

A Mathematical Framework that Matches Power Density of Nanoporous Membranes with Experimental Literature

Pravalika Avugaddi*¹, Shriram Elangovan*², Sharad Kumar Yadav³, Vishal V. R. Nandigana⁴

^{1,2,3,4}Membrane Technology and Deep Learning Laboratory, Fluid Systems Laboratory, Department of Mechanical Engineering, Indian Institute of Technology, Madras, Chennai 600036, India

*Authors contributed equally to the manuscript

⁴Corresponding author: [nandiga\[at\]iitm.ac.in](mailto:nandiga[at]iitm.ac.in)

Abstract: *In this paper, we develop a mathematical framework to predict ion-transport across thick nanoporous membrane. The framework includes 1) force between the applied voltage and the ion 2) interaction of the ion with the surface charge density of the nanoporous membrane 3) electrostatic force between the applied voltage and the surface charge density of the nanoporous membrane. The framework neglects the ion-ion correlations and treats the ionic correlations as a cumulative sum of ions calculated from a single counter-ion. The mathematical framework matches well with the experimental ion transport I-V results of various published experimental literature with respect to thick nanoporous membranes.*

Keywords: Blue Energy, Nanofluidics, Membrane Technology, nanopores, mathematical framework

1. Introduction

Nanofluidics is the study of the transport of fluids within 1-100 nm scale. Over the last two decades, nanoporous membranes have found their use in various applications like DNA sequencing [1–3], protein sensing [4,5], fluidic circuits [6–10], desalination [11–14], and energy [15,16]. In all these applications the ion transport across the nanoporous membrane is characterized from the I-V characteristics. It was found that the ionic current inside nanoporous membranes cannot be predicted using the pore dimensions and the bulk conductivity alone but the surface charge density of the nanopore plays a dominant role [17]. There have been a lot of experimental studies over the last two decades on understanding the ion transport across nanoporous membranes. For instance, Smeets et al. [17] conducted experiments using a thick silicon nitride nanoporous membrane of length 34 nm and diameter 10 nm and reported the conductivity measurements. Their results indicated, across the nanoporous membrane the conductivity deviates the bulk conductivity and surface charge density of the nanoporous membrane influences the ion transport. Smeets et al. postulated a two transport model with bulk and surface conduction terms contributing to the ion transport inside the nanoporous membrane. Similarly, Balme et al. [18] also conducted experiments on nanoporous membranes made of PET coated with Al₂O₃ and ZnO using the atomic layer deposition technique and concluded that surface charge density influences the ion transport resulting in surface-charge governed transport. Similarly, Ho et al. [19] performed experiments on 10 nm length SiNx nanoporous membrane with angstrom scale pore diameter of the order of 0.5 nm to 1.5 nm. They concluded that the surface charge density of the nanoporous membrane influences the ion transport and surface conduction dominant mode exists because of the surface charge density, and the pore conductivity is greater than the bulk conductivity. However, no mathematical framework is

available that can match and predict the experimental literature.

In this paper, we propose a mathematical framework that matches the experimental literature. Our mathematical framework considers 1) the electrostatic force between the applied voltage and the ion 2) electrostatic interaction of the ion with the surface charge density of the nanoporous membrane 3) electrostatic interaction between the applied voltage and the surface charge density of the nanoporous membrane. The framework neglects the ion-ion correlations and treats the ionic correlations as a cumulative sum of a single counter-ion interaction. Our mathematical framework matches the experimental literature.

2. Mathematical Framework

The mathematical framework for the ionic current is given by,

$$\vec{I} = \frac{ezn^{total}}{L_{nano}} \frac{\partial \vec{x}}{\partial t} \quad (1)$$

where e is the electronic charge, z is the valence of the ionic species, n^{total} is the total number of ions. The velocity of the ion dictates the transport of the ion and the magnitude of the current. L_{nano} is the length of the nanoporous membrane. The velocity, $\frac{\partial \vec{x}}{\partial t}$ is calculated by solving Newton's equation of motion, considering all the forces influencing the ionic transport inside the nanoporous membrane.

