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# Electroconvection instability and shocks in complex geometries



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### Abstract

The precise and efficient control of ion transport in an electrochemical system is essential for desalination, water treatment, and energy conversion and storage. With the recent progress of electroconvection in microstructures and shock electrodialysis in porous media, here, we review the emergence of intriguing physical phenomena related to electroconvection and shocks for complex geometries in theory and experiments. In a circular channel, equilibrium electroconvection instability of concentration enrichment, rather than instabilities of concentration depletion, is realized in an aqueous electrolyte. Additionally, the propagation of a deionization shock wave is driven by electroconvection up to millimeter scales, offering more opportunities for desalination. Conformal mapping is employed to explore the effect of symmetry broken in more complex geometries, including an eccentric annulus, a concentric ellipse, and a corner geometry. Lastly, in a multi-component electrolyte, a remote electroconvection is formed, while the concentration valley of inert cations occurs.

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# Introduction

The electrochemical system has been playing an increasingly important role in the sustainable world development, including energy conversion and storage, desalination for water treatment, and biomedical applications [1-5]. In order to precisely control the ion transport, one of the typical approaches is designing the specific sophisticated or complex geometries. For

example, in classical electrodialysis, a stack of alternating cation- and anion-exchange membranes is designed in order to produce the fresh and brine stream for desalination [6-8]. More recently, with the advancement in microfluidics [9], enrichment/depletion resulting from overlapping electric double layers (EDLs) in micro/nanochannels has been observed and subsequently applied to biomolecular separation [10,11]. Polarizable porous electrodes or particles under applied voltages can also induce capacitive deionization in a variety of geometries [12,13].

Historically, in the 1940s, Prof. Benjamin G. Levich (an internationally known physicist and electrochemist and the founder of the discipline known as physicochemical hydrodynamics) built the theory of diffusion-limiting current and concentration polarization. When a current passes through a charge-selective interface (such as a membrane, an electrode, and also the recently studied nanochannel), the charge neutrality is maintained by rejecting the co-ions [14–16]. In practice, overlimiting current (OLC), which exceeds the diffusion-limiting current, was simply measured at a high voltage in experiments [17,18]. The microscopic mechanism responsible for OLC, however, was debated for decades in theory. Early theory in the 1960s considered the chemical effects that produce excess ions, such as the water splitting, chemical reactions, or the degradation of membranes interface [19-22].

The theoretical breakthrough of underlying physical mechanism for OLC has been carried out by Prof. Isaak Rubinstein and Prof. Boris Zaltzman in Israel. They considered the extended space charge, which is related to the formation of a peculiar structure at a chargeselective interface next to the diffuse EDL at limiting current [23-28,28,29]. At a microscopic level, diffusionlimiting current corresponds to the nearly vanishing interface concentration, and the extended space charge appears as a vicinity of the counter-ion concentration minimum from which the co-ions have been expelled by the electric field [27-29]. Subsequently, based on the extended space charge, they proposed the nonequilibrium electroconvection instability (ECI) at a smooth permselective interface, causing the overlimiting conductance through it [30-33]. Experimentally, ECI has been verified by the observation of the vortices at the interface directly (Figure 1a) [34–38]. They further explored equilibrium ECI in theory by simply relaxing the assumption of the perfect or ideal interface [39].

At the reduced length scale such as microchannels in the microfluidic devices, surface charge effects, namely surface conduction and electro-osmotic flow, might become dominant to contribute OLC [40-44]. The transient response to OLC can involve the shock-like propagation of a sharp drop in salt concentration, as investigated by Prof. Juan G. Santiago group in Stanford University [45-47]. The propagation of "deionization shocks" in charged porous media has been exploited by Prof. Martin Z. Bazant group at MIT for water desalination and purification in the emerging process of "shock electrodialvsis" (Figure 1b) [5,41,48-50] and for control of metal growth in "shock electrodeposition" [51,52]. Particularly, shock electrolysis has been demonstrated for promising applications, including small-scale desalination system [53], separation of radionuclides from contaminated water to reduce the nuclear pollution [54], and removal of lead from drinking water [55].

