and back. The three-electrode microfluidic cell is used under the ionic current traveled through the full cross section of the channel, at $0.3$ cm/s in dilute electrolyte of $1.8$ M KOH and $0.018$ M ZnO.17 Using an RDE in the dendritic regime, Moshtev and Zlatilov reported agreement with Tafel slopes of $115$ mV and $i_b = 150$ mA/cm².18 Dirks and Hampson determined kinetic parameters via potential steps, reporting $b = 118$ mV and $i_b = 140$ mA/cm² at KOH and Zn concentrations similar to those in the present work.19 Hendrikx et al. reported values for deposition on Zn from $7$ M KOH and $0.1$ M ZnO as $b = 120$ mV and $i_b = 15$ mA/cm².20 The variation in values can be attributed to the wide spectrum of experimental methods employed, e.g., WE areas, mass transport, substrate materials, etc. A general clustering of values suggests a Tafel slope of $120$ mV, which agrees with the lower current range presented here. However, for the testing of electrodes, the Tafel slopes observed in the $10$–$300$ mA/cm² range were more relevant. Kinetic values reported by Cachet et al. of $b = 30$ mV more closely agree with the present work, although the methods employed are quite different, relying on long-time deposition and ohmic correction of the results.21 Despí et al. similarly reported two Tafel regions in studies concerning deposition on zinc amalgam. Their values of $b = 65$ mV and $i_b = 4$ mA/cm² for $9$ M KOH and $0.1$ M Zn agree with those found here.22

The polarization curves in Fig. 2 showed deviation from Tafel behavior at high current densities, where flow rate-dependent slope-ringing regimes were evident. At $0.3$ cm/s, this transition occurred at $730$ mA/cm² and $480$ mA/cm² at $3.1$ cm/s. Growth in a dendritic mode is likely the cause of this slope, with active areas being poorly defined. The inset to Fig. 2 shows subplateau-like features near $50$ mA/cm², which may relate to the state of the oxide layer, as described by Cachet et al.22

The three-electrode microfluidic cell was designed to minimize ohmic losses (IR), which can dominate during electrodeposition at high current, while also allowing hydrodynamic control of the electrolyte. As IR is linear with WE area, $A = 7.85 \times 10^{-5}$ cm² for this cell, IR was $25$ times lower than with a typical RDE configuration. Total resistance of the cell, which is a function of the WE/CE spacing $L = 800 \mu$m and the conductivity of the zincate electrolyte $\kappa = 3.5 \times 10^{-2} \text{S/cm}$, was higher than when using an RDE ($260$ vs $2.9$ Ω), but this was more than offset by the differences in WE areas. Assuming the ionic current traveled through the full cross section of the channel, at $i = 1000$ mA/cm², IR = $20$ mA, as opposed to $570$ mA with an RDE with a $5$ mm WE diameter. Applying ohmic correction to RDE results with IR values this large can result in overcompensation errors. The three-electrode microfluidic cell is used under the assumption that minimizing ohmic loss and leaving the data uncorrected is a preferable method. This aspect of the three-electrode cell has been reported previously.13 For the analysis to follow, kinetic parameters for the oxygen formation reaction were also assessed, resulting in $\alpha = 0.43$ and $i_b = 7.7$ mA/cm².

Lateral microfluidic cell.—Evolution of zinc layers during electrodeposition was monitored in lateral microfluidic cells, as shown in Fig. 3. The electrolyte flow rate was $0.3$ cm/s and the galvanostatic current density was as indicated in the caption, increasing from top to bottom. The electrodeposited zinc morphologies were as follows: (a) porous zinc grown at $110$ mA/cm² for $3600$ s; (b) dense zinc in a compact layer grown at $170$ mA/cm² for $2400$ s; and (c) dense zinc in an initially compact layer that became ramified, which was grown at $220$ mA/cm² for $1800$ s. For each panel in Fig. 3, an equal charge of $Q = 0.72$ $\text{C}$ was passed. At short times ($t < 60$ s), only minor hydrogen formation was observed at these current densities, which stopped entirely upon formation of a visible zinc layer. This is in contrast to the acidic electrolyte experiments of Hsu et al., during which massive hydrogen formation was observed at $200$ mA/cm².24 As hydrogen formation was minor, the experi-

