# Understanding Conduction Mechanisms in Nano-Structures

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## ABSTRACT

Many emerging technologies require the understanding of charge transport mechanisms through nanostructures. Our previous research has revealed unusual and enhanced conduction properties in pores whose width is significantly less than 1μm over a range of +10V to -10V. The conduction current, as a function of voltage, of a NaCl electrolyte within a 150-nm pore has been measured and characterized using an atomic force microscope (AFM). A double-layer conduction model has been devised to explain the experimental results.

*Keywords*: atomic force microscopy, nano-conduction, nanopore, double-layer model, electrolyte

## 1 BACKGROUND

The Naval Surface Warfare Center, Dahlgren Division, has been involved in interface-research issues with liquid dielectrics for three decades [1]. Modeling efforts for water electrolytes have progressed through traditional mechanisms to include charge injection [2] as well as double-layer models [3], [4], [5], and [6]. Recently work has extended into the field of nanotechnology and resulted in measurement of conductance through water-electrolyte-wetted nanostructures [7], [8].

Traditional theoretical investigations into water-electrolyte conductance include classic works [9], [10] and double-layer calculations [11]. More recent investigations into nano-pores include impressive experimental measurement of diffusion and transport [12] (under similar conditions to our work) as well as sophisticated theoretical electrochemistry-based investigations that focus on the effects of double layers and surface potentials on charge transport in nanopores [13]. Still, it would be useful to know if simpler calculations can explain the existing experimental data, especially given the large number of unknown variables in actual nanopore experiments, including actual profile through the material, concentration gradients within the electrolyte, surface charge distribution along the nanopore wall, etc.

## 2 MEASUREMENT

The nanopores used were samples produced by the Naval Research Laboratory and kindly donated to NSWC Dahlgren Division. The nanopores are well documented [14]. The conduction measurement using the nanopores can be described quite simply but is difficult to do and involves considerable art as well as science. There are some dynamic processes going on simultaneously which will affect results including the rate of solvent evaporation and drift of the Atomic Force Microscope (AFM) tip across the surface of the sample. Fluctuation in the data is significant from experiment to experiment, even on the same sample. Yet, such experimental probes are necessary to characterize the unique behavior found in nanopores.

The procedure consists of:
1. Preparing the electrolyte solution.
2. Cleaning or preparing the nanopore sample.
3. Electrowetting the sample to insure filling the nanopore with the electrolyte solution. (This often requires voltage ~ 100 VDC.)
4. Quickly transporting the sample to the AFM and conducting a contact scan.
5. Simultaneously capturing conductance data during the contact-contour surface scan.
6. Quickly deciding on a representative nanopore. Positioning the tip over the selected pore and conducting a semi-DC sweep of voltage over a range of roughly plus-minus 12 Volts.

## 3 MODEL

Numerous models have been proposed for conduction in nanostructures. In general, they are adaptations of Debye-Hückel theory [15], [16], [17]. The model chosen to analyze the nanopore conduction behavior seen in this paper is an adaptation of previous pulsed-power research by one of the authors. Instead of relying on an ionic atmospheric to represent "drag" on an ionic conductor moving in a dielectric, polar fluid under the impetus of a semi-DC electric field, the mobility value is assumed to be enhanced directly. Other modifications are certainly possible and reasonable, including concentration alterations, mobility as a function of electric field (the Wien effect), etc. But the first-order correction has been assumed to be a mobility enhancement in the double layer near the walls of the nanopores. Therefore, two regions of conduction exist within the cylindrical nanopore: the bulk region (with standard conduction values) and the double layer region near the edge where enhanced mobility is fit to the data. Please see Figure 1.
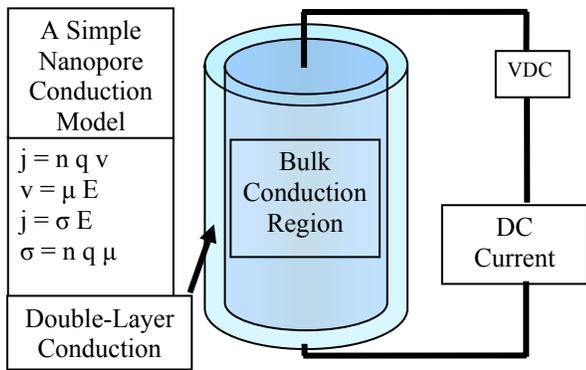
Figure 1: Schematic of a simple conduction model for a nanopore.