In this review, we will focus on the recent progress of ECI and shocks in complex geometries, particularly in a circular channel (Figure 1c) [56-59]. Some intriguing phenomena have been observed, such as equilibrium ECI of concentration enrichment, as opposed to one of concentration depletion (Section 2) and deionization shock driven by electroconvection (Section 3). For more complex geometries, the conformal mapping approach is employed to investigate the effect of the broken symmetry, providing physical insight into ECI and deionization shock (Section 4). Lastly, an intriguing remote ECI and inert-cation concentration valley are identified within supporting electrolyte (Section 5).

# Equilibrium ECI of concentration enrichment

Physically, for quasi-equilibrium EDL, a seeding vortex is suppressed by a negative feedback in the concentration depletion region near the interface (such as the cathode), since the descending portion of the vortex toward the interface brings the high bulk concentration to the cathode [32]. In the concentration enrichment region, the opposite is true, making the instability possible.

In spite of few literature on equilibrium ECI, the timeline for its development is quite interesting, and the theory itself of course is quite thought provoking as well. In 1996, hydrodynamic instability for concentration polarization was ruled out in Zholkovskij model [60]. Nearly 20 years later, in 2015, equilibrium ECI was proposed to be possible by relaxing the assumption of perfect charge selectivity [39]. In 2020, equilibrium ECI of concentration enrichment was found in a circular channel driven by the strong electric field and can be generalized to more curved geometries [57].

# Zholkovskij model for stable concentration polarization

In a plane-parallel electrochemical cell, Zholkovskij et al. carried out the linear stability analysis for a binary electrolyte solution around the limiting current (Figure 2a) [60]. Two natural assumptions are imposed in this model. One is a perfectly permselective interface allowing only counter-ions passing through electrode, ion exchange membrane, and micro-nanochannel junction for the sake of simplicity in theory. The other is the geometry of plane-parallel electrodes, which is reasonably applicable for the typical experimental setup.



Sketch for electrokinetic instabilities in various geometries. (a) Electroconvection in a straight microchannel [38]; (b) electro-osmotic flow in a porous medium [41]; and (c) remote electroconvection in a circular channel [59].

#### Figure 1



Equilibrium ECI. Top panel for ECI of concentration depletion: (a) Parallel-plate cell with a binary electrolyte solution [60]; (b) dependency of the parameter *m* from wavenumber *k* contains a one minimum corresponding to k = 2.5, m = 5.526 [60]; (c) scheme of three-layer setup with flanked membrane with a fixed charged density (*N*) [39]; (d) scaled critical voltage dependent on *N* [39]. Bottom panel for ECI of concentration enrichment: (e) sketch of the anode vortex near the inner anode in a circular channel [57]; (f) nearly inverse dependence of Pe<sub>min</sub> on the maximum electric field on the anode,  $E_{max} = -(\chi \ln \chi)^{-1}$  [57]; (g) numerical simulation demonstrating equilibrium ECI of concentration enrichment; and (h) experimental observation of the streamlines at the inner anode interface and the associated particle image velocimetry [57].

The dimensionless number of the material Peclet number, Pe (the notation m = 2Pe/3 in Ref. [60]), was used to evaluate the instability,

$$\operatorname{Pe} = \frac{\epsilon}{4\pi\eta D} \left(\frac{RT}{zF}\right)^2,\tag{1}$$

where  $\epsilon$  is the dielectric constant, and  $\eta$  is the dynamic viscosity of the solution. Dependency of Pe on wavenumber showed the instability of one-dimensional solution, and a minimum of Pe was found  $Pe_{min} = 8.28$  (m = 5.526) (Figue 2b). For a low molecular or inorganic electrolyte in an aqueous solution,  $D \approx 10^3 \,\mu\text{m}^2/\text{s}$ ,  $\text{Pe}_{aqu} = 0.5 \ (m = 0.34)$  is one order of magnitude smaller than the required minimum value. Hence, with a perfectly permselective interface, no bulk ECI was feasible for а low molecular electrolyte.