![Figure 2. Polarization curves of zinc electrodeposition as a function of electrolyte flow rate. The electrolyte is $8.9$ M KOH with $0.6$ M ZnO. Data are recorded using the three-electrode microfluidic cell with a copper WE. The RE is Ag | AgCl. Tafel fit to is to the $0.3$ cm/s outbound scan data.](image_url)
ments in Fig. 3 resulted in equal quantities of zinc deposited on the WE. Higher current densities resulted in earlier ramification of the zinc layer. At a current density of 830 mA/cm², dendrite formations with nonsplitting tips resulted, with significant hydrogen bubble co-formation.

Potential data for galvanostatic lateral cell experiments are shown in Fig. 4. In all cases, oxygen formation was the CE reaction as given by

\[ 4 \text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \]  

Electrolyte flow was sufficient to remove oxygen bubbles, which were confined to within 15% of the channel width near the CE. Flow rates of <0.1 cm/s were avoided, as oxygen bubbles became persistent and affect the zinc morphology by blocking current paths to the WE. As oxygen bubbles caused a fluctuation in cell potential (40 mV below 200 mA/cm²) the data in Fig. 4 were taken from bubble-free conditions. Theoretical cell potentials calculated from three-electrode cell data via \( E_{\text{cell}} = E_{\text{O}_2} - E_{\text{Zn}} \) agreed with lateral cell experiments, and are shown as solid lines.

The transition from porous to dense zinc correlated with an average \( E_{\text{cell}} > 2.4 \) V, shown by a dotted line in Fig. 4, with morphology indicated as porous by open markers and dense by filled markers. From the 0.3 and 3.1 cm/s three-electrode data, this corresponds to zinc surface overpotentials of \( \eta = -34 \) and \(-38 \) mV, respectively. Transitions in zinc morphology have previously been reported as dependent on critical overpotentials, e.g., a dendrite transition at \( \eta = -173 \) mV reported by Popov et al. However, the porous–dense transition observed here also corresponds to the predicted onset of mass transport limitations (see below).

The micrometer-scale dimension in lateral cells is the channel height (90 μm), to allow analysis of the metal layers as two-dimensional. Images of the in situ zinc layers were processed using ImageJ to render zinc in solid black with the flow channel in white, to determine the fraction of the channel occupied by zinc. The zinc layers in Fig. 3a and b occupied 0.43 and 0.15 fractions of the channel at their full length, respectively, revealing a 3 times bulk density difference between the porous and dense morphologies.

Figure 3. (Color online) In situ lateral cell images of galvanostatic zinc electrodeposition at equivalent passed charge of 720 mC. Electrolyte flow rate is 0.3 cm/s and from right to left. (a) \( i = -110 \) mA/cm², \( t = 3600 \) s; (b) \( i = -170 \) mA/cm², \( t = 2400 \) s; and (c) \( i = -220 \) mA/cm², \( t = 1800 \) s.

Figure 4. Zinc–oxygen galvanostatic cell data recorded using a lateral microfluidic cell at 0.3 and 3.1 cm/s electrolyte flow rate. Each data point represents one experiment, with error bars being the standard deviation. Cell potentials are ohmic-corrected, although the correction is small. Solid lines show the theoretical cell potential as calculated from the zinc and oxygen half-cells referenced to Ag | AgCl (as in Fig. 2). Porous zinc layers are indicated by open markers and dense zinc layers by filled markers. At \( E_{\text{cell}} > 2.4 \) V, compact zinc is formed at both flow rates. At extremely high deposition rate (\( i_{\text{cell}} = 820 \) mA/cm²), gas formation prevents a stable cell potential.
comparable to the flow rate in the reported kWh scale system, which was ~0.5 cm/s. In the literature, this flow rate was optimized to accomplish the goals of flow assist, which are (i) suppression of ramifications, (ii) gas bubble removal, and (iii) heat removal, while minimizing the loss in round trip efficiency due to electrolyte pumping. This finding has implications for zinc flow batteries, namely that the maximum amount of zinc that can be stored with practical electrolyte flow rates is electrodeposited just beyond the porous-to-dense regime transition.