The mathematical framework for the ion transport inside nanoporous membrane is given as,

$$m \frac{\partial^2 \vec{x}}{\partial t^2} + \lambda \frac{\partial \vec{x}}{\partial t} = F \quad |_{t_n} \quad (2)$$

Where the first term is the inertial term, m is the mass of a single counter-ion traveling inside the nanoporous membrane. Note, we have coarse-grained the ion-ion correlation effect and considered only a single ion to understand the transport of the ions inside the nanoporous membrane with various electrostatic -only forces acting on the ion. The total ionic current is calculated by multiplying the single ion current with the total charge contributed by all ions (both positive and negative ions) calculated from the concentration of the solution. The second term in Eq. (2) is the diffusive term, leading to the mobility changes of the ion because of the ionic diffusion effects. The diffusive constant, λ is given by the Einstein's relation, $\lambda = \frac{k_B T}{D}$, where D is the diffusion coefficient of the single counter-ion considered, k_B is the Boltzmann constant and T is the temperature. $F|_{t_n}$ is the conservative electrostatic force acting on the ion to drive the ion transport at each time t_i to t_n , where t_i is the start time, t_n is the time when the ion motion has reached steady and the dynamics can be considered quasi-equilibrium. In this paper, we have considered three conservative electrostatic forces in the framework that is acting on the coarse-grained single ion. First, we have the electrostatic force between the ion and the applied voltage given in Eq. (3a).

$$F_1 = \frac{ezV_0}{L_{nano}} (\text{Applied voltage} - \text{ion interaction force}) \quad (3a)$$

where V_0 is the applied voltage. The second force is the electrostatic force between the ion and the surface charge density. This force is derived by considering the total surface charge of the nanoporous membrane calculated from the surface charge density, $Q_{surface} = \sigma 2\pi R_{nano} L_{nano}$, where $Q_{surface}$ is the total nanoporous surface charge, σ is the surface charge density of the nanoporous membrane, R_{nano} is the radius of the nanoporous membrane. We assume, $Q_{surface}$ is located on the nanoporous cylinder wall, at a distance of R_{nano} from the center of the nanopore and L_{nano} from the entrance of the nanopore. Further, we assume, the ion is initially located at $x = 1nm$ from the entrance of the nanopore. Under, this condition, the electrostatic force between the ion and the surface charge of the nanoporous membrane, is given by a dynamical forcing term, $F_2(t)$, as,

$$F_2(t) = \frac{ez|Q_{surface}|}{4\pi\epsilon_r\epsilon_0((L_{nano} - x(t))^2 + R_{nano}^2)} (\text{ion} - \text{nanopore surface charge interaction force}) \quad (3b)$$

where the absolute value of the surface charge density is considered as we are considering only a single counter-ion transport, we account only for absolute forces.

Finally, the third and last electrostatic force accounted for while deriving the ion transport mathematical framework inside the nanoporous membrane, is the electrostatic force between the surface charge density and the applied voltage. The force is given as,

$$F_3 = \frac{|Q_{surface}|V_0}{L_{nano}} (\text{nanopore surface charge} - \text{applied voltage force}) \quad (3c)$$

Combining the three electrostatic conservative forces, we arrive at the total force, given as,

$$F|_{t_n} = \frac{ezV_0}{L_{nano}} + \frac{ez|Q_{surface}|}{4\pi\epsilon_r\epsilon_0((L_{nano} - x(t))^2 + R_{nano}^2)} + \frac{|Q_{surface}|V_0}{L_{nano}} \quad (3)$$

Solving the mathematical framework, Eq. (2) with the total force derived in Eq. (3), we obtain the position and velocity of the single ion. The ion transport dynamics helps us to calculate the ionic current using Eq. (1) after substituting the velocity obtained from Eq. (2). The mathematical framework Eq. (2) is solved using velocity verlet algorithm [20] in which the position and velocity of the ion is obtained at time $t + \Delta t$,

$$\vec{x}(t + \Delta t) = \vec{x}(t) + \vec{\dot{x}}(t)\Delta t + 0.5\vec{\ddot{x}}(t)\Delta t^2 \quad (4)$$

$$\vec{\dot{x}}(t + \Delta t) = \vec{\dot{x}}(t) + 0.5(\vec{\ddot{x}}(t) + \vec{\ddot{x}}(t + \Delta t))\Delta t \quad (5)$$

The acceleration at time $(t + \Delta t)$ is calculated using (2) and (3) at time $(t + \Delta t)$. Here, the initial position is taken to be $1nm$ and the time step Δt as $1fs$. The simulation is performed for 1000 time steps, until $1ps$.