#### Equilibrium ECI of concentration depletion

By relaxing the perfect charge selectivity for an ideal interface in theory, Rubinstein and Zaltzman reported the equilibrium ECI in a three-layer setup for a membrane flanked by two concentration polarized diffusion layers (Figure 2c) [39]. Since the current is under or near limiting current, this instability is called equilibrium ECI to be distinctive from the nonequilibrium ECI in OLC, where the structure of EDL at the interface is transformed into nonequilibrium one [32]. But this instability still appears in the depletion region at the interface, similar to the non-equilibrium counterpart.

The charge selectivity is characterized by the fixed charge density N in the membrane (a perfect membrane corresponding to  $N \gg 1$ ). The linear instability analysis suggested the dependence of the neutral stability curve on the fixed charge density N, and the scaled critical voltage  $(V_{cr}^*)$  for the onset of instability decreases as N decreases (Figure 2d). The numerical solution of governing equations for a poorly selective membrane (N = 2) found the transition to oscillations turning chaotic upon further increase of voltage.

#### Equilibrium ECI of concentration enrichment

In an annular channel with an inner anode of radius  $R_1$ and outer cathode of radius  $R_2$  (the ratio  $\chi = R_1/R_2$ ) (Figure 2e), the electric field near the inner anode at  $r = \chi$  is as below,

$$E_{\max}(\chi) = -1/\chi \ln \chi. \tag{2}$$

This  $E_{\text{max}}$  at  $r = \chi$  becomes singular as  $\chi \to 0$ , providing the sufficient driving force for ECI. In other words, the limitation of unrealistically high Pe in planar geometry

might be eliminated by the strong electric field due to the singularity of line charges.

**Linear stability analysis:** The linear stability analysis was performed, and the neutral stability curve for growth rate  $\omega = 0$  indicated a minimum material Peclet number  $\text{Pe}_{\min}$  for various  $\chi$ . Pe<sub>min</sub> decreases with  $\chi$ , and once  $\chi < \chi_{cri}$  ( $\chi_{cri} \approx 0.045$ ), Pe<sub>min</sub>  $< Pe_{aqu}$  (Figure 2f). Therefore, equilibrium ECI of concentration enrichment for an aqueous electrolyte is possible in a circular channel.

**Numerical simulation:** In order to explore the nonlinear evolution of the instability, a numerical simulation of the coupled Nernst–Planck–Poisson and Navier–Stokes equations was done for the circular geometry. Simulation results showed the formation of vortex in concentration enrichment region near the inner anode ( $\chi = 1/120 < \chi_{cri}$ ), demonstrating the development of equilibrium ECI (Figure 2g).

**Experimental observation:** A circular channel embedded in a PDMS device was designed, the channel height  $H \approx 40 \ \mu\text{m}$ , the outer copper ring  $2R_2 = 24 \ \text{mm}$ , the inner copper wire  $2R_1 = 0.4, 0.2 \ \text{mm}$  corresponding to  $\chi = 1/60, 1/120$ , the concentration of the aqueous CuSO<sub>4</sub> 1 mM, and the voltage at inner anode  $\Phi = 6\text{V}$ . The observed streamlines from 20-*s* time-lapse imaging and the associated PIV evidently reveal the existence of equilibrium ECI of concentration enrichment in a circular channel ( $\chi < \chi_{cri}$ ).

**Generalization to more curved geometries:** The criterion for equilibrium ECI in the circular geometry in terms of a critical electric field can be generalized to any curved geometries, and the local electric field on the anode  $\overline{E}_{max}$  should be larger than  $\alpha/Pe$ , *i.e.*,

$$\bar{E}_{max} \ge \alpha / \text{Pe},$$
 (3)

where  $\alpha \approx 14.34$  and  $\overline{E}_{max}$  for any anode geometry can be obtained by conformal mapping accordingly [57].

# Electroconvection-driven deionization shock

In a circular channel (Figure 3a), the bulk ECI drives the propagation of a deionization shock up to millimeter scales [56]. Here, we briefly present the related theory of EC-driven deionization shock in OLC.

