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

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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 cellular patterns that silica colloidal spheres form on a horizontal electrode when electrokinetic forces act in the same direction as gravity. We suggest that these cellular patterns form as a result of bulk electroconvection mediated by charge injection into the supporting aqueous electrolyte. This charge-injection mechanism also accounts for some aspects of electroconvective pattern formation in our earlier reports. Cellular patterns reorganize themselves into distinct transient pattern patterns after the driving voltage is turned off. These transients 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 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 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 electroconvection [22, 23] when the applied DC voltage exceeds water’s decomposition voltage of ~2.5 V [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 dispersions 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 attract each other through their influence on ionic flows, and thus form epitaxial colloidal crystals [15, 18, 21].

In Sec. III, we report that field-induced epitaxial crystals can further assemble into cellular patterns on the electrode at voltages high enough to induce electroconvection in the bulk electrolyte. Section IV introduces a charge-injection model that may account for the onset of electroconvection in aqueous suspensions. The same mechanism also provides an explanation for dynamic pattern formation in the bulk of confined dispersions, which we have reported previously [20–22]. It suggests that electroconvective instabilities may be far more common in aqueous systems than has been suspected.

Although electroconvection may explain many aspects of colloidal clustering and dynamics under constant drive, it does not obviously explain the patterns described in Sec. V that form once the driving voltage is turned off. Rather than relaxing directly to a disorganized state, the particles in interfacial cellular patterns instead transiently pass through distinct cellular patterns that can persist for minutes. These unexplained transients promise new insights into the mechanism of electroconvection during electrolysis.

II. EXPERIMENTAL SYSTEM

Our experimental system has been described in detail previously [21, 22]. Briefly, the sample consists of an aqueous dispersion 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 electrolysis is roughly 1 V higher when 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 electrolysis 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 φ of sedimented colloidal spheres is reported relative to that of a close-packed layer. For example, φ = 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. Dispersed spheres are driven to the lower electrode by gravity and electrokinetic forces, as shown in Fig. 1(a). Their presence distorts the ionic currents near the electrode and thus induces 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 electrolysis. Increasing the bias beyond the threshold for electrolysis, 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 µm 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 clus-
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 electroconvective 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 electrolysis 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. CHARGE INJECTION AND ELECTROCONVECTION OF WATER

In considering what physical properties influence the length scale of electroconvective pattern formation in colloidal dispersions and the time scales governing their appearance and relaxation, we first draw attention to unresolved questions in the electroconvection of pure water. In Ref. [22], we reported the onset of bulk convection during electrolysis in a thin layer of water at strong bias $|V| \gtrsim 3\,\text{V}$, even when there were no colloids in the field of view. The few isolated colloidal spheres in these observations appear to have acted as passive tracers of electroconvection without substantially influencing the flow pattern. Despite the simplicity of the system and the ease with which the phenomenon may be observed, electroconvection of pure water appears not to have been reported previously.

We conjecture that many, if not all, of the electroconvective instabilities we observe can be attributed to the charge injection mechanism that typically is applied to apolar solvents [27]. The effect may have been overlooked because most experimental studies of hydrolysis make use of added salts to enhance electrical conductivity. Our experiments, by contrast, are performed in deionized water whose low conductivity enhances the charge-injection mechanism.

In charge injection, a high voltage is applied across an insulating liquid. The resulting electric field induces charge separation, breaks local electroneutrality, and thereby allow current to flow [27]. The injected current generally strongly dominates conduction by intrinsic mobile charges. Spatially separated flows of injected charges can cause the fluid medium to flow through viscous coupling, and can lead to a convective instability above a threshold voltage. Because water has a reasonably high inherent conductivity, injected current must compete with conventional conduction. Whether local electroneutrality is broken to the point that the internal electric field can drive convection is analyzed as follows.