The key to the validity of the enhanced-conduction double-layer model is whether 'reasonable' values for the double-layer thickness and enhanced mobility can account for experimental observation. Those parameters are fitted through a trial-and-error process bounded by physical expectations for water electrolytes. Some expected boundaries include:

1.   Limit of the enhanced mobility equal to the ratio of the dielectric constant in the bulk to that in the double layer. In practice this means less than a factor of 78 at room temperature, but since the dielectric constant of the double layer is more often calculated to be between 2 and 6, an upper limit of 40 would be better.

2.   Limit the thickness of the double layer to some reasonable multiple of the Debye Length in a water electrolyte, which is 3.033 nm at room temperature in 0.01M NaCl.

$$\lambda_D = \sqrt{\frac{\varepsilon k T}{e^2 \sum_{i=1}^{N} Z_i^2 n_i}} , \qquad (1)$$

with $\lambda_D$   as the Debye Length,

$\varepsilon$   = dielectric constant of water, 78 at room temperature of 25C,

k = Boltzmann constant = 1.380658 x 10-23 J/K,

T = Temperature in K, room temperature = 298.15K,

e = electronic charge = 1.60217733 x 10-19 Coulombs,

$Z_i$ = valence of the i$^{th}$ conducting ion in the water electrolyte,

$n_i$ = number density of the i$^{th}$ conducting ion in the water electrolyte, in terms of number of ions per cubic meter.

For this calculation there are assumed to be four conducting ions in the electrolyte: Na+, Cl-, H3O+ and OH-. Although the mobilities of all are within an order-of-magnitude, the number density for the hydronium and hydroxyl ions are five orders-of-magnitude less than the

sodium and chloride ions for 0.01M salt. Therefore, the conductance is dominated by sodium and chlorine.

# 4   ANALYSIS

Figure 2 shows two experimental data curves as well as two theoretical calculations. The experimental data curves do not overlap and give a good indication of the difficulty of the measurement. As stated previously, the AFM tip must be positioned over one of the 150-nm, water-electrolyte-filled nanopores and held there while a slow, semi-DC sweep of voltage and corresponding current measurements are made through the tip. While the tip may be drifting, it is also the case that water is evaporating. Both of these phenomena affect the current measurement. Furthermore, the two curves are not symmetric about 0 Volts, which may mean that there are some other voltage potentials present (e.g., electrochemical mismatch between the platinum-coated silicon tip and the copper grounding plate). It is hardly surprising that the data reflect a degree of uncertainty.

The two theoretical calculations in Figure 2 do not fit the data well at all. The traditional theory represents a calculation using bulk values for 0.01M salt water within a right-circular cylinder 150-nm in diameter and 2-mm long. The traditional theory also has a voltage correction built in to account for the platinum-copper potential difference noted above. However, the asymmetry of the data is still not well explained. The double-layer calculation assumes a double-layer thickness equal to a Debye Length in 0.01M salt water, 3.033 nm, and a mobility enhancement of 10 times. Clearly parameter changes are necessary to fit the data.
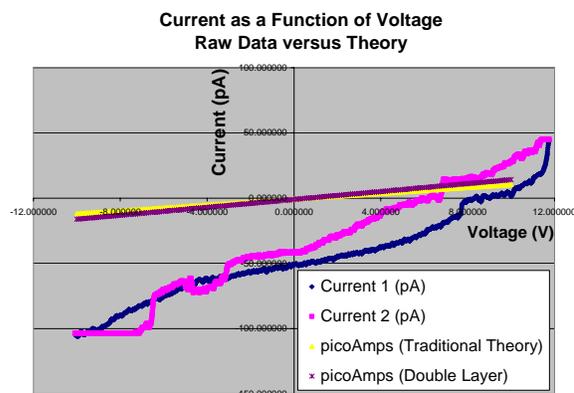


Figure 2: Experimental data plotted versus theoretical calculations of current versus voltage for a nanopore. Double-layer parameters are mobility enhancement is 10 times and Debye Length is 3.033 nm.