# 1D model for EC-driven OLC

A dilute, binary z : z electrolyte with concentration ( $c_0$ ) fills a circular channel with an inner radius ( $R_1$ ) and outer radius ( $R_2$ )( $\chi = R_1/R_2 < 1$ ) under applied voltage V. In the steady state, under the assumption of the azimuthal symmetry and charge neutrality, the



Concentration shock driven by electroconvection in a circular channel [56]. (a) Sketch of a circular channel, potential  $\varphi$  at the outer electrode, while being 0 at the inner electrode; (b) OLC dependent on  $\tilde{c}_{d}$ ; (c) concentration distribution along the radius( $\tilde{V} = 35$ ,  $\tilde{c}_{d} = 0.1$ ); I - V curve for (d) positive voltage bias, indicting limit current around 0.4  $\mu$ A, and (e) negative voltage bias, showing limit current around 2.25  $\mu$ A at  $\chi = 1/30$ ; (f) the time-lapse snapshot from a top-down view to observe electroconvection near the inner cathode in OLC; (g) snapshots of fluorescent signals at OLC, demonstrating the spatiotemporal evolution of concentration shock, and shock propagation front marked by the red circular contour; and (h) radial profiles of fluorescent intensity at t = 0, 20, 40, and 60 s, the steep jump of fluorescent intensity due to concentration shock.

Nernst-Planck equations can be simplified into a 1D dimensionless form:

$$\frac{\mathrm{d}\tilde{c}}{\mathrm{d}\tilde{r}} + \tilde{c}\frac{\mathrm{d}\tilde{\varphi}}{\mathrm{d}\tilde{r}} + \tilde{\sigma}_{EC}\frac{\mathrm{d}\tilde{\varphi}}{\mathrm{d}\tilde{r}} = -\frac{\tilde{I}}{2\pi\tilde{r}},\tag{4a}$$

$$\frac{\mathrm{d}\tilde{c}}{\mathrm{d}\tilde{r}} - \tilde{c}\frac{\mathrm{d}\tilde{\varphi}}{\mathrm{d}\tilde{r}} + \tilde{\sigma}_{EC}\frac{\mathrm{d}\tilde{\varphi}}{\mathrm{d}\tilde{r}} = 0, \qquad (4\mathrm{b})$$

where  $\tilde{c} = \tilde{c}_+ = \tilde{c}_-$  is the (equal) dimensionless mean concentration of cations and anions scaled by  $c_0$ ,  $\tilde{r}$  the dimensionless radius scaled by  $R_2$ ,  $\tilde{\varphi}$  the dimensionless potential scaled by thermal voltage,  $k_BT/ze$ , and  $\tilde{I}$  is the dimensionless current scaled by  $zeDc_0$ , assuming equal diffusivity D for cations and anions. A residual bulk conductivity  $\tilde{\sigma}_{EC}$  is introduced to capture the electroconvection.

## Concentration depletion and deionization

When the electroconvection occurs, the intense vortex will enhance the ion transport locally and increase the conductivity. Therefore, conductivity ( $\tilde{\sigma}_{\rm EC}$ ) can be used in Nernst–Planck equation (3.1) to describe the electroconvection (EC). EC causes the formation of an extended depletion zone ( $\tilde{r} \leq \tilde{r}_d$ ) with a nearly constant area-average concentration ( $\tilde{c}_d$ ), resulting in residual conductivity( $\tilde{\sigma}_{EC} \sim \tilde{c}_d$ ), while convection is negligible in the bulk region far away from the vortices. By matching the concentration and potential in two regions at  $\tilde{r}_d$ , I - V relationship and concentration distribution can be obtained,

$$\tilde{V} = \ln\left(1 + \frac{\tilde{I}}{4\pi\tilde{c}_d}\ln\tilde{r}_d\right) - \frac{\tilde{I}}{4\pi\tilde{c}_d}\ln\left(\frac{\tilde{r}_d}{\chi}\right), \quad (5)$$

$$\tilde{c} = \begin{cases} \tilde{c}_{d,} & \tilde{r} \leq \tilde{r}_{d,} \\ \frac{\tilde{I}}{4\pi} \ln\left(\frac{\tilde{r}_{d}}{\tilde{r}}\right) + \tilde{c}_{d,} & \tilde{r}_{d,} \leq \tilde{r} \leq 1. \end{cases}$$
(6)

The calculated I - V curves (Figure 3b) show OLC is sustained by  $\tilde{\sigma}_{EC}$ , and the concentration distribution (Figure 3c) presents concentration depletion region (shock) with constant  $\tilde{c}_d$  after the front  $\tilde{r}_d$  ( $\tilde{r} \leq \tilde{r}_d$ ).

