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Nowzesh Hasan, *Louisiana Tech University* Wenli Zhang, *Louisiana Tech University* Adarsh D. Radadia, *Louisiana Tech University*



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Characterization of Nanodiamond Seeded Interdigitated Electrodes using Impedance Spectroscopy of Pure Water



Nowzesh Hasan, Wenli Zhang, Adarsh D. Radadia*

Institute for Micromanufacturing, Center for Biomedical Engineering and Rehabilitation Services, Louisiana Tech University, Ruston, LA 71272, USA

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ABSTRACT

We have recently demonstrated enhancement in sensitivity of an impedance biosensor by seeding detonation nanodiamonds (DNDs) at the interdigitated electrodes (IDEs). Here, impedance spectroscopy of pure water is carried out at such IDEs to reveal the role of the DNDs. The impedance data is fit to an equivalent circuit model consisting of a geometrical resistance in series with a distributed element for Havriliak-Negami (HN) relaxation, and in parallel with a geometrical capacitance. Concurrently, the motion of charges across the IDEs is modeled as Plank-Nerst-Poisson anomalous diffusion across two partially blocking conductive electrodes. Results show that the DNDs (having a positive zeta potential) at the IDEs reduce the geometrical resistance to less than half, and the time constant for the HN relaxation to less than one-fourth. These changes propose doubled diffusion coefficient and mobility of the charged species, and reduced dielectric relaxation time constant. The diffusion modeling suggests insignificant increase in charged mobile species upon DND seeding. It is hypothesized that the DNDs, which have a positive zeta potential, when seeded on gold and oxide surfaces with a negative zeta potential, reduce the electrostatic force acting on the diffuse layer ions, and increase their mobility.

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1. Introduction

Nanodiamonds (NDs) are 2–10 nm wide crystals with sp³hybridized carbon atoms in the core arranged as the corners of a repeating tetrahedral structure, while the surface carbon atoms are either sp³-hybridized with a variety of functional groups or sp²hybridized into a graphene plane [1]. Presently, NDs are commercially synthesized via detonation [2], laser ablation [3], or high-energy ball milling of high pressure high temperature diamond microcrystals [4], while other techniques such as plasmaassisted chemical vapor deposition [5], ultrasound cavitation of organic compounds or graphite [6,7], autoclave synthesis from supercritical fluids [8], chlorination of carbides [9], ion radiation of graphite [10], and electron irradiation of carbon onions [11] also exist. The use of detonation NDs (DNDs) in biosensing has gained widespread attention, primarily due to its moderate cost, the relative ease with which a wide variety of functional groups can be decorated on DNDs for bioconjugation [1,12], its excellent biocompatibility [13,14], and the induction of fluorescence through doping [15].

E-mail addresses: radadia@latech.edu, radadia@gmail.com (A.D. Radadia).

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Recently, the use of DNDs to decorate biosensing electrodes has shown unique advantages. For example, the use of oxidized DNDs at electrodes has shown to enhance the electrochemical response of different redox probes in solution such as $Fe(CN)_6^{3-/4-}$ [16–18], $IrCl_6^{3-/2-}$ [17], $Ru(NH_3)_6^{3+/2+}$ [16], and ferrocene methanol [19]. This enhancement is either due to the favorable interaction between the redox active functional groups on the DNDs with the redox species in the solution, or the concentration of the redox probes at the electrodes due to its adsorption on the DND surface. Oxidized DNDs and nitrogen-doped DNDs on *n*-doped silicon have shown to improve the sensitivity of enzymatic detection of glucose [20]. The enhanced electrochemical response of ferrocene methanol on gold electrodes decorated with oxidized DNDs has recently been used to create sensitive enzymatic sensors for glucose and lactate [21]. The use of DNDs was also observed to improve the distribution of the enzyme on the electrode, and promote the electron transfer between the enzyme and the redox probe. While most of the work reported uses the oxidized DNDs that have a negative zeta potential, recently we reported the use of DNDs with a positive zeta potential (>20 mV) to create a non-faradaic impedance biosensor [22]. The purification method of the DNDs plays a major role in determining their zeta potential [23,24]. The liquid phase oxidation using strong acids typically results in the

^{*} Corresponding author. Tel.: +1 318 243 8394.

DNDs with a positive zeta potential, while the gas phase oxidation in air or ozone results in the DNDs with a negative zeta potential.