3. Results

We considered three sets of experimental results from the literature, Smeets et al. [17] data, Balme et al. [18] data, and Ho et al. [19] data to match our mathematical framework. The I-V characteristics and the corresponding conductance Vs concentration are compared with the experimental literature.

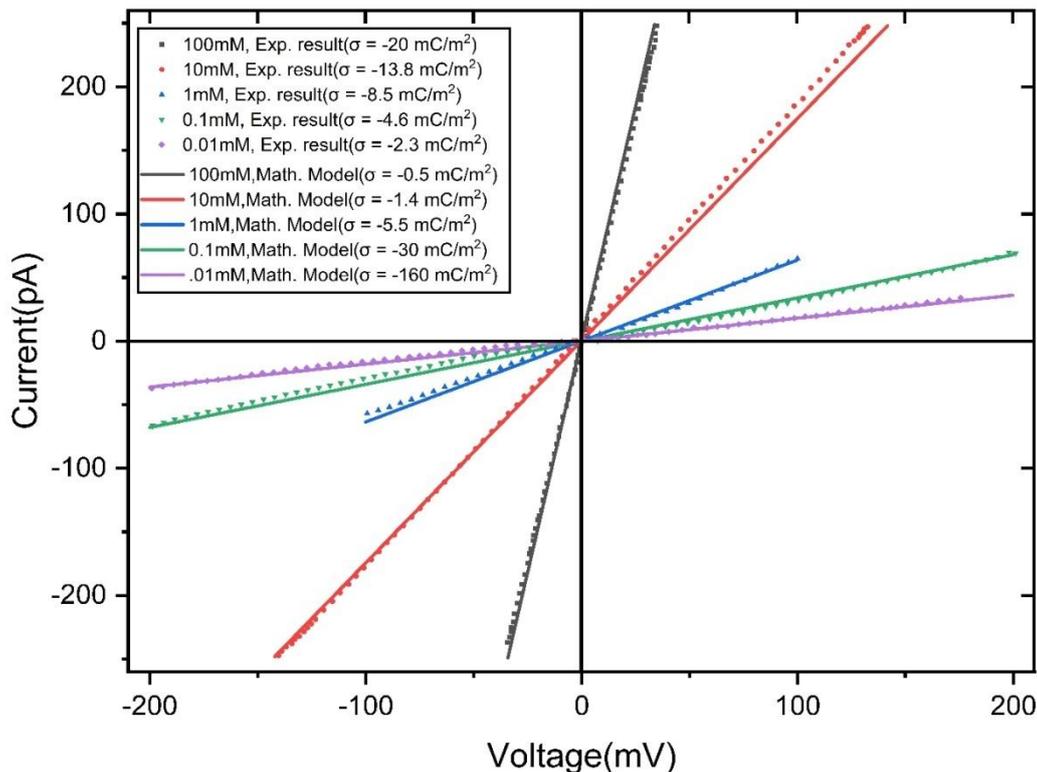
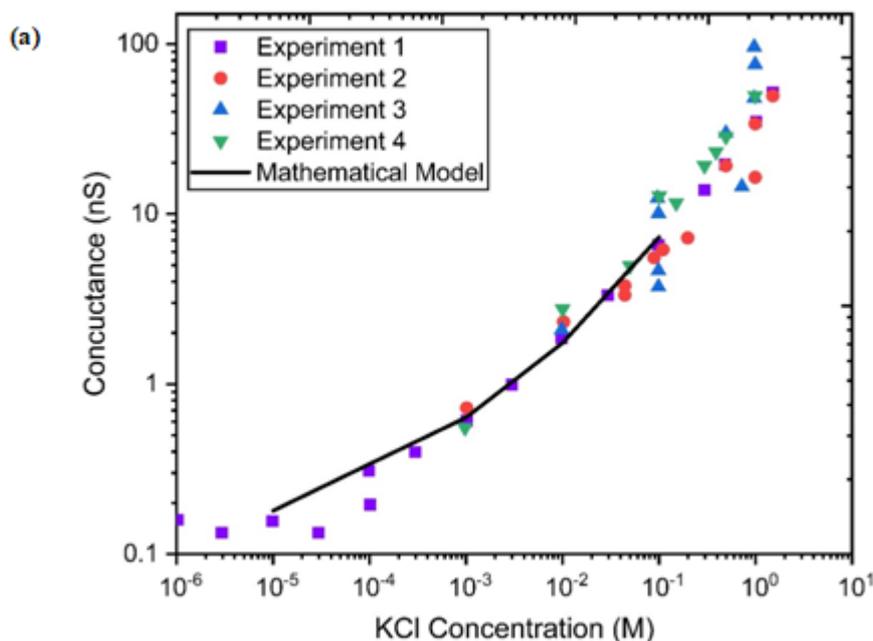


Figure 1: Comparison of I-V plots between Smeets et. al [17] experimental data and our mathematical framework for concentrations from 0.01 mM to 100 mM for KCl electrolyte solution.