#### Limiting current dependent on voltage bias

Since the translational symmetry is broken in the annular geometry, current-voltage curve will be related to the voltage bias, *i.e.*, the positive voltage bias  $(\tilde{r}_{cathode} = \chi, \tilde{I} < 0)$  or the negative voltage bias  $(\tilde{r}_{cathode} = 1, \tilde{I} > 0)$ .

For  $\tilde{\sigma}_{EC} = 0$ , EC is absent and the residual conductivity vanished, and then quiescent solution of concentration polarization can be solved from Eq. (3.1) together with concentration conservation,

$$\tilde{c} = 1 - \frac{\tilde{I}}{4\pi} \left( \ln \tilde{r} + \frac{1}{2} + \frac{\chi^2 \ln \chi}{1 - \chi^2} \right), \tag{7a}$$

$$\tilde{\varphi} = \ln \tilde{c} + \text{const.}$$
 (7b)

An analytic solution of the limiting current under positive or negative voltage bias is obtained from Eq. (7a) as the concentration approaches to zero at cathode,

$$\tilde{I}_{pos} = -8\pi \frac{(1-\chi^2)}{1+2\ln\chi-\chi^2}, [\tilde{c}(\chi)=0],$$
(8a)

$$\tilde{I}_{neg} = 8\pi \frac{(1-\chi^2)}{1+2\chi^2 \ln \chi - \chi^2}, [\tilde{c}(1) = 0],$$
(8b)

$$\tilde{I}_{bias} = \frac{\tilde{I}_{neg}}{\tilde{I}_{pos}} = -\frac{1 + 2\ln \chi - \chi^2}{1 + 2\chi^2 \ln \chi - \chi^2}.$$
 (8c)

The measured I - V curves depend on the voltage bias, and the associated ratio of limit current is about 5 (Figure 3d and e).

#### **Observation of EC-driven deionization shock**

Because of the symmetry broken and the consequent effect of voltage bias, the aforementioned equilibrium ECI (Section 2.3) is under the operation of the *negative* voltage bias (the inner central electrode acting as the anode) [57], while the following EC-driven deionization shock is under the operation of the *positive* voltage bias (the inner central electrode acting as the cathode) [56]. Experimentally, in an aqueous CuSO<sub>4</sub> solution, an array of the vortices (Figure 3f) was confined within the horizontal plane with circumferential length up to millimeters and is attributed to non-equilibrium electroconvection with the positive voltage bias. By adding the fluorescent indicator (Phen Green SK dipotassium salt, the intensity quenched by Cu<sup>2+</sup> ions), the spatiotemporal evolution of concentration is visualized. The initial homogeneous distribution of fluorescent intensity is separated into two distinct regions marked by the red circular contour (Figure 3g). The radial intensity (Figure 3h) demonstrates the propagation front with a sharp intensity jump, in a fashion reminiscent of the deionization shock.

# Conformal mapping in complex geometries

The asymmetry or symmetry breaking provides another degree of freedom to manipulate the ion transport. The complicated geometries together with asymmetries might offer opportunities to further unravel more electrokinetic phenomenon. However, the complex geometries not only hinder the direct derivation of analytical solutions in the mathematic analysis but also increase the computational cost and numerical difficulty of the numerical simulation. As one of the elegant mathematical approaches, conformal mapping has the unique capacity to tackle the complicated irregular geometries in electrokinetics [61,62].