In our previous report, we used mild-sonication to seed the DNDs with a positive zeta potential, and optimized the solvent type, the DND concentration, and the sonication time to create a surface coverage as high as \sim 35%. The original motivation was to anchor the biomolecules to the seeded DNDs using our previously published UV-alkene chemistry [12,14], and thereby improve the hydrolytic stability of the immobilization at the interdigitated electrodes (IDEs) of the biosensor. But to our surprise we found that the use of the DNDs improved the sensitivity of the charge transfer resistance to the capture of target bacteria. The impedance measurements in solutions of varying conductivity before and after DND seeding elucidated that the resistive or the charge transfer contribution to the overall impedance decreased with DND seeding; further this reduction was masked as the solution became more conductive. On hypothesis we had then postulated that the DNDs were nanometer scale electrically conductive islands between the electrode fingers forming a surface conduction pathway, which was more sensitive to bacteria capture. The electrical conductivity in DNDs has been observed in its powder or cluster form [25,26], analogous to the electrochemical transfer doping observed on hydrogen-terminated diamond surfaces [27]. However, recent investigation of surface electronic properties of transfer-doping in single isolated NDs by Asaf et al. using scanning tunneling spectroscopy and Kelvin force microscopy shows that as the size of single ND shrinks, especially below 10 nm, the surface electron affinity, following hydrogenation and exposure to air, becomes less negative, and the surface band bending is lower than that obtained on the surface of the bulk diamond exposed to the same hydrogenation procedure [28]. This warrants the search for an alternative mechanism for the reduction in the resistive or the charge transfer contribution to the overall impedance with DND seeding in our previous report.

In this article, we use impedance spectroscopy (IS) of pure water to probe the contributions of DNDs to the charge transport across the IDEs. The presence of low charge carriers in pure water prevents masking the small changes induced by the DNDs. In IS, a small alternating electrical stimulation is used to probe the changes in electrical properties of a system [29]. The IS data is collected over a frequency range of interest, then it is converted into the Fourier transform domain, and an equivalent circuit model is hypothesized that fits the impedance data as well as explains the physically relevant changes in the system. Several softwares like LEVM [30,31], MEISP (Kumho Petrochemical Co., Korea), Zview[®] (Scribner Associates, USA), EIS300[™] (Gamry Instruments), ZMAN (Xeno Systems, Korea), FRA2 (Metrohm Autolab B.V., Netherlands), and more have been used for equivalent circuit modeling. The choice of software has been primarily driven by the list of equivalent circuit models and the types of elements offered, the cost and the availability, the acceptance within the particular research field, the user friendly interface, the documentation and the support, the fitting algorithm, and the method for parameter estimation [32]. LEVM or its counterpart with a graphical user interface, LEVMW stands out amongst those as an open source, freely available package that performs complex nonlinear least squares (CNLS) fitting with Levenberg-Marquardt method for parameter estimation. This program was written by Dr. J. Ross Macdonald, and specifically developed for analyzing electrochemical, dielectric, highly resistive or highly conductive system data. We chose LEVMW due to the availability of more than 37 distributed elements and numerous models with physical significance.

In this article, we fabricate DND-seeded IDEs as previously reported, perform impedance spectroscopy of pure water on the IDEs before and after DND seeding, and use LEVMW to interpret the physically relevant changes at the IDEs due to DND seeding. Specifically, we elucidate the type of charge that is affected, its diffusion coefficient, and the changes in the dielectric relaxation time constant. Through the changes in the equivalent circuit model, we hypothesize a couple of mechanisms by which DNDs are enhancing the charge transport across the IDEs.

