Ion Current Oscillations Caused by Femtoliter Volume Precipitation in a Nanopore

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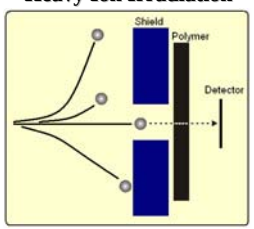
Abstract

The fixed negative surface charges inside single conical polymer nanopores result in transport properties not encountered in micrometer-scale counterparts. A notable example of an effect caused by these permanent negative charges is the enhancement of ionic concentration inside the pore when compared to the bulk solution. The nanopores described here are created with the track etching technique resulting in a conical geometry having a large opening of hundreds of nanometers and a small opening of several nanometers. A new phenomenon is presented detailing an oscillating ionic current through our conical nanopore when a small amount of a divalent cation is added to a buffered monovalent ionic solution. An ionic current enhancement brought on by the superposition of the electric field from the fixed negative surface charges and the externally applied electric field causes a formation and redissolution of nanoprecipitates that temporarily block the ionic current through the pore. The frequency and character of these ionic current oscillations is regulated by the transmembrane potential and the chemistry of the nanoprecipitate. This oscillating system could be used as a model for studying nonlinear electrochemical processes and early stages of crystallization.

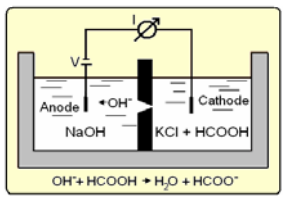
Nanopore Fabrication

Heavy Ion Irradiation



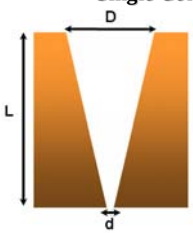
A high energy single heavy ion creates a damage track through the polymer film.

Chemical Etching

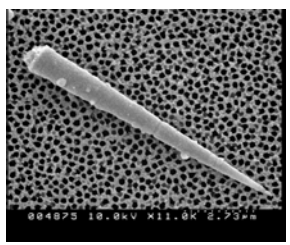


Sodium hydroxide etches along the damage track until breakthrough occurs and the etching is stopped.

Single Conical Nanopore Dimensions

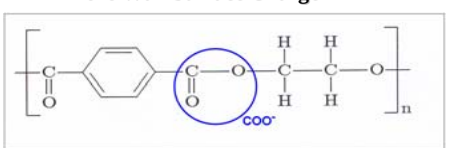


L = 12 micrometers
D ~ 450 nanometers
d ~ 3 nanometers



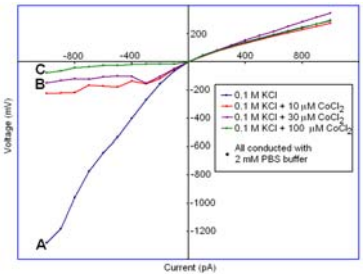
A gold electroless deposition "negative" of a conical PET nanopore. (Univ. of Florida)

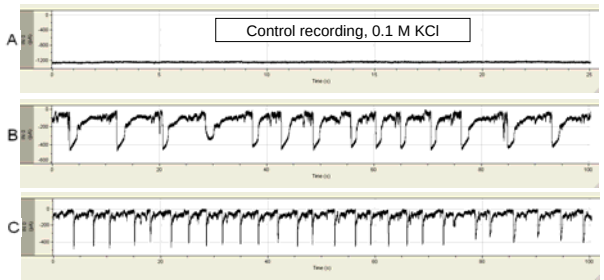
Pore Wall Surface Charge



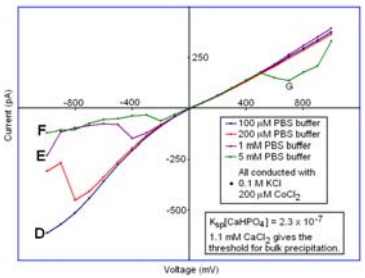
Etching PET with NaOH produces carboxyl groups on the polymer surface. Surface density of these groups is estimated at ~1.5 per nm².