# An eccentric annulus

Considering an eccentric annulus with an inner radius  $\chi$ , an outer radius 1 and an eccentricity *e* in a *z* plane,

$$\{\Omega_{z} | \|z\| < 1, \|z - e\| > \chi, 0 < e < 1 - \chi\}.$$
(9)

By function  $\zeta = f(z)$ , the eccentricity ring is conformally mapped to a concentric annulus (an inner radius  $\kappa$  and outer radius 1) in  $\zeta$  plane { $\Omega_{\zeta} |\kappa < ||\zeta|| < 1$ } (Figure 4a). The formation of the mapping is

$$\zeta = f(z) = \frac{z - \alpha}{\alpha z - 1}, \|\alpha\| < 1, \tag{10}$$

where  $\alpha$  is a function of *e* and  $\chi$ .

The annulus with the different eccentricity is conformally mapped to a concentric annulus with a different inner radius  $\kappa$ . Then, the limit current corresponds to the vanished concentration or zero concentration at cathode and can be obtained from conformal mapping. Figure 4b shows the experiment measurements agree well with the theory for limiting current dependent on the eccentricity. The concentration distribution is presented in Figure 4c, while the distribution of electric field is demonstrated in Figure 4d, indicating electric



Electrokinetics in complex geometries [58]. For an eccentric circle, (**a**) the eccentric circle  $\Omega_z$  being conformally mapped to a concentric circle  $\Omega_{\zeta}$ ; (**b**) comparison between theory and experiment for the limit current with different eccentricity *e*; (**c**) concentration distribution and (**d**) electric field in an eccentric circle ( $\chi = 1/30$ , e = 1/2); (**e**) electric field intensity at the inner cathode dependent on  $\theta$ ; electroconvection along  $\theta = 0$  (**f**) having a larger size, and (**g**) occurring earlier; (**h**) more pronounced deionization shock along  $\theta = 0$ . For a concentric ellipse, the concentration distribution of (**i**) concentric ellipse and (**j**) the inner ellipse degenerated to a stripe. For a corner geometry, (**k**) the electric field distribution in a corner geometry and (**l**) the electric field intensity changes from isotropy to anisotropy with increasing distance from the corner cathode.

field at the inner cathode along  $\theta = 0$  is stronger than that along  $\theta = \pi$  (Figure 4e).

Although this anisotropic electric field is calculated under the limit current, one can reasonably argue that a similar anisotropic distribution of electric field still holds for OLC. As a result, EC most likely appears along  $\theta = 0$  direction. Indeed, the vortices appear earlier along  $\theta = 0$  in most experiments, as shown by the PIV image (Figure 4f and g). The size of vortices along  $\theta = 0$  is larger than that along  $\theta = \pi$  (Figure 4f), and the deionization shock along  $\theta = 0$  is stronger, since the fluorescence signal is stronger as well (Figure 4h).

When the inner radius is anode, the ECI of enrichment region occurs in a circular channel because of the singularity of electric field. In an eccentric annulus, the electric field along  $\theta = 0$  is strongly enhanced, making it easier to achieve ECI of concentration enrichment.

### A concentric ellipse

In addition to the eccentric annulus, conformal mapping can be applied to other complicated geometries, such as a concentric ellipse. The Joukowski transformation

$$z = g(\zeta) = \zeta + \frac{\gamma^2}{\zeta}, \qquad (11)$$

maps an annulus  $\Omega_{\zeta}$  in  $\zeta$  plane  $\{\Omega_{\zeta}|\kappa < \|\zeta\| < 1\}$  to a concentric ellipse  $\Omega_z$  in physical z plane,

$$\left\{\Omega_{z} \left| \frac{x^{2}}{(1+\gamma^{2})^{2}} + \frac{y^{2}}{(1-\gamma^{2})^{2}} < 1, \frac{x^{2}}{\left(\kappa + \frac{\gamma^{2}}{\kappa}\right)^{2}} + \frac{y^{2}}{\left(\kappa - \frac{\gamma^{2}}{\kappa}\right)^{2}} > 1 \right\}.$$
(12)

The concentration distribution is shown in Figure 4i. When  $\gamma = \kappa$ , the inner ellipse in  $\Omega_x$  is degenerated into a stripe with length of  $4\kappa$ , and the electric field at the tips of stripe forms a singularity, likely drives ECI of concentration enrichment as well (Figure 4j).