2. Experimental

2.1. Device fabrication

The process for device fabrication and DND seeding have been detailed in our previous publication [22]. Briefly, a silicon wafer $(525 \pm 25 \,\mu\text{m}$ thick, 1–10 Ω -cm) coated with a 280 nm-thick thermal oxide was used for device fabrication. The IDE layer was formed by sputter depositing a 25 nm-thick Cr adhesion film and a 200 nm-thick Au film, and patterned them using the lift-off process with S1813 as the photoresist. Each electrode in the IDE pairs contained sixty-five fingers, each 2.5 mm long, 9 µm wide and spaced 9 µm apart. Subsequently, a 300 nm thick insulating oxide layer was deposited by plasma enhanced chemical vapor deposition. The IDEs were then exposed by opening circular windows (2.4 mm diameter) in the insulation layer using photolithography and buffered oxide etching. The silicon wafer was diced to obtain individual devices, each having a 3×3 array of IDEs. For DND-seeding, the as received 0.5 (w/v) % DND solution in DMSO was diluted in 1:1 ratio with methanol; the fabricated devices were sonicated in the diluted DND solution for 30 minutes in a Branson bath sonicator. According to the manufacturer (Adamas Nanotechnologies), the NDs were size separated by centrifugation and were found to be within 3-10 nm while the peak of the distribution was around 5 nm. These NDs show a positive zeta potential and DMSO as a solvent provides strong resistance to settling of these NDs [23]. Post-sonication, the devices were rinsed with deionized water (DI), acetone, and isopropyl alcohol, and blow-dried under a gentle nitrogen stream. The surface morphology of DND-seeded IDE was investigated using scanning electron microscopy (SEM, Hitachi S-4800) and image processing (2D fast Fourier transform filtering) of the SEM images using the Gwyddion software package.

2.2. Measurement setup

The fabricated IDE array devices were electrically connected using a high-density card edge connector (Sullins GBB10DHLD as shown in Fig. 1) to an impedance analyzer (CompactStat, Ivium Technologies). The working electrode lead from the CompactStat was short circuited to the sense electrode lead, and the reference lead was short circuited to the counter to make two two-electrode



Fig. 1. Optical image of a 3×3 IDE array device that was fabricated and seeded with the DNDs with a positive zeta potential. The IDE array device is plugged into the card edge connector, which then allows addressing each individual IDE using alligator clips. Pure water obtained from the deionization unit was used to create a puddle over the IDE during the measurement.

measurements. The device was set inside a grounded Faraday cage. Impedance measurements were made with a puddle of deionized water (20 °C, 3 μ S/cm) sitting over the device without touching the sides of the chip. The magnitude of the impedance and the phase lag across each of the IDEs was average from three readings using a 10 mV excitation at 52 frequencies over a frequency range of 100 to 10^5 Hz.

3. Results and discussion

To examine the structure of the data, the physical processes present that led to the data and any outliers, it is generally a good practice to examine the data graphically. Whether the data for deionized water represents that for a leaky dielectric or intrinsically conducting character with mobile charges dominating the response with partial or complete blocking at the electrodes. The two extreme types of electrode models are the conducting electrode model and the fully blocking electrode model. The impedance, $Z_{Conduct}(\omega)$ for a conducting electrode model as shown in Fig. 2a, can be expressed as,

$$Z_{Conduct}(\omega) = \left(\frac{R_b}{1 + \omega^2 R_b^2 C_b^2}\right) - j\left(\frac{\omega R_b^2 C_b}{1 + \omega^2 R_b^2 C_b^2}\right) \tag{1}$$

where R_b is the bulk resistance, C_b is the bulk capacitance and $j = \sqrt{(-1)}$. The impedance, $Z_{Block}(\omega)$ for a fully blocking electrode model as shown in Fig. 2b, can be expressed as,

$$Z_{Block}(\omega) = \left(\frac{R_b}{1 + \omega^2 R_b^2 C_b^2}\right) - j\left(\frac{\omega R_b^2 C_b}{1 + \omega^2 R_b^2 C_b^2} + \frac{1}{\omega C_D}\right)$$
(2)

where C_D is the Debye layer capacitance. From Eq. (1) and (2), it can be inferred that the real part of the impedance expression is same for the conducting and the fully blocking electrode models; however, the imaginary part of the impedance plays the decisive role in determining the appropriate model. Fig. 2c shows the plot of the imaginary part of the impedance versus the frequency using Eqs. (1), (2), and the experimental data from one of the sensors. As shown in Fig. 2c, the experimental data from the IDEs suggested the use of a partially blocked electrode model as shown in Fig. 3



Fig. 2. Plots showing the equivalent circuit diagram of (a) the simplified conductive electrode model, (b) the simplified fully blocking electrode model, and (c) the imaginary part of the impedance, |Im(Z)| plot versus the frequency for (a) using the brown dots, (b) using the blue dots, and the experimental data obtained from one of the IDE sensors using red dots. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



 DE_2 consists of four elements as follows: R_{DE2} : Resistance of DE_2 T_{DE2} : Time constant of DE_2 U_{DE2} : An exponent of DE_2 which when equal to 1 reduces the HN model to the Cole-Davidson model.

