Colloidal electroconvection in a thin horizontal cell III: Interfacial and transient patterns on electrodes

Yilong Han
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China

David G. Grier
Department of Physics and Center for Soft Matter Research
New York University, 4 Washington Place, New York, NY 10003
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Previously we have reported a family of convective patterns formed by charge-stabilized aqueous colloidal suspensions under constant (DC) vertical electric fields (J. Chem. Phys. 122, 164701 (2005); 125, 144707 (2006)). These patterns form in the bulk when electrokinetic forces act in the opposite direction to gravity. Here we report on qualitatively different cellular patterns that silica colloidal spheres form on a horizontal electrode when electrokinetic forces act in the same direction as gravity. We also describe transient patterns that form after the driving voltage of the cellular patterns is turned off. These transient patterns cast new light on the complex interplay between the motions of charged colloidal spheres and the ionic relaxation of water undergoing electrolysis.

I. INTRODUCTION

Charged fluids can develop a wide variety of electrohydrodynamic instabilities when driven by external electric fields [1]. The resulting flows play a central role in such varied applications as electrospray, microfluidics and electrohydrodynamic pumping [2]. Colloidal particles often are used as passive tracers for such flows. Their presence, however, can strongly influence the underlying instabilities, particularly when the particles themselves carry electric charge. Electric fields exert forces on colloidal particles both directly through their coupling to the particles’ charges and indirectly through their influence on the surrounding electrolyte [3]. Neighboring particles also interact electrostatically and hydrodynamically with each other as they move. The resulting cooperative motion in many-body suspensions gives rise to clearly distinguishable categories of patterns and structures in both oscillatory (AC) [4–17] and constant (DC) [15, 17–22] electric fields. Even pure water undergoes electroconvective pattern formation [22, 23] when the applied DC voltage exceeds the water decomposition voltage of ∼2.5V [24, 25].

We previously have reported on remarkable hierarchically structured colloidal clusters that can form during the electrolysis of aqueous colloidal dispersions [20, 21] when electrokinetic forces counteract the tendency of dense colloidal spheres to sediment under gravity. We also have reported on the macroscopic patterns [22] that arise in such suspensions when the water itself becomes electrohydrodynamically unstable.

These studies complemented earlier investigations [15, 18] of colloidal pattern formation in electric fields that act in the same direction as gravity. Colloidal spheres pushed against the lower electrode at low voltages are observed to attract each other through their influence on ionic flows, and thus form epitaxial colloidal crystals [15, 18, 21].

Here, we report that the epitaxial crystals can further assemble into cellular patterns on the electrode at still higher voltages. After the voltage is turned off, moreover, the cellular patterns relax into an unstructured sedimented layer of particles. Interestingly, silica spheres of 1.58 μm in diameter can form various transient patterns during this relaxation process. These results provide new insights into the mechanism of electroconvection during hydrolysis.

II. EXPERIMENTAL SYSTEM

Our experimental system has been described in detail previously [21, 22]. Briefly, the sample consists of an aqueous suspension of silica spheres of 1.58 μm in diameter (Duke Scientific Lot 24169) or 3.0 μm in diameter (Duke Scientific Lot 4740) confined to a thin horizontal layer approximately 100 μm thick between two parallel glass slides. Both inner surfaces are coated with 10-nm-thick gold electrodes on 10-nm-thick titanium wetting layers. These electrodes are optically thin so that colloidal patterns can be imaged onto a charge-coupled device camera (NEC TI-324A) outfitted with a macro lens (Vivitar Series 1, φ = 52 mm Macro Telephoto) for low-resolution imaging, or mounted on an optical microscope for high-resolution imaging. We apply DC voltages across the electrodes to produce vertical electric fields, and record the resulting time evolution of the distribution of colloids in the cell. The typical current density used to create patterns is on the order of 10 μA/cm² [21] and the resistivity of the electrodes is roughly 50 Ω/□. These values are small enough to avoid temperature gradients due to Ohmic heating across the 4 cm² sample area.