Fig 1. shows the comparison of I-V characteristics between Smeets et al. experimental results (symbols) and our mathematical framework (lines) for silicon nitride, SiN_x nanoporous membranes of length 34nm, and pore diameter 10nm. The I-V characteristics follow Ohm's law and shows linear characteristics. The only fitting parameter in our mathematical framework is the surface charge density and same is the case in the experiment-theory fit results of

Smeets et. al observations. Fig. 2a shows the conductance variation with the concentration. The mathematical framework calculates the conductance value for each concentration by calculating the slope of the I-V data available in Fig 1. Our proposed mathematical framework matches well with the experiments for the concentrations considered.



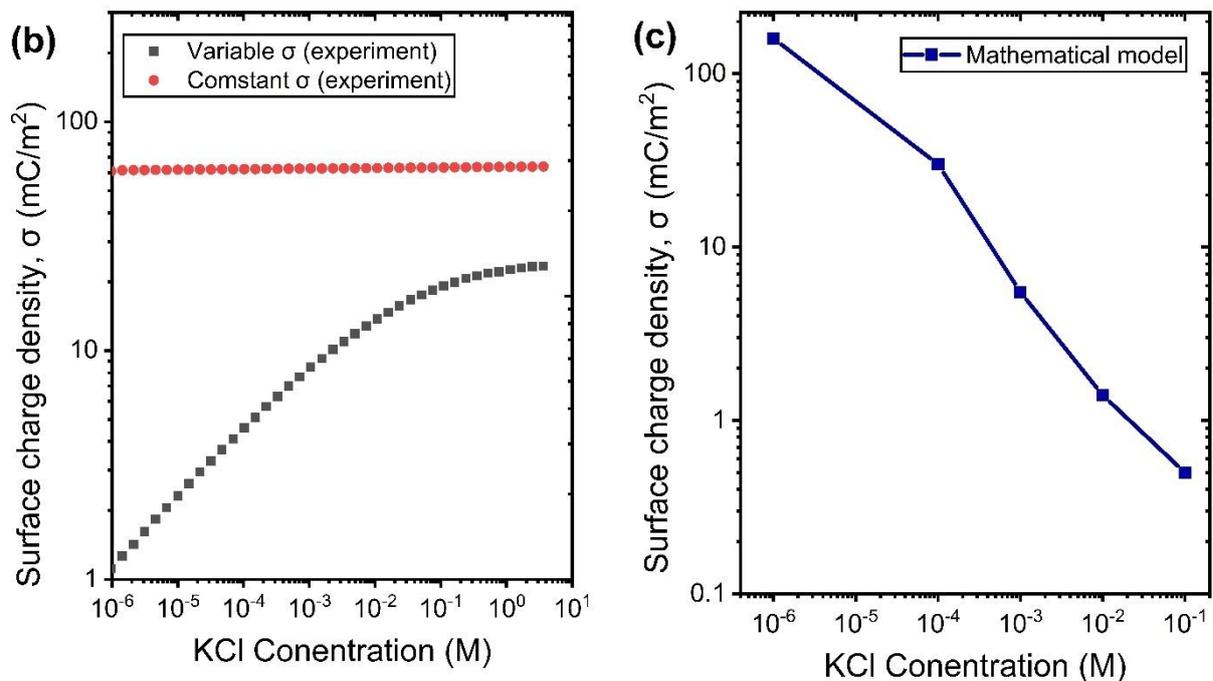
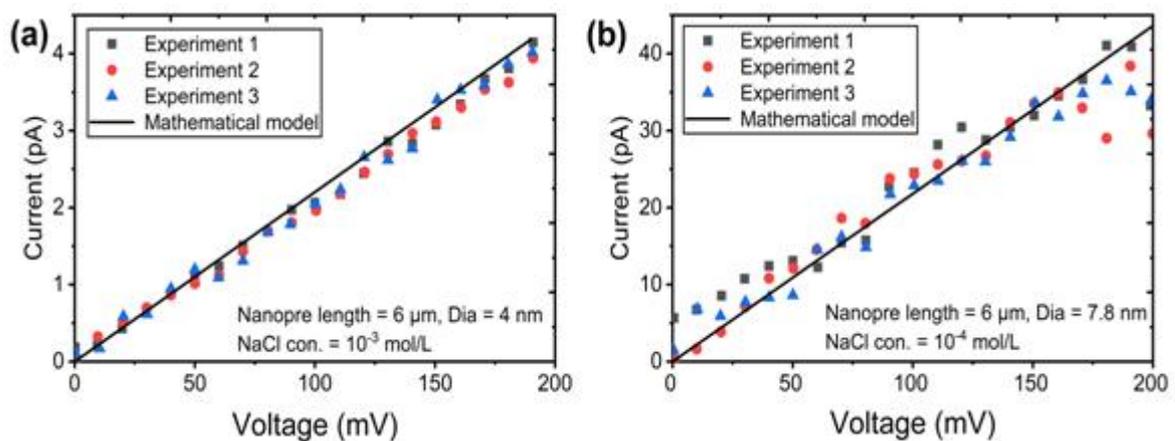


