Selection of Non-Equilibrium Over-Limiting Currents: Universal Depletion Layer Formation Dynamics and Vortex Instability

Gilad Yossifon and Hsueh-Chia Chang

Department of Chemical and Biomolecular Engineering, Center for Microfluidics and Medical Diagnostics, University of Notre Dame, Notre Dame, Indiana 46556, USA

We report the first experimental verification of an electrosmotic vortex instability, first predicted by Rubinstein and Zaltzman (1988), at a micron-sized extended polarized layer on the depleted side of a homogenous nanoporous membrane, when the current through the membrane exceeds the limiting current. The vortex instability is shown to select the extent of the polarized layer and a thicker diffusion layer beyond it, and thus specify the over-limiting current. The requisite conductivity gradient across the ion-selective membrane is reproduced by a fabricated nano-microchannel junction with the former/latter having a depth smaller/larger than the Debye length. The extended polarized layer and the accompanying diffusion layer, whose much larger dimension allows fluorescent tracking, are sustained quasi-steadily with an AC field. Beyond a critical instantaneous field strength, the diffusion layer dynamics is shown to be self-similar at all scales, independent of the frequency and field strength, until the vortices arrest its growth. The vortex pair wavelength doubles in time sequentially in this self-similar region before saturation and is roughly on the order of the diffusion layer thickness.

Previous theories on ionic conduction from an electrolyte solution into an ion selective nanoporous membrane have suggested that the steady conduction flux through the membrane becomes unstable beyond the diffusion-controlled limiting current when the electrolyte concentration near the interface approaches zero (Rubinstein & Zaltzman, 2000). Unlike the Poisson-Boltzmann distribution at zero flux, which is globally stable, the polarized layer is unstable to transverse perturbations in a manner reminiscent of Rayleigh–Benard and Marangoni instabilities in thermal conduction. With any local increase in the polarized layer thickness, the diffusion layer thickness decreases and the field at the outer boundary of the polarized layer increases. This positive feedback further extends the local polarized layer thickness and the local electric field. The resulting transverse gradient in the polarized layer thickness produces a transverse field that drives a non-equilibrium and non-uniform electro-osmosis slip flow in the extended polarized layer. This vortex instability hence has its own selected length scale — the evolving diffusion layer thickness. This is in contrast to the classical electro-osmotic vortices of the 2nd time (Dukhin, 1991) around a granule, which occur because of inhomogeneous polarization due to granule curvature and exhibit length scales comparable to the granule radius (Mishchuk & Takhistov, 1995; Ben & Chang, 2002). In the theories of Rubinstein and co-workers, however, the diffusion layer thickness is pre-imposed and specified by external stirring. The implication is then the over-limiting current is stirring dependent.

Secondary instability of the steady vortices has also been predicted (Rubinstein & Zaltzman, 2000) and has been speculated to be the origin of significant noise in the measured current beyond the limiting current conditions. This mechanism is consistent with some indirect experimental observations: if the depleted diffusion layer is immobilized by a gel, a plateau is reached at saturation, and the excess electric noise disappears (Maletzki et al., 1992). However, a direct confirmation of the vortex instability of extended polarized layers and their role in determining the overlimiting current has yet to be reported.

In recent years, with the development of micro- and nano-fabrication technologies, increasing experimental evidence for this instability has been reported at the entrance of a single array of nanochannels. As in membrane nanopores, the permselectivity of a nanochannel stems from the existence of EDL overlap since nanochannels approach double layer dimensions. Effects such as concentration polarization across an array of nanochannels have been reported by several groups (e.g. Pu et al. (2004), Plecis et al. (2005) and Kim et al. (2007)). The latter group also reported electro-osmotic vortices of the 2nd time that arise from non-uniform polarization at the micro-nano junction and with dimensions comparable to the channel width. Hence, definitive and quantitative connection to true vortex instabilities with intrinsic length scales has yet to be established.

A unique universal and self-similar diffusive evolution of the field-driven diffusion layer dynamics, independent of the frequency and the instantaneous field strength, allows us to sustain and examine the vortex instability quasi-steadily with an AC field in our experiments. In the process, we confirm the predicted relationship between the instantaneous vortex pair wavelength and the evolving diffusion layer thickness (Rubinstein & Zaltzman, 2000). However, we also demonstrate from the data that, at low frequencies, the growing diffusion layer thickness saturates at an asymptotic thickness due to the vortex instability at a value that is dependent only on the field strength and the liquid mobility. This asymptotic thickness is also expected to be the one selected under DC conditions. This result has the important implication that, if hydrodynamic resistance is not too severe to suppress vortex formation (viz. too shallow a channel), the over-limiting current is independent of external stirring and is actually intrinsic to the system. We are hence able to produce the first a priori estimate of the overlimiting current that is consistent with our measured current through the nanochannel. We are also able to produce a dimensionless electro-osmotic Rayleigh number based on the quasi-diffusion layer thickness for the onset of vortices in a microfluidic slot.

The application of AC electric field is a key factor in our success to quasi-steadily sustain diffusion layers of different thickness and capture this instability. The same AC field can also suppress the instability altogether with frequencies higher than the inverse vorticity-diffusion time scale such that the macroscopic vortical flow pattern has no time to evolve. This corresponds to subcritical conditions below the critical Rayleigh number. Hence, our result has further implications on how to dynamically control (by AC forcing) the overlimiting current such that it deviates from the DC value. The Rayleigh number for the onset of vortices is dependent on the depth of the microchannel (through hydrodynamic resistance or vorticity diffusion time) and one can hence also design specific DC and AC I-V characteristics with proper adjustment of the channel geometries. Being able to control the flux through an ion-exchange membrane is both scientifically interesting because of the myriad of pertinent physics, and also important in many engineering and biological applications.

References

[1] Ben Y. & Chang H.-C., Nonlinear Smoluchowski slip velocity and micro-vortex generation, J. Fluid Mech., 461, 229-238 (2002).

[2] Dukhin S.S., Electrokinetic phenomena of the second kind and their applications, *Advances in Colloid and Interface Science*, 35, 173-196 (1991).

[3] Kim S.J., Y.C. Wang Y.C., Lee J.H., Jang H., and Han J., Concentration Polarization and Nonlinear Electrokinetic Flow near a Nanofluidic Channel, *PRL* 99, 044501 (2007).

[4] Maletzki F., Rosler H.-W. and E. Staude, Ion transfer across eelctrodialysis membranes in the overlimiting current range: stationary voltage current characteristics and current noise power spectra under different conditions of free convection*, J. Memebrane Science*, 71, 105-115 (1992).

[5] Mishchuk N.A, Takhistov P.V, Electroosmosis of the second kind, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 95, 119-131 (1995).

[6] Plecis A., Schoch R.B., and Renaud P., Ionic Transport Phenomena in Nanofluidics: Experimental and Theoretical Study of the Exclusion-Enrichment Effect on a Chip, *Nano Lett*., 5, 1147-1155 (2005).

[7] Pu Q., Yun J., Temkin H., and Liu S., Ion-Enrichment and Ion-Depletion Effect of Nanochannel Structures, *Nano Lett*., 4, 1099-1103 (2004).

[8] Rubinstein I., Staude E. and Kedem O., Role of the membrane surface in concentration polarization at ion exchange membrane, *Desalination*, 69, 101 (1988).

[9] Rubinstein I. and Zaltzman B., Electro-osmotically induced convection at a permselective membrane*, Physical Review E*, 62, 2 (2000).