Figure 3 displays the same experimental curve and traditional calculation. The new double-layer calculation

increases the mobility enhancement to 78 times while keeping the thickness at 3.033 nm. The slope of the line is better but not acceptable yet.
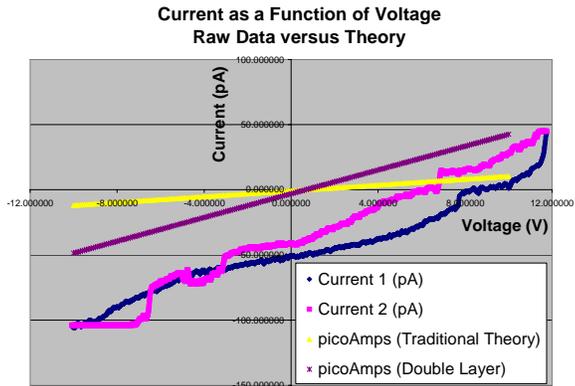


Figure 3: Experimental data plotted versus theoretical calculations of current versus voltage for a nanopore. Double-layer parameters are mobility enhancement is 10 times and Debye Length is 3.033 nm.

Figure 4 maintains most of the parameters as Figure 3, but the double-layer thickness is increased roughly three times to 10 nm. These parameters clearly overestimate the conductance, which is comforting since they represent the outer limits of acceptability for our model of dielectric-dominated conductance effects.
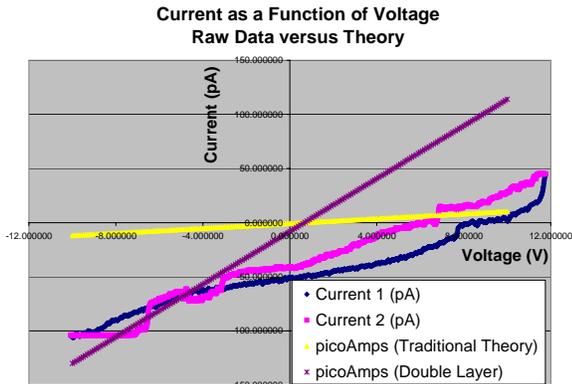


Figure 4: Experimental data plotted versus theoretical calculations of current versus voltage for a nanopore. Double-layer parameters are mobility enhancement is 78 times and Debye Length is 10 nm.

Figure 5 keeps the 10-nm double-layer thickness but reduces the mobility enhancement factor to 40 times. Here

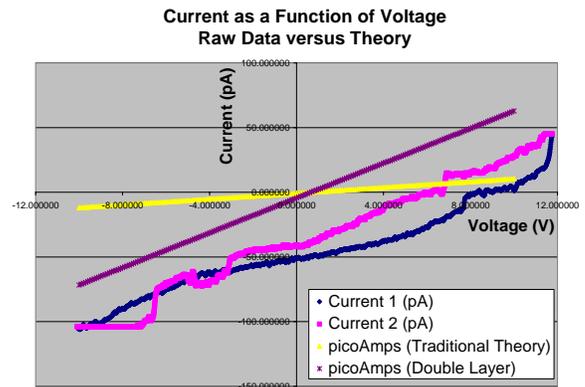the slope is quite acceptable but the voltage offset is not present.



Figure 5: Experimental data plotted versus theoretical calculations of current versus voltage for a nanopore. Double-layer parameters are mobility enhancement is 40 times and Debye Length is 10 nm.

Finally, Figure 6 represents a small tweak of the double-layer thickness from 10 to 6 nm. While a least-squares fit has not been done yet, it is clear that this fit is roughly as good as or perhaps a little worse than Figure 5.
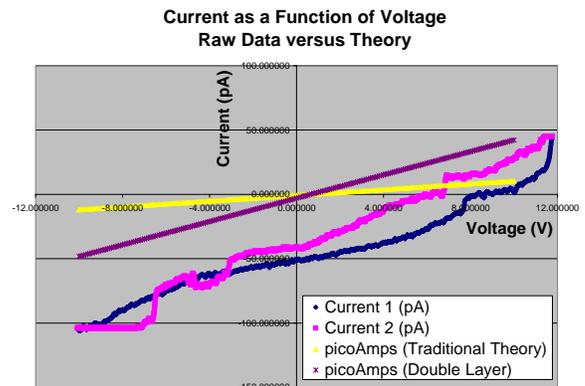


Figure 6: Experimental data plotted versus theoretical calculations of current versus voltage for a nanopore. Double-layer parameters are mobility enhancement is 40 times and Debye Length is 6 nm.

## 5 CONCLUSIONS

The intent of this paper was to determine if an enhancement of the ionic mobility within a small, reasonable double layer next to the wall could adequately explain experimental data for conductance measurements over 150-nm diameter nanopores filled with 0.01M salt water.