 P_{DE2} : An exponent of DE_2 which when equal to 1 reduces the HN model to the Cole-Cole model.

Fig. 3. The equivalent circuit model for impedance between the interdigitated electrodes deduced from circuit H, where C_1 is the geometrical capacitance, R_1 is the geometrical resistance or also known to define the high-frequency plateau of the real part of the impedance, and DE_2 is a distributed element accounting for the Havriliak-Negami (HN) relaxation of the Debye layer.

[33]. The circuit shown in Fig. 3 represents the charge conducting medium between two electrodes. Differing from a conventional electrochemical experiment with parallel electrodes where motion of charges is forced perpendicularly through the bulk water, here motion of charges is somewhat parallel to the surface of the electrodes and hence we include the role of charge carrier conduction in the diffuse layer or the surface along with the bulk. This is something that has not been considered before. The impedance arising from the geometrical capacitance C_1 , can be written as,

$$Z_C = \frac{1}{j\omega C_1} \tag{3}$$

The distributed element DE_2 followed the HN relaxation model and the expression of impedance for this element can be written as,

$$Z_{HN} = \frac{R_{DE2}}{\left\{1 + (jT_{DE2}\omega)^{U_{DE2}}\right\}^{P_{DE2}}}$$
(4)

So, the overall equivalent impedance of the circuit in Fig. 3 was, $Z_{eq} = (Z_{HN} + R_1)||(Z_C)$ or

$$Z_{eq} = \left[j\omega C_1 + \frac{\left\{ 1 + (jT_{DE2}\omega)^{U_{DE2}} \right\}^{P_{DE2}}}{R_{DE2} + R_1 \left\{ 1 + (jT_{DE2}\omega)^{U_{DE2}} \right\}^{P_{DE2}}} \right]^{(-1)}$$
(5)

The LEVMW software is unique as it helps solve the Eq. (5) in conjunction with the Poisson-Nernst-Planck anomalous (PNPA) diffusion model for the motion of the charged species between the two electrodes in the IDEs [34]. In order for LEVMW to simultaneously solve for the equivalent circuit model as well as the PNPA diffusion model, a few values needed to be calculated to make initial guess or define limits. The capacitance of the empty IDE cell (*CELCAP*) was calculated as,

$$CELCAP = \frac{A\varepsilon_o}{L} \tag{6}$$

where A is the effective electrode area, ε_0 is the permittivity of vacuum and L is the electrode separation distance. In our experiment, $A = 1.16 \times 10^{-2} \text{ cm}^2$, $L = 9 \times 10^{-4} \text{ cm}$, $\varepsilon_{\odot} = 8.854 \times 10^{-14}$ F/cm and thus, CELCAP = $1.141 \times 10^{-06} \,\mu$ F. CELCAP serves as the lower limit for C₁. Estimation of dissociated charged species plays an important role in impedance spectroscopy when the medium is not significantly dielectrically dispersive. Considering that our experiments were conducted at 20 °C, the corresponding value of the ionization constant for water dissociation: $2H_2O \rightarrow H_3O^+ + OH^-$, $K_W = 6.81 \times 10^{-15} \text{ mol}^2/L^2$ [35]; so, the total molar concentration of the dissociated charged species calculated

to be, $c_{\text{max}} = 2 \cdot \sqrt{K_W} = 1.65 \times 10^{-07} \text{mol/L}$. and the maximum molar concentration of the negative or the positive charged species being $M_{n,max} = \frac{c_{max}}{2} = 8.25 \times 10^{-08} \text{ mol/L}$. Further, the maximum density of each intrinsic dissociated species was calculated as, $|N_{o,max}| = M_{n,max} \cdot N_A$, where N_A is the Avogadro's number (6.022 × 10²³ per mole). This $|N_{o,max}|$ (= 4.97 × 10¹³ per cm³) formed the upper limit of our guess for the concentration of each charged species, N_{\odot} used in LEVMW, while the ratio of the rate constant of generation of charged species (k_g) to the rate constant of recombination (k_r) was set as, $k_{gr} = \frac{k_g}{k_r} = 9.35 \times 10^{35}$, and the ratio of the generation-recombination relaxation time (τ_{GR}) to the Debye relaxation time (τ_d) set as, $\xi = \frac{\tau_{GR}}{\tau_d} = 2.28 \times 10^{25}$. These high values for ξ and k_{gr} ensured ignoring recombination [36]. All positive and negative charged species were considered as univalent and thus the valence number ratio of negative to positive charged species was kept fixed as, $\prod_Z = 1$. Cases of one mobile charged species were simulated by fixing the value of mobility ratio of the negative (μ_n) to the positive (μ_p) charged species as, $\prod_m = \frac{\mu_n}{\mu_p} = (3.388 \times 10^{38})$, and cases of two mobile charged species were simulated with $\prod_m = 1$.

