Desalination shocks in microstructures

Salt transport in bulk electrolytes occurs by diffusion and convection, but in microfluidic devices and porous media ("microstructures"), surface conduction and electro-osmotic flow also contribute to ionic fluxes. The classical theory assumes linear response to a small voltage, but what happens when a large voltage is applied? This talk describes some surprising nonlinear electrokinetic phenomena that result from the competition between bulk and interfacial transport in a microstructure, triggered by the removal of ions at a boundary (e.g. by electrodialysis or electrodeposition). At constant voltage, the microstructure can sustain an over-limiting current (exceeding diffusion limitation) without any hydrodynamic or chemical instability. At constant current, a "desalination shock" can propagate through the microstructure, leaving behind a macroscopic region depleted of ions and particles. These nonlinear phenomena are explored by mathematical analysis (homogenization, similarity solutions, stability, characteristics) and experiments on copper sulfate desalination in glass frits, which suggest a new approach to water desalination and purification ("shock electrodialysis").