Clearly the data can be explained by this mechanism. However, no other conclusive proof for this mechanism has yet been collected. Other hypotheses by other researchers are clearly still in play. In fact, much remains to be done for this hypothesis including:

1. Accounting for the voltage offset in the experimental data.

2. Allowing the theory to provide for other phenomena observed in past electrochemical and pulsed-power experiments, including:

a. electric-field-enhanced conductance,

b. electric-field-enhanced dissociation,

c. improved calculation for dielectric constant and thickness within the nanopore, especially as a function of surface charge,

d. measurement of surface charge within the nanopore and any other properties that will affect conductance,

e. measurement of conductance for smaller nanopores with theoretical analysis, and

f. determination of the classical-quantum boundary for small nanopores wherein classical water-electrolyte theory fails to explain conductance.

Enhanced conductance within nanopores is still an important phenomenon with many potential uses in technology as well as lessons-to-learn in science. Characterization of conductance is the key to future utilization.

## 6   ACKNOWLEDGEMENTS

## REFERENCES

[1] V. Gehman and D. Fenneman, "Experiments on Water-Capacitor Electrode Conditioning by Ion Bombardment", 1980 Fourteenth Pulsed Power Modulator Symposium, Orlando, Florida, June 3-5, 1980.

[2] M. Zahn, Y. Ohki, D. Fenneman, R. Gripshover and V. Gehman, "Dielectric Properties of Water and Water/Glycol Mixtures for Use in Pulsed Power System Design", Proceedings of the IEEE, September 1986, p 1182-1221.

[3] Gehman, Jr., V.H., Berger, T.L., and Gripshover, R.J., "Theoretical Considerations Of Water-Dielectric Breakdown Initiation For Long Charging Times," Proceedings of the 6th IEEE International Pulsed Power Conference, Arlington, Virginia, June 29-30 and July 1, 1987.

[4] Gehman, Jr., V.H. and Gripshover, R.J., "Water-Based Dielectrics for High-Power Pulse Forming Lines," NATO Advanced Study Institute on The Liquid State and Its Electrical Properties, poster session, Sintra, Portugal, July 5-17, 1987.

[5] Bowen, S.P., Gehman, Jr., V. H., and Gripshover, R.J., "Microscopic Theory Of Dielectric Breakdown In Liquids," Poster Paper at the Gordon Conference on Dielectric Phenomena, Holderness School, Plymouth, NH, July 25-29, 1988.

[6] Gehman, Jr., V. H., Impulse Electrical Breakdown of High-Purity Water, Doctoral Dissertation at Virginia Tech, May 1995.

[7] Boulais K., Santiago F., Long K., Gehman, Jr. V.H., "Conduction Measurements of Electrolyte Filled Nanostructures Using Conducting AFM", 2005 Fall Meeting of the Materials Research Society, Boston, Massachusetts, November 27 to December 1, 2005.

[8] K. J. Long, V. H. Gehman, F. Santiago, K. A. Boulais and A. Rayms-Keller, "Conduction Measurements of Electrolyte-Filled Nanochannel Glass Using Conducting AFM," Submitted to the Seeing at the Nanoscale IV International Conference, University of Pennsylvania, Philadelphia, PA, 17-20 July 2006.

[9] H. Frohlich, Theory of Dielectrics, London, England, Oxford University Press, 1968.

[10] F. Booth, "The Dielectric Constant of Water and the Saturation Effect", Jour. Chem. Phys., Vol. 19, No. 4, 391. April 1951.

[11] J. O'M. Bockris, M.A.V. Devanathan and K. Muller, "On the Structure of Charged Interfaces", Proc. Roy. Soc. (London), A274, 55, 1963.

[12] J.V. Macpherson, C.E. Jones, A.L. Barker and P.R. Unwin, "Electrochemical Imaging of Diffusion through Single Nanoscale Pores", Analytical Chemistry, Vol. 74, No. 8, 1841, April 15, 2002.

[13] S. Pennathur and J.G. Santiago, "Electrokinetic Transport in Nanochannels. 1. Theory", Analytical Chemistry, Vol. 77, No. 21, 6772, November 1, 2005.

[14] R.J. Tonucci, B.L. Justus, A.J. Campillo and C.E. Ford, "Nanochannel Array Glass", Science, Vol. 258, pp.783-785, 30 October 1992.

[15] P. Debye and E. Hückel, Physik. Z., 24, (1923), 311.

[16] L. Onsager, Physik. Z., 27, (1926), 388.

[17] G. Kortüm, Treatise on Electrochemistry, Second, Completely Revised English Edition, pp. 186-191, Elsevier Publishing Company, 1965, LOC 63-19824.