Nonlinear ion transport at high electric currents in shock electrodialysis and ion-intercalation memories

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This thesis studies the nonlinear ion transport at high electric currents, in two applications: shock electrodialysis (shock ED) for ion separation, and ion-intercalation memories for in-memory computing. The two studies are both related to the concept of concentration polarization (CP) in electrochemistry, which describes the formation of ion concentration gradient in an electrolyte adjacent to a charge-selective interface. CP leads to linear concentration profiles at small current in ideal electrolyte. However, CP in shock ED and ion-intercalation memories can be very nonlinear. It has been well studied that CP at over-diffusion-limiting current in charged porous media can lead to the formation of deionization shock, which is the key physics for shock ED. The main contribution of this thesis to shock ED is the modeling of multicomponent ion separation. In addition, in this thesis, it is proposed that the CP in multiphase ion-intercalation materials can lead to phase re-distribution and can be used for non-volatile memories. A general phase-field model has also been developed in this thesis to study the multiphase CP behaviors. The details of the two studies are described as below.

Shock ED is a new electrochemical method for water treatment utilizing deionization shocks generated by over-diffusion-limiting current, developed by the Bazant group. Previous models have qualitatively described the desalination of binary electrolytes. However, they cannot quantitatively predict experiments, or explain the selective ion removal of multicomponent electrolytes recently observed in experiments. In this thesis, a depth-averaged model is developed for shock ED. Compared with previous homogenized models, the depth-averaged model includes the effect of pore-scale ion distribution by integration in the pore cross-sections. The model applies to multicomponent electrolytes and any electrical double layer (EDL) thickness, captures the phenomena of electroosmosis, diffusioosmosis, and water dissociation, and incorporates more realistic boundary conditions. The model is well consistent with experiments of binary electrolytes, and can explain the selective removal of multivalent cations from electrolytes. In addition, this thesis also includes experiments to for removal of trace amounts of lead from dilute solutions of model tap water by shock ED, showing approximately 95% of dissolved lead (to safe levels below 1 ppb), compared to 40% of sodium ions, at 60% water recovery and at an electrical energy cost of only $0.01\,\mathrm{kW\,h\,m^{-3}}$. These experimental results are quantitatively consistent with the predictions of our depth-averaged model. In summary, this thesis significantly improves the understanding of ion separation in shock ED, and can guide the optimization and scale-up of the process for industrialization.

Resistive switching (RS) memories (including two-terminal memristors and three-terminal synaptic transistors) with multiple, nonvolatile states tunable by electric fields are promising for in-memory computing. In recent years, ion intercalation materials have attracted increasing attention for RS because of the ion-modulated electronic conductivity. In 2020, the Rupp and Bazant group developed LTO memristors made from LTO4 or LTO7 nanofilms sandwiched by ion-blocking Pt electrodes. The RS behaviors for such systems cannot be explained by existing models like the dielectric breakdown model. In this thesis, an interfacial RS mechanism, multiphase polarization (MP), is proposed to explain the LTO memristors and other similar systems made from multiphase, ion-intercalation nanofilms sandwiched by ion-blocking electrodes. In the first step, a preliminary 1D model is developed to analyze the switching time and energy, and resistance ratio for MP-induced RS. Next, a general phase-field model is developed, for coupled ion-electron transport

with surface effects like non-neutral wetting condition, dynamic contact angle and surface charge. Then, 2D MP with complex surface conditions is simulated and compared with the simple 1D model. This thesis also discusses the comparison between the MP mechanism and other RS mechanisms, as well as the prospects of MP-based memristors. This work is inspired by the memory application but should also benefit other fields as a general theoretical study.