We did not notice a significant difference in the fit obtained with the one mobile charge or the two mobile charges. Hence for the rest of the paper we consider only negative mobile species to compare the effect of DND seeding at the IDEs. We found that the best fits were obtained with $|N_o|$ value around 3.31×10^{13} per cm³, regardless of the presence of DNDs at the IDEs; this $|N_o|$ value corresponds to a molar concentration value of $M_n = 5.50 \times 10^{-08}$ mol/L, a total molar concentration of $c_o = 1.10 \times 10^{-7}$ mol/L, and an ionization constant of $K'_w = 3.02 \times 10^{-15}$ mol²/L², which are within the same order magnitude as that predicted by the theory of water ionization.

Fig. 4 shows the Nyquist plots calculated from the experimental data, and the best fit obtained using the above calculated constants and initial guesses for the PNPA diffusion model with one mobile charged species between two partially blocking conductive electrodes. At the high excitation frequency regime (lower real part values), both real and imaginary parts were found to increase with the reduction of frequency, which resembles the response of pure water as described by Macdonald [37]: subsequently, a plateau was noticed where the imaginary part did not change values while an increase in the real was noticed with the reduction in frequency. Then, a sharp rise in the imaginary part of the impedance was observed with further reduction of the frequency. Overall, we found that DND seeding lowered the absolute impedance for most of the sensors like we reported previously [22]. Fig. S2 shows the real and imaginary part of the impedances with and without DND seeding, plot versus the excitation frequency. We noticed that the values for the real part with, and without DND seeding were close at frequencies larger than 10 kHz, but were found to be lower for DND-seeded IDEs at frequencies below 10 kHz, with the biggest shift due to DND seeding found around 1 kHz. Similarly, the values for the imaginary part with and without DND seeding converged at frequencies higher than 50 kHz, but were found to be lower for DND-seeded IDEs at frequencies below 50 kHz, with the biggest shift due to DND seeding noticed around 5 kHz. It is believed that the ion conduction property of the charge transfer pathway, and the ohmic characteristics of the electrode play a significant role in the low frequency part of the spectra [38–40]. Thus our data is indicative that the DND seeding causes differences in conduction behavior of the dissociated ions [38].

The values for the components of the equivalent circuit shown in Fig. 2 as obtained from LEVMW are summarized in Fig. 5, Fig. S3, Fig. 5a, b, and c show plots of R_1 , C_1 and T_{DE2} values, respectively,



Fig. 4. Nyquist plots of impedance data obtained from eight different sensors before and after seeding with DNDs. Experimental data from Au electrodes is represented by the blue dots and the equivalent circuit model fitting represented by the blue line. Experimental data from DND-seeded Au electrodes is represented by the red dots and the equivalent circuit model fitting represented by the rol line. DND-seeding lowered the overall impedance of most of the sensors and the fittings perfectly followed the experimental data at higher frequency (lower Re(Z)), but at the lower frequency, it shows slight deviation in some sensors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Plots showing the values of (a) the geometric/bulk resistance, R_1 (b) the geometric capacitance, C_1 and (c) the time constant, T_{DE2} obtained from the fitting of the impedance data of all the eight sensors before (blue columns) and after seeding (red columns) on the Au electrodes with DNDs. The error bars indicate the standard deviation in parameter estimation. Overall, 57% reduction in R_1 is observed through the DND seeding on an average for each of the sensor, which indicated the DND-seeding process had reduced the geometrical resistance of the Au electrodes. The geometrical capacitance, C_1 exhibits an incremental trend for each sensor before and after DND-seeding with on an average 3.4% increment as after the DND-seeding on the Au electrodes, DND grains with conducting surfaces and non-conducting cores augmented the overall capacitance. The time constant, T_{DE2} was showing a reduction in values about on an average of 72% after the DND-seeding. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

which showed distinct trend due to DND seeding. The values of R_1 were found to decrease 57% on an average with DND-seeding at the IDEs, while an average 3.4% increment was found in C_1 , which was expected due to the capacitive nature of the DND