Current-Induced Membrane Discharge

Possible mechanisms for overlimiting current (OLC) through aqueous ion-exchange membranes (exceeding diffusion limitation) have been debated for half a century. Flows consistent with electro-osmotic instability have recently been observed in microfluidic experiments, but the existing theory neglects chemical effects and remains to be quantitatively tested. Here, we show that charge regulation and water self-ionization can lead to OLC by “current-induced membrane discharge” (CIMD), even in the absence of fluid flow, in ion-exchange membranes much thicker than the local Debye screening length. Salt depletion leads to a large electric field resulting in a local pH shift within the membrane with the effect that the membrane discharges and loses its ion selectivity. Since salt co-ions, H+ ions, and OH- ions contribute to OLC, CIMD interferes with electrodialysis (salt counterion removal) but could be exploited for current-assisted ion exchange and pH control. CIMD also suppresses the extended space charge that leads to electroosmotic instability, so it should be reconsidered in both models and experiments on OLC.