Figure 2: (a) Comparison of conductance plots between Smeets et. al [17] experimental data and our mathematical framework for concentrations from 0.01 mM to 100 mM for KCl electrolyte solution. (b) shows the surface charge density values proposed by Smeets et. al. theory fit to experiments (c) shows the surface charge density values used in our mathematical framework.

We observe that the surface charge density contribution is more pronounced for low concentration regime below 1 mM as the nanoporous membrane becomes more counter-ion selective, reaching a near ideal-ion-selective membrane. Above 1 mM concentration, the nanoporous membrane is non-ideal-ion-selective membrane. The exact surface charge density is not fully clear and a direct evidence of surface charge density of the nanoporous membrane from image processing in which the partial charge of the nanoporous membrane material exposed to the ionic solution over the entire length of the nanopore is measured. The partial charge is integrated over the pore length to calculate the total surface charge density of the nanoporous membrane. Fig. 3 shows the I-V plot characteristics of Balme et. al. experimental data on hydrophobic high-aspect-ratio

nanoporous membranes of length $6\mu\text{m}$ with diameters ranging from 1 nm to 10 nm. The experiments were carried out with NaCl electrolyte solution of concentrations varying from 10^{-2} mol/l to 10^{-4} mol/l. Fig. 3. shows that the mathematical framework matches very well with Balme et. al. experimental data. The surface charge density used for concentration = 10^{-3} mol/L is $\sigma = -4.5 \text{ mC/m}^2$, for concentration = 10^{-4} mol/L is $\sigma = -4.5 \text{ mC/m}^2$ and for concentration = 10^{-2} mol/L is $\sigma = -0.6 \text{ mC/m}^2$. Fig. 4. shows the I-V characteristics of silicon nitride (SiN_x) nanoporous membrane of Ho et. al experimental data for angstrom size pore diameters ranging from 0.5 nm to 1.5 nm.



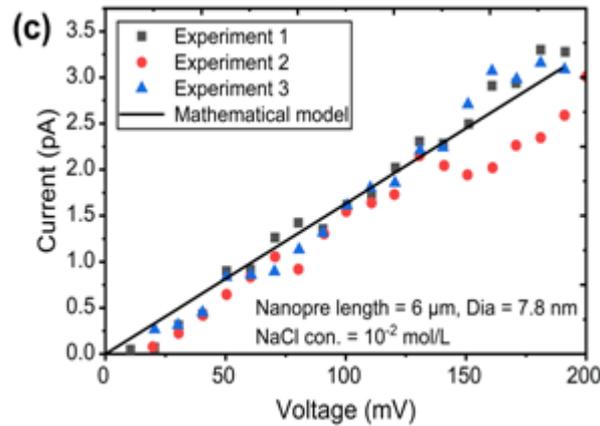


Figure 3 (a-c): Comparison of I-V plots between Balme et al. [18] experimental data and our mathematical framework for concentrations from 10^{-4} mol/l to 10^{-2} mol/l for NaCl electrolyte solution and different pore diameters.