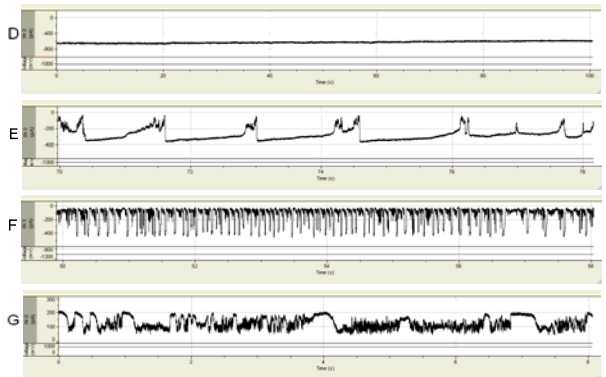
Cobalt Induced Oscillations with PBS Buffer



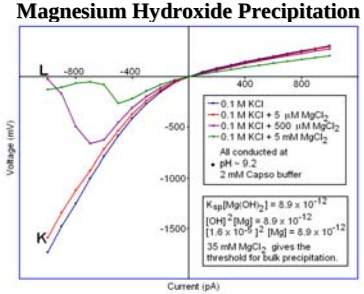


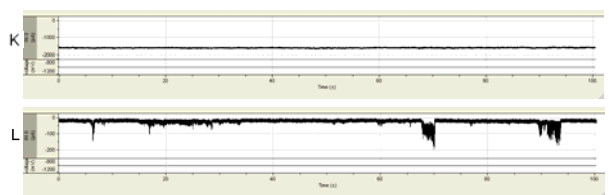
PBS Buffer Dependence on Calcium Induced Oscillations

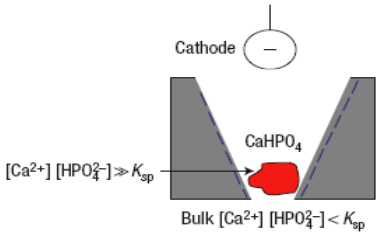




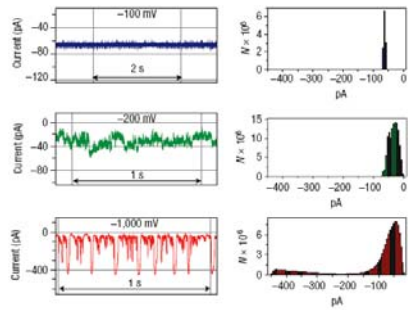
Magnesium Hydroxide Precipitation



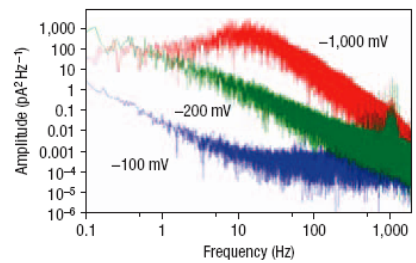




When the negatively biased electrode (cathode) is at the larger opening of a conical nanopore, cations will move from the narrow opening towards the larger opening of the cone. The activities of Ca^{2+} and HPO_4^{2-} ions inside the nanopore then rise above the solubility product K_{sp} of CaHPO4, allowing nanoprecipitation to occur.

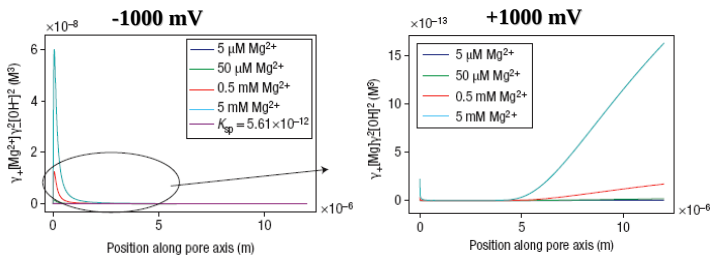


Ion current time series along with current histograms for various applied voltages as indicated, with 0.1 M KCl, 0.2 mM $CaCl^2$ and 5 mM PBS.



Power spectra of the ion current recordings above. The peak between 10 Hz and 20 Hz for the -1,000 mV time series corresponds to oscillations of that frequency, which can be clearly seen from the time series.

Modeling of the Theoretical Concentration for the Magnesium Hydroxide Precipitation



Theoretical results from the one-dimensional Poisson–Nernst–Planck model mapping the products of the magnesium and hydroxide activities for -1,000 mV (left), +1,000 mV (right), along the pore axis. Position 0 corresponds to the tip of the pore. The modelling confirms that the ionic concentrations in the pore are very different for the two voltage polarities, allowing the nanoprecipitates to form for negative voltages.

Acknowledgements:

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