Galvanostatic zinc electrodeposition was also studied at a flow rate of 3.1 cm/s. At that flow rate, porous zinc formed at higher current densities than at 0.3 cm/s (see Fig. 4) and dense compact layers were formed to larger sizes before developing ramifications. At a current density of 560 mA/cm², Q = 3.6 was achieved with the zinc layer occupying a fraction of only 0.64 of the channel width.

All dense zinc morphologies formed projections that lead to cell shorting, even if a compact layer was maintained initially (as in Fig. 3 and 5). For parallel plate flow batteries, it is desirable to avoid critical growth at protrusions caused by a nonuniform current distribution. Potentiostatic deposition in lateral cells was used to evaluate the electrolyte flow rate effect on critical growth. During potentiostatic experiments, as shown in Fig. 6, zinc was deposited with constant values of \( E_{\text{cell}} \), as defined by the Zn−O₂ cell. Cell current oscillated due to periodic bubbles much as the cell potential did in the galvanostatic case. Figure 6a and b shows results from electrolyte flow rates of \( v = 0.3 \) and \( 3.1 \) cm/s, respectively. Rates of zinc deposition increased as a function of time, with the increases being dramatic in the periods directly before critical growth and cell shorting. In Fig. 6b, with an electrolyte flow rate of \( v = 3.1 \) cm/s, high values of \( |E_{\text{cell}}| = 2.55 \) and 2.6 V resulted in runaway current densities well in excess of \( 1 \) A/cm² based on the original geometric area of the WE. Increasing \( |E_{\text{cell}}| \) values generally resulted in increasing zinc growth rates, with the exception of the 2.6 V and 0.3 cm/s case. In this experiment, oxygen bubble formation was vigorous and obstructed the channel, resulting in compact zinc nodules on the WE. Moshtev and Zlatilova reported that increases in current on the WE accomplished the goals of flow assist, which are (i) suppression of ramifications, (ii) gas bubble removal, and (iii) heat removal, while minimizing the loss in round trip efficiency due to electrolyte pumping. This finding has implications for zinc flow batteries, namely that the maximum amount of zinc that can be stored with practical electrolyte flow rates is electrodeposited just beyond the porous-to-dense regime transition.

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In the lateral cell, the analogous electrochemical features corresponded roughly to ramification lengths of half the channel width. Boundary layers for OH⁻ (D = 5.3 × 10⁻⁵ cm²/s) at both the anode and the cathode were calculated to be on the order of 1 μm in 0.3 cm/s and smaller at higher flow rate.16 For this reason, the major effect of anode−cathode proximity was the generation of oxygen bubbles, which were removed rapidly at all flow rates considered, as discussed above.

Zinc morphologies resulting from the experiments in Fig. 6 were mixed porous/compact at −2.4 V and highly ramified at all other conditions other than the exception mentioned above. Figure 7 shows results for −2.55 V at both flow rates as a function of time. The images were processed to depict the zinc layer as solid black, with the flow channel in white. Times of the black traces \( t = t_{\text{black}} \) increased from top to bottom, with the bottom image being directly before cell shorting, at the shorting location. For this reason, they represented the areas of highest local current density in the cell. Images 100 s in the future were superimposed in red, \( t_{\text{red}} = t_{\text{black}} + 100 \) s, to reveal the locations of electrochemically active interfaces with time. A flow rate of 0.3 cm/s resulted in ramified morphologies that were narrow initially and broadened near the half-width of the channel. With a flow rate of 3.1 cm/s, ramifications were evenly placed on the WE and broader than the 0.3 cm/s case. With a flow rate of 0.3 cm/s, experiments shown in Fig. 6 shorted at values of 1.9 C charge passed. At 3.1 cm/s, wider ramifications more densely packed on the WE achieved coulombic values of 3.1 C for −2.5 V and 3.7 C for both −2.55 and −2.6 V.
current densities. However, micrometer-scale bubbles may be present at all times from top to bottom of the solution for mass transport limited current at parallel plate electrodes in a flow stream. The zincate limiting currents observed in the three-electrode microporous cell agreed with the expected values from the analytical solution for mass transport limited current at parallel plate electrodes.