The length of the nanoporous membrane is 10 nm and the experiments were carried out at 1M KCl electrolyte solution. Further, linear I-V characteristics are observed for 1M KCl concentration. Fig 4. shows the mathematical framework I-V results compared to experimental results. We observe that for angstrom diameter size nanoporous membranes, $d = 0.5$ nm, a fitting surface charge density value of $\sigma = -2 \text{ mC/m}^2$ shows a good match between the experimental

and the mathematical framework. However, the mathematical framework was not able to predict the experimental data for higher diameter pores of $d = 1 \text{ nm}$ and $d = 1.5 \text{ nm}$ even when the surface charge density contribution is switched off, i.e., taking $\sigma = 0 \text{ mC/m}^2$.

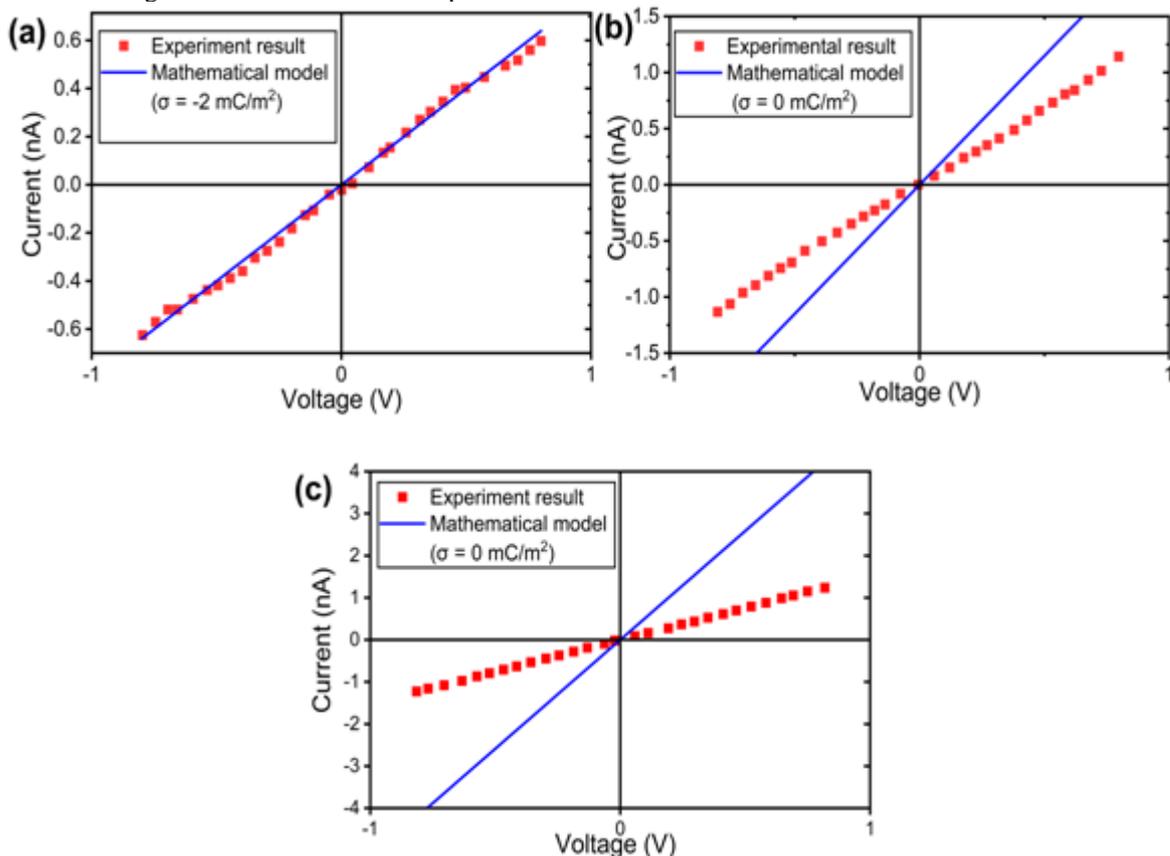


Figure 4 (a-c): Comparison of I-V plots between Ho et al. [19] experimental data and our mathematical framework for concentration 1 M KCl electrolyte solution and pore diameters, $d = 0.5 \text{ nm}$, $d = 1 \text{ nm}$, and $d = 1.5 \text{ nm}$, respectively

4. Conclusion

Here, a mathematical framework that matches power density of nanoporous membranes with experimental literature. Direct evidence of the surface charge density measurements

with image processing method will provide exact surface charge density of nanoporous membrane.

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