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Anomalous ionic transport at nanometer-scale electrodes DIEGO KRAPPF, Delft University of Technology, BERNADETTE QUINN, MENG-YUE WU, HENNY ZANDBERGEN, CEES DEKKER, SERGE LEMAY — We probe the transport of charged species in high ionic strength solutions on the scale of a few nanometers by monitoring electrochemical reactions at correspondingly sized electrodes. The electrical current through the nanoelectrode provides a direct measure of the flux of ions across the diffuse double layer. Because both the concentration gradient and the electric field are localized in the immediate vicinity of the nanoelectrode, this provides very local information. Furthermore, when the electrode dimensions are in the order of a few nanometers, very steep concentration gradients are achieved. To carry out these experiments, we have developed a method for fabricating nanoelectrodes with a well-defined size and geometry. A pore is first drilled in an insulating membrane with a focused electron beam and it is then filled with a noble metal yielding conically shaped, convex electrodes with radii as small as 2 nm. We observe pronounced non-linearities of ion flux versus concentration when transport is localized within a region smaller than 10 nm in size. We numerically calculate the predicted ion flux using the Stern-Poisson-Nernst-Planck formalism. We show that our observations cannot be explained using this widely applied mean-field description of ionic transport.

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