#### A corner geometry

A corner geometry is taken as another example of the complex geometry applicable for conformal mapping. The following transformation

$$\zeta = \frac{z^n - i}{z^n + i},\tag{13}$$

maps the infinite  $\Omega_z$  region in a physical z plane.

 $\{\Omega_z | r > 0, 0 < \theta < \frac{\pi}{n}\}$  to a unit circle  $\Omega_{\zeta}$  in a mathematical  $\zeta$  plane  $\{\Omega_{\zeta} | 0 \le r < 1\}$ . For n = 3, the electric

field in corner geometry is shown in Figure 4k. For a given red circle centered around the cathode, the electric field is determined by both the distance away from the point electrode  $r_n$  and its azimuthal direction  $\theta$ . As shown in Fig. 4l, the electric field appears isotropic near the cathode and becomes anisotropy with increased distance. These results provide the guidance for precise regulation of electric field for electrophoresis [63].

# Remote electrokinetic instability within supporting electrolyte

While binary electrolyte has been widely studied in different complex geometries, such as the intriguing interfacial instabilities [64], the multi-component electrolyte is less examined [65]. Based on the classical Cu |CuSO<sub>4</sub>|Cu electrochemical system, the effect of supporting electrolyte is systematically investigated by highlighting the inert cations [59]. ECI is suppressed by the inert cation, while an array of remote electroconvection (REC) emerges, which is correlated with the inert-cation concentration valley.

### **REC** along an azimuthal direction

In an annular geometry, ECI in CuSO<sub>4</sub> working electrolyte is expected to occur at the central cathode (Figure 5a and b). However, by adding the secondary supporting electrolyte of Na<sub>2</sub>SO<sub>4</sub> into the CuSO<sub>4</sub>, the traditional ECI is suppressed, while an array of REC or remote vortices along the azimuthal direction emerges away from the electrodes (Figure 5c and d). The location of remote vortex  $R_{\text{vortex}}$  is about 2 mm away from the inner cathode, and the size of each vortex is about 50 µm. The typical velocity and vorticity for ECI and REC are on the same order of 30 µm/s and 0.3 s<sup>-1</sup>. But different from ECI, REC is transient and lasts for a period with a limited lifetime  $\tau_{life} \approx 100$  s, then gradually disappears after 2 min.

The transition from ECI to REC is determined by the supporting concentration (Figure 5e). For 1 mM CuSO<sub>4</sub> working electrolyte under 5 V, a critical concentration value of Na<sub>2</sub>SO<sub>4</sub> supporting electrolyte is  $c_{cri} \approx 0.4$  mM. At the lower concentration [c(Na<sub>2</sub>SO<sub>4</sub>) <  $c_{cri}$ ], ECI near the cathode is observed; but at the higher concentration [c(Na<sub>2</sub>SO<sub>4</sub>) >  $c_{cri}$ ], an array of REC emerges along the azimuthal direction. Once REC is formed, both  $\tau_{life}$  around 100 s and  $R_{vortex}$  around 2 mm are nearly insensitive to the concentration. By further checking with different combinations of the working and supporting electrolyte, the presence of the inert cations is arguably accountable for the suppression of ECI and appearance of REC (Figure 5f and g).

# Inert-cation concentration valley

In order to reveal spatiotemporal evolution of the inert cations, Rhodamine 6G (Rh6G) is chosen as the supporting electrolyte, allowing the characterization of





Observation of remote electroconvection [59]. (**a**, **b**) Snapshot and PIV image of ECI at cathode for the working electrolyte of CuSO<sub>4</sub> only (**c**, **d**) snapshot and PIV image of REC in CuSO<sub>4</sub> (1 mM)-Na<sub>2</sub>SO<sub>4</sub>(0.9 mM) with the supporting electrolyte; (**e**) REC for  $c(Na_2SO_4)$  and the associated  $R_{vortex}$  and  $\tau_{life}$ ; (**f**) REC in CuCl<sub>2</sub> (1 mM)-NaCl (0.9 mM) with inert cations; and (**g**) ECl in Cu<sub>2</sub>SO<sub>4</sub> (1 mM)-CuCl<sub>2</sub> (0.9 mM) without inert cations.