Ex situ SEM images of zinc layers are seen in Fig. 8. Figure 8a shows the same sample as that in Fig. 7a, grown potentiostatically at −2.55 V and 0.3 cm/s. Two characteristic porous lengths can be seen, the larger being 1.5–2.5 μm in diameter, as indicated in the figure, and smaller pores on the order of hundreds of nanometers in size. The larger mode may be the result of codeposited hydrogen gas. Visible hydrogen appears only at the zinc limiting current. Figure 8b shows porous zinc grown potentiostatically at −2.4 V and a flow rate of 3.1 cm/s. On the macroscale, this zinc appeared dark and mossy, as in Fig. 3a. Two characteristic porous lengths can be seen, larger pores 1.5–2.5 μm in diameter, as indicated in the figure, and smaller pores on the order of hundreds of nanometers in size. The larger mode may be the result of codeposited hydrogen gas. Visible hydrogen appears only at the zinc limiting current. However, micrometer-scale bubbles may be present at all current densities.

Discussion

The zincate limiting currents observed in the three-electrode microfluidic cell agreed with the expected values from the analytical solution for mass transport limited current at parallel plate electrodes in a flow stream

\[ i_{L}(s) = 0.9783nFDe_{0} \left( \frac{v}{hD_{e}} \right)^{1/3} \]  

where \( i_{L} \) is the mass transport limited current density at a distance \( s \) along the electrode, \( D \) is the active species diffusion coefficient, \( e_{0} \) is the bulk concentration, \( v \) is the average electrolyte velocity, and \( h \) is the channel height. For comparison, the circular WE in the three-electrode cell may be approximated as a square electrode with equivalent area. The leading edge of the WE is under kinetic or ohmic control under virtually all conditions due to the flow of fresh electrolyte. Further along the WE length, a diffusion layer is established and a flux of zincate controls the current density. For flow rates at 0.3 and 3.1 cm/s, average limiting currents of \( i_{L,av} = -880 \) and \( -1800 \) mA/cm\(^2\) were expected based on the literature value for zincate diffusion, \( D = 8 \times 10^{-6} \) cm\(^2\)/s. This agreed with the \( i_{L} \) observed in Fig. 2 for inbound scans. Local \( i_{L} \) values at the trailing edge of the WE were expected to be a factor of 0.65 of this.

For the lateral cell experiments, lower average \( i_{L,av} \) values were expected due to the increased electrode length and cell characteristic size. From Eq. 4, flow rates at 0.3 and 3.1 cm/s result in \( i_{L,av} = -120 \) and \( -260 \) mA/cm\(^2\), respectively. These values correspond generally to the porous–dense zinc transition seen in Fig. 4 for galvanostatic experiments. Calculated diffusion layer thicknesses at the midpoint of the WE for these cases were 95 and 45 μm, respectively. In Fig. 7a, ramification appeared to begin after 30–40 μm of growth, well within the expected mass transport limiting diffusion layer value of 95 μm. Flow rate was not correlated with the initial
decreases, the tips approach the kinetically limited current density independent of flow rate. As distance to the CE decreases, the tips approach the kinetically limited current density independent of image analysis of the ramifications in Fig. 7. As distance to the CE becomes more complicated. Although the local limiting current is a function of distance from the leading edge and the electrode remains planar, with the addition of zinc protrusions two factors change: (i) flow rate becomes a function of both morphology and time as protrusions constrict the channel and (ii) there is a possibility of changes in the concentration boundary layer between protrusions. Protrusions are typically on the order of 100–200 μm in width, which is a short enough distance to result in high local limiting currents as in the three-electrode cell microelectrode.

The current density at protrusion tips \(i_d\) was calculated using the relation:

\[
i_d = \frac{A_d}{\ell} \frac{nF}{V \Delta t}
\]

where \(A_d\) is the area deposited, which is shown in red, \(\ell\) is the interfacial length between black and red areas, \(V\) is the molar volume of zinc, and \(\Delta t = 100\) s for all images. This method has been reported previously as an ex situ technique to determine current distribution in copper-plated trenches. The \(i_d\) values for three protrusions in each of Fig. 7a and b, labeled 1, 2, and 3, are shown as functions of time in Fig. 9. \(i_d\) is generally a nonlinear function of time as the cell approaches a shorting condition. Also, protrusions may be characterized by rapid growth followed by sudden deactiva-

tion, as with protrusion 3 in the 3.1 cm/s case. These calculations were also performed using the one-dimensional tip velocity as the growth length; however, in some cases, such as protrusion 3 in Fig. 7b, this simplified calculation differed significantly from the method using \(A_d/\ell\).\(^{9,31}\)