We first estimate the space-charge density $\rho$ that characterizes the small departure from electroneutrality by balancing two competing effects: electroneutrality favors overlap of the $\text{H}^+$ and $\text{OH}^-$ distributions; viscous dissipation is minimized, however, if the counterpropagating ionic fluxes are separated. To estimate the scale of each effect, we introduce a simple model, illustrated in Fig. 3,
that consists of an $n \times n$ array of cylinders representing spatially resolved flows of OH$^-$ ions. The distance between cylinders, $\ell$, is the characteristic length of the pattern. Assuming that each cellular domain in a pattern reflects the flows associated with one cylinder, the scale of the observed patterns suggests that $\ell$ ranges from 50 $\mu$m [20–22] to 1 mm, as in Fig. 2(a). We take the lower end of this range, $\ell = 50$ $\mu$m, to model the onset of electroconvection. In this model, the H$^+$ flux flows in the opposite direction in the region between the cylinders. The contribution to the electrostatic energy due to one of the charged cylinders in the array is

$$U_C(\ell) = \alpha \frac{\pi \rho^2 (\ell/2)^4 H}{16 \epsilon \epsilon_0},$$

(1)

where $H$ is the height of the cylinder and $\alpha$ is a geometric constant of order unity. Given $\ell^{-2}$ cylinders per unit area, the areal electrostatic energy density of the system is

$$u_c(\ell) = \ell^{-2} U_C(\ell) = \frac{\pi \rho^2 \ell^2 H}{2 \epsilon \epsilon_0}.$$  

(2)

Reducing $\ell$ thus reduces the cost in Coulomb energy of separating the oppositely charged ion fluxes. This, however, increases the energy dissipated by viscous drag between the opposite flows. We model this as the energy dissipated by water flowing along the length of a cylinder at speed $v$,

$$U_d(\ell) = \beta \frac{6 \pi \eta \ell v H}{\ell},$$

(3)

where $\eta = 10^{-3}$ kg/s/m is the viscosity of water, and where $\beta$ is another constant of order unity. From tracer measurements, we estimate $v \approx 10$ $\mu$m/s. The areal density of dissipated energy is then

$$u_d(\ell) = \beta \frac{6 \pi \eta \ell v H}{\ell}.$$  

(4)

The optimal separation between charge streams minimizes $u(\ell) = u_C(\ell) + u_d(\ell)$ at $du(\ell)/d\ell = 0$. If we further assume that the observed cell separation corresponds to this optimal value of $\ell$, and if we identify this length scale with the observed scale of the pattern, the associated charge density is

$$\rho = \sqrt{\frac{\alpha 24 \epsilon \epsilon_0 \eta v}{\beta \ell^3}} \approx 0.04 \text{ C/m}^3.$$  

(5)

Equilibration with airborne CO$_2$ lowers the water’s pH to roughly 5.5, which corresponds to a charge density of anion or cation roughly $\rho_0 = 300$ C/m$^3$. The relative departure from charge neutrality estimated in Eq. (5) thus is of the order of $10^{-4}$, which is reasonably small.

By comparison, the charge density associated with the measured conduction current density $j = 1$ A/m$^2$ [22] is

$$\rho_c = j/v_c,$$

(6)

where $v_c$ is the drift speed of an ion. Taking the net voltage across the electrolyte at the onset of electroconvection to be $\Delta V = 1$ V [20, 21] and the mobilities of the ions to be $b_{H^+} = 2.3 \times 10^{12}$ m/N s and $b_{OH^-} = 1.3 \times 10^{12}$ m/N s [28], the typical drift speed is $v_c = b_h \Delta V/H \approx 10^{-3}$ m/s so that $\rho_c \approx 10^3$ C/m$^3$, which is substantially larger than the estimate for $\rho$ from Eq. (5). From this, we conclude that the conduction current dominates the injection current in water under our experimental conditions, as expected.