The redox potential of water is 1.23 V. In practice, however, the threshold for hydrolysis is roughly 1 V higher once account is taken of the voltage drop across the electrode-electrolyte interfaces. This overpotential depends on the current density, temperature, and the
roughness and composition of the electrode [24], and is approximately 0.43 V for gold electrodes. In our samples, the measured effective water decomposition potential [24, 25] is around 2.5 V [21], above which H₂ and O₂ molecules are generated at the electrodes by hydrolysis faster than they can be transported away by diffusion. Bubbles consequently form at the electrodes after several minutes [21]. All the colloidal patterns reported here were observed before macroscopic bubbles formed.

The applied DC voltage is defined to be positive when the upper electrode is positive so that the negatively charged silica spheres are driven upward. In this study, a negative bias is used to push spheres against the bottom electrode.

The areal density \( \phi \) of sedimented colloidal spheres is reported relative to that of a close-packed layer. For example, \( \phi = 2 \) refers to two close-packed layers.

III. INTERFACIAL CELLULAR PATTERNS

The applied DC bias breaks water down into hydronium and hydroxyl ions at the electrodes. Ions then flow across the cell to the oppositely charged electrodes, where they recombine into hydrogen and oxygen gas. The flowing ions draw the negatively charged colloidal spheres toward the anode where they form a layer, such as the example in Fig. 1(a), which is formed from 3.0 \( \mu \)m diameter silica spheres. The spheres distort the ionic currents near the electrode and thus induce structured flows in the water. These structured flows in turn mediate strong and long-ranged hydrodynamic attractions among the colloidal spheres [3, 26], which accordingly are drawn together into crystalline domains [15, 18, 21]. Typical examples can be seen in Fig. 1(b).

Electrokinetically bound interfacial colloidal crystals persist indefinitely for biases below the threshold for hydrolysis. Increasing the bias beyond the threshold for hydrolysis, as in Fig. 1(c), dramatically increases the range and strength of electrokinetic attractions and causes monolayer crystalline domains to buckle and collapse into multi-layered three-dimensional colloidal clusters. The clusters of 3.0 \( \mu \)m diameter spheres in Fig. 1(c) formed from the domains in Fig. 1(b) when the bias was abruptly changed from \(-0.8\) V to \(-1.8\) V. The clusters themselves are mobile at such a large bias and coalesce into millimeter-scale crystalline domains. The example in Fig. 1(d) formed after 10 min from the isolated clusters in Fig. 1(c).

Smaller silica spheres also form clusters on the bottom electrode under negative bias. Figure 2 shows clusters of 1.58 \( \mu \)m diameter silica spheres in an \( H = 300 \mu \)m thick cell at a constant bias of \(-8\) V. Rather than coalescing into macroscopic interfacial crystals, however, these smaller spheres form macroscopic cellular patterns, such as the example shown at low magnification in Fig. 2(a). Particles are concentrated in the brighter regions of this reflection-mode image. Dark rings thus denote depleted boundaries surrounding cellular domains. Viewing the same pattern under transmission mode microscopy in Fig. 2(b) reveals a tracery of densely packed particles sandwiched between the depleted boundaries of neighbor-
ing cells. Although individual particles are not resolved in this image, regions of higher particle concentration appear darker. Zooming in to a still higher magnification view of the inter-cellular boundary in Fig. 2(c) resolves individual spheres and reveals a multi-layered structure with a high degree of crystalline order. This is quite remarkable given the rounded contours and dynamically mobile nature of the inter-cellular boundaries. The dense region at the center of each cell, by contrast typically consists of a monolayer crystal, such as the example shown in Fig. 2(d).

Cellular patterns translate smoothly across the electrode surface. On occasion, they also spontaneously break into mechanical oscillation, their crystalline regions rhythmically expanding and contracting by a few micrometers at frequencies of about 1 Hz. Oscillations at similar frequencies have been observed in bulk colloidal clusters levitated into the electrolyte by constant positive bias [20, 21]. Such DC-driven oscillations are believed to result from the interdependent motions of particles and ionic fluxes near the electrode during electrolysis [20, 21]. Their mechanism, however, is not yet fully understood.