Rh<sup>+</sup> concentration from the fluorescent intensity. From the snapshot, a darker front corresponds to a lower fluorescent intensity or the local reduction of the inert cation Rh<sup>+</sup> in 0.2 mM CuSO<sub>4</sub> - 0.2 mM RH6G electrolyte at 5 V (Figure 6a). The time-dependent radial distribution of fluorescent intensity clearly presents the concentration valley with a local concentration reduction or dip, as marked by  $R_{\text{valley}}$  (Figure 6b). The propagation velocity of this front is nearly a constant about 40 µm/s (Figure 6c), which is compared with the calculated electromigration-limited velocity [59].

Moreover, the coexistence of the concentration valley and REC is revealed by the simultaneous visualization of spatiotemporal evolution for concentration and flow by adding fluorescent particles (Figure 6d). As shown by zoom-in view, the size of vortices is around 100  $\mu$ m, and their location is around the darker region associated with the lower concentration of Rh<sup>+</sup>. At a later stage, the propagation front is distorted by the array of remote vortices, and the azimuthal symmetry of the concentration valley indeed is broken. Their coexistence directly indicates the strong correlation between concentration and REC at the microscopic level.

## Phase diagram

Dependent on the concentration of working and supporting electrolyte, the different instabilities such as

ECI or REC might take place, and the phase diagram of  $CuSO_4 - Na_2SO_4$  electrolyte at 5 V is constructed (Figure 6e). For a low  $c(Na_2SO_4)$  and  $c(CuSO_4)$ , ECI is generated due to the extended space charge at the cathode. For a high  $c(Na_2SO_4)$ , such as  $CuSO_4$  (1 mM)-Na\_2SO\_4 (10 mM), bubbles are produced by water splitting at the cathodes to sustain the current. For a low  $c(Na_2SO_4)$  and high  $c(CuSO_4)$ ,  $Cu^{2+}$  ions might dominate the ion transport in a way that their fast deposition leads to the dendrite growth. For an intermediate  $c(Na_2SO_4)$  and low  $c(CuSO_4)$ , REC is formed. By comparing the two transportation timescales for the inert cations (charging timescale into EDL at the cathode interface, and migration timescale within the bulk), the transition from ECI to REC has 1/2 scaling [59].

# Outlook and future direction

In this review, we briefly present the recent progress of ECI and shocks. (1) In a circular channel, the limitation of an unrealistically high material Peclet number in planar geometry is eliminated by the strong electric field, and equilibrium ECI of concentration enrichment is formed in an aqueous electrolyte. (2) Deionization shock can be driven by electroconvection up to millimeter scales. (3) Conformal mapping is applied to tackle the symmetry broken in more complex geometries, providing insight into ECI and deionization shock. (4) Additionally, in a multi-component electrolyte, the inert





Observation of inert-cation concentration valley and phase diagram [59]. (a) Spatiotemporal evolution of the inert-cation  $Rh^{nbsp;+}$  fluorescent intensity, and the propagation front with a nearly well-preserved circular contour as marked in red; (b) the radial profile of the fluorescent intensity, indicating a pronounced concentration valley with a local dip at  $R_{valley}$ ; (c) propagation of  $R_{valley}$  at an electromigration-limited velocity  $v_{em} = 40 \mu m/s$ ; (d) strong correlation between REC and concentration valley; and (e) phase diagram of various instabilities depending on the concentration of working and supporting electrolyte at 5 V.

cations of support electrolyte can induce the remote electroconvection and form the concentration valley.

More raised questions might be addressed along the path in future as below: (1) How to practically implement the discovered equilibrium ECI of concentration enrichment for the technological advancement to prevent the undesirable salt enrichment? (2) Is it possible to intergrade EC-driven deionization shock into shock electrodialysis for the purpose to boost the desalination performance of shock electrodialysis? (3) What is the role of inert cations and the physical mechanism of remote electroconvection within supporting electrolyte? These results might not only push the current boundaries of fundamental understanding but also have relevant technological implications for desalination, water treatment, and energy storage in batteries.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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