Next we estimate whether such a small departure from electroneutrality can account for the onset of convection. In the theory of charge injection, the dimensionless parameter

$$C = \frac{\rho H^2}{\epsilon \epsilon_0 \Delta V}$$

is a measure of the injection level, and

$$T = \frac{\rho (\Delta V/H)}{\eta \nabla_s^2 v}$$

(8)

characterizes the instability condition [27]. No-slip boundary conditions for flows on the electrosurfaces suggest $\nabla_s^2 v \approx u/H^2$ [27]. The present system has $C \approx 0.5$ which corresponds to weak charge injection [27]. The small Reynolds number $Re \approx 0.1$ in our system [27, 29]. In this regime of $C$ and $Re$, convection occurs for $T \gtrsim 350$ [29]. Using the value for $\rho$ obtained from Eq. (5), the present system has $T \approx (\rho \Delta V/H)/(\eta \nabla_s^2 v) = 360 > 350$. The estimated value for the magnitude of the charge separation therefore is consistent with the onset of convection at the length scales observed in our experiments. Electroconvection due to charge injection thus appears to explain both the bulk patterns reported in Ref. [22] and also the surface patterns reported here.

This result also suggests that charge-injection instabilities can play a previously unsuspected role in the transport properties of conducting solutions, even when the conduction current dominates the charge-injection current. Moreover the small oscillation predicted in weak charge-injection regime [30] could be responsible for the oscillations observed in Sec. III and in our previous work [20, 21]. To further confirm this mechanism, a direct measurement of the predicted spatial charge density $\rho$ would be desirable in the future.
V. 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 structures 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 rates.

The images in Fig. 4 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. 4(a) rapidly relax when the bias is switched off. Rather than dissipating altogether, though, the muted cellular pattern in Fig. 4(b) gradually evolves into the very distinct polygonal pattern shown in Fig. 4(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. 5 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. 5(a) reorganizes into the more labyrinthine pattern shown in Fig. 5(b) within a few seconds after the bias is abruptly reversed to +2 V. This transient state somewhat resembles the polygonal pattern in Fig. 4(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. 5(c) after the bias is increased to +4 V. At +10 V, in Fig. 5(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 restores the original cellular pattern, and fur-
the negative bias is abruptly removed from the cellular pattern in Fig. 7(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. 7(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 vortices temporarily stop once they 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. Electrostatic screening by 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.

VI. DISCUSSION

The present study complements related work, including Refs. [20–22], that demonstrate the very rich variety of quasistatic and dynamic patterns that can emerge during electrolysis 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 general feature of ionic conduction in colloidal dispersions, and may be related to the small current oscillations predicted for conduction by charge injection in the weak-injection regime [30].
In addition to the varied patterns that charged colloids display in steady state, still more patterns 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 [31], 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 electrolysis 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 are reminiscent of electrohydrodynamic instabilities that have been studied in apolar fluids charged by ion injection [27, 32, 33]. 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 non-linear physics.

In summary, we report two new classes of interfacial patterns that arise in confined colloidal dispersions subject to constant electric fields: (1) cellular patterns that emerge at strong negative voltages, and (2) transient patterns that form after the voltage is removed. Both types of patterns form under negative biases that push charged particles against the electrode surface. They differ in this respect from the patterns reported in our previous studies [20–22], which formed in the bulk under positive biases. We attribute both types of pattern formation under high bias to electroconvection mediated by charge injection, a model that previously has not been applied to aqueous systems. This mechanism agrees quantitatively with estimates based on the measured properties of the emergent patterns, and suggests that the spheres distribute themselves on the electrode as tracers of spatially separated ionic flows that are stabilized by a reduction in viscous dissipation. This model also is consistent with earlier observations of colloidal electroconvection in the bulk [22]. Perhaps the most striking conclusion of this study is that electroconvection induced by charge injection should arise far more commonly than previously suggested, even in fluids with moderate conductivity.

Although electroconvection driven by charge injection appears to explain the dynamic colloidal patterns we have observed under constant driving, the transient patterns reported in Sec. V remain unexplained.

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