Reversing the applied bias to +3 V pushes particles off of the lower electrode and into the bulk, where they generate electroconveeating labyrinthine patterns on the millimeter scale. We previously have discussed such bulk labyrinthine patterns as an electrokinetic analog of Rayleigh-Bénard convection [22]. Applying a higher positive voltage (> +6 V) drives particles all the way to the top electrode where they again form crystalline cellular patterns qualitatively similar to those shown in Fig. 2. The iridescent colors of these colloidal crystals under white light illumination can easily be observed with the unaided eye.

Interfacial cellular patterns form over a broad range of particle densities (0.05 < φ < 2) and are not sensitive to the electrode separation \( H \). In this sense, interfacial cellular patterns are robust against variations in driving conditions. They differ, therefore, from the bulk electroconveceiveing patterns that form at low positive biases, which are sensitive to the applied voltage, the electrode separation, and the particle density [20–22].

Despite their differences, both interfacial and bulk patterns arise from the same underlying electrohydrodynamic instability. In all cases, opposing ionic fluxes generated by hydrolysis become spatially separated through their interaction with charged colloidal spheres. Viscous coupling to the ions' hydration spheres then gives rise to counterpropagating fluid flows that enhance ionic transport and reduce dissipation. These flows also convey the colloidal spheres and thus mediate effective long-ranged interactions that contribute to the dynamic patterns we observe.

IV. PATTERNS FORMED DURING TRANSIENTS

Based on the scale of the patterns we observe, we infer that the quasi-steady-state distributions of ions, ionic currents, particles, and flowing streams of electrolyte are structured on scales extending to millimeters. The time required for these nonequilibrium structure to relax therefore establishes the rate at which one of these patterns can respond to changes in driving conditions. The relaxation process, in itself, can create distinctive and interesting patterns whose lifetime therefore casts further light on these distributions and their relaxation rate.

The images in Fig. 3 show how a cellular pattern of 1.58 μm diameter polystyrene spheres formed at −8 V, responds to having the bias abruptly set to zero. The strong gradients in particle concentration visible in quasi-steady-state in Fig. 3(a) rapidly relax when the bias is switched off. Rather than dissipating altogether,
FIG. 4: Response of a polygonal pattern such as that in Fig. 3(c) to positive bias. 1.58 µm diameter silica spheres in a $H = 390$ µm thick cell at density $\phi \approx 1.5$. (a) 2 s after the bias in Fig. 3(c) was increased to $+2.0$ V. (b) After 10 sec at 2.0 V, the particles were levitated into the bulk and formed tumbling clouds. (c) $+4.0$ V: convective tumbling clouds. (d) $+10$ V: labyrinthine convection in the bulk. (e) Cellular pattern reestablished by switching the bias back to $-10$ V.

though, the muted cellular pattern in Fig. 3(b) gradually evolves into the very distinct polygonal pattern shown in Fig. 3(c). Remarkably, the relaxation process coalesces the separate depleted regions around each of the original cells into a sharply defined network of depleted boundary layers between uniformly dense polygonal domains of colloidal crystal. This polygonal pattern dissipates into a uniform layer of colloidal spheres over the course of several minutes.

This relaxation process is taken further in Fig. 4 with the initial $-8$ V bias being reversed abruptly to a positive bias that should tend to lift the particles off the lower electrode altogether. The initial cellular pattern in Fig. 4(a) reorganizes into the more labyrinthine pattern shown in Fig. 4(b) within a few seconds after the bias is abruptly reversed to $+2$ V. This transient state somewhat resembles the polygonal pattern in Fig. 3(c), with a network of dark depleted region separating bright domains of concentrated particles. This structure, however, appears much more quickly under reverse bias than it did by relaxation alone. The labyrinthine nature of this transient is more apparent in Fig. 4(c) after the bias is increased to $+4$ V. At $+10$ V, in Fig. 4(d), the particles are entirely lifted from the lower electrode and form a quasi-stationary labyrinthine electroconvective pattern in the bulk of the electrolyte. Reversing the voltage back to $-8$ V restored the original cellular pattern, which highlights the robustness of their formation mechanism. Further cycling the bias from $-8$ V to $+2$ V yields a new pattern of rings with dots in the centers as shown in Fig. 4(e). Similar rings can also be generated in the first cycle of the voltage under a lower density, see Fig. 5. These observations demonstrate that the transient patterns are sensitive to history.

No transient patterns form if the bias is abruptly increased from the quiescent state at 0 V to $+2$ V. When the negative bias is abruptly removed from the cellular pattern in Fig. 6(a), by contrast, the interfacial particles “rebound” into the bulk electrolyte for several seconds. Ionic fluxes within the bulk of the cell thus appear to lag changes in the applied bias, presumably because time is required to restructure the electrochemical gradients in the double layers near the electrodes. In this process, the patterns traced out by observed particle trajectories qualitatively resemble the fingers and plumes in the convective Rayleigh-Taylor instability. Such plume-like flows prefigure the development of the ring-like pattern in Fig. 6(b).

We also observe a slower relaxation process in which particles’ Brownian motion temporarily stops once they settle onto the lower electrode. Formerly dynamic patterns such as the annular vortexes in Fig. 6(b) become
frozen in place. Brownian motion typically resumes after several minutes, allowing the initially frozen patterns to diffuse into uniform layers of spheres. The mechanism of this transient adhesion is not yet understood. Electrostatics and high concentrations of ions near the electrode could permit adhesion through van der Waals attraction. Were this the case, though, it would be somewhat surprising for the spheres to become free once the ionic distributions relaxed. Ionic currents associated with relaxation of concentration gradients similarly might press particles against the electrode. The minutes-long duration of the transient, however, seems inconsistent with such an explanation. A mechanism incorporating a combination of such effects would have to account for the observation that all of the immobilized spheres resume to free motion more or less simultaneously.

V. DISCUSSION

The present study complements related work ([20–22], for instance) that demonstrate the very rich variety of quasistatic and dynamic patterns that can emerge during hydrolysis under a constant electric bias. Dispersed colloidal spheres can act as passive tracers for intrinsic electrokinetic flows and also can contribute to the initiation and propagation of hierarchically structured flow patterns. We have shown in the present study that charged colloidal particles can be swept into cellular patterns on electrode surfaces by electrohydrodynamic convection in the bulk electrolyte. These cellular patterns qualitatively resemble some of the bulk electroconvective patterns we reported in Ref. [22].

Like their small-scale bulk counterparts [20, 21], the millimeter-sized cellular domains that form at high negative biases also undergo small-amplitude oscillations at frequencies of roughly 1 Hz. Such collective oscillations thus appear to be a very general feature of ionic conduction in colloidal dispersions.

In addition to the varied patterns that charged colloids display in steady state, still more patterns reproducibly form during the relaxation process after the driving field is turned off. For example, metastable colloidal crystal-like patterns have been observed after an oscillating voltage is switched off [27], and ring-like patterns have been observed after a constant voltage was switched off [21]. Here we have reported additional types of transient patterns that form for negatively charged colloidal spheres near the cathode of a horizontal parallel-plate hydrolysis cell once the bias is turned off. Observing the evolution of these patterns offers insights into the time-scales that characterize the relaxation of electrohydrodynamic convection. These observations suggest that the relaxation time for bulk flows can extend to several seconds and that the relaxation time for ionic diffusion can extend to several minutes. Further studies on the transient relaxation process promises to cast new light on the mechanism of electrolysis under oscillatory bias.

The cellular and plume-like patterns we have observed also are reminiscent of electrohydrodynamic instabilities that have been studied in fluids charged by ion injection [28]. Ion injection, however, does not capture the intricate chemistry of electrolytic dissociation [29]. Electroconvective instabilities in colloidal dispersions, however, exhibit a much wider range of pattern formation, indicating a central role for the particles themselves in forming patterns. Transient patterns, anomalous oscillations and slow ion relaxations all challenge our current understanding of convection and relaxation in electrolysis and pattern formation in nonlinear physics.

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