Figure 9 shows that as \(i_d\) became large on a given protrusion and that protrusion neared the CE, a value of \(i_d\) independent of electrolyte flow rate was achieved. During a condition of runaway growth, \(i_d \approx -1600\) mA/cm\(^2\) corresponded to the expected kinetically controlled current density calculated from Tafel curves for the Zn–O\(_2\) reactions at 3.1 cm/s, as discussed in the Three-electrode microfluidic cell section above. As the protrusion tips were \(\sim 100\) to 200 μm in width, not subject to an established zincate boundary layer (see below) and in an accelerating flowfield, they grew under kinetic control upon approach to the CE. Comparing the \(i_d\) values in Fig. 9 to the electrode average data in Fig. 6, for the 0.3 cm/s case \(i_d > i\) as the protrusions were localized on a small area of the WE. The 3.1 cm/s case was more uniform across the WE and \(i_d = i\). At high deposition rates, increasing electrolyte flow did not eliminate zinc protrusions but increased their thickness and density on the electrode.

Simulations of the parallel plate cell were performed in COMSOL using kinetic parameters for the electrode reactions as shown in Table 1. This confirmed that as protrusions became long with respect to the cell width, zincate diffusion layers became compressed, making limiting current values high. This corresponds to a transition to kinetic control. Figure 10 shows simulations for 0.3 and 3.1 cm/s flow rates. In the upper images, model zinc protrusions 100 μm wide and 25 μm tall originate from the WE (lower electrode). In a less rapid flow rate, the zincate diffusion layer grows to significant thickness along the electrode length. At a given protrusion height, a vortex forms between protrusions, which homogenizes the local zincate concentration. This results in zincate diffusion layers that are comparatively uniform at all protrusion tips, thus explaining the appearance of flow rate-independent kinetic current densities on protrusion tips, as shown in Fig. 7 and 9. This vortex formation is observed for 0.3 cm/s at 600–800 μm protrusion height and 3.1 cm/s at 100–200 μm, as shown in the lower panels. At \(\sim 100\) μm protrusion height, current distribution is entirely localized at protrusion tips for both flow rates.

**Conclusions**

This work focused on zinc layers that were grown to thicknesses near the channel width either at or near the shorting condition. A single-use microfluidic electrochemical cell was designed, intended for monitoring a metal layer electrodeposited from a flowing electrolyte stream, with WE and CE in a lateral configuration and separated by a flow channel. The current–potential relationship in a Zn–O\(_2\) lateral cell was the same as that observed in a three-electrode microfluidic cell. At low overpotentials, a dark, porous zinc was formed, often termed mossy or spongy zinc. At a cell potential of \(E_{cell} = -2.4\) V, the morphology changed to a dense and crystalline zinc. Zinc grown in this mode invariably leads to ramification, producing protrusions and cell shorting when the layer thickness became large.

At a flow rate of 0.3 cm/s, zinc layers electrowon galvanostatically packed most densely into the flow channel at a current density just above the transition from porous or mossy zinc to dense zinc, \(i = 170\) mA/cm\(^2\), although these conditions lead to eventual ramification of the zinc layer. Greater zinc packing was possible at a flow rate of 3.1 cm/s, although flow rates of this order are impractical for flow-assisted zinc batteries. Potentiostatic growth resulted in nearly equivalent zinc storage at this flow rate. At higher deposition rates, zinc ramifications resulted more rapidly, although the micromorphology remained compact and nonporous. Under potentiostatic growth, protrusion tips reached a kinetically limited growth rate, independent of electrolyte flow rate. Increased flow rate resulted in a higher density of protrusion tips at equivalent cell potential. At high deposition rates, increasing electrolyte flow did not eliminate zinc.
protrusions but increased their density on the electrode, increasing the total charge stored in the zinc layer. For this reason, increased flow rate cannot be used to reduce critical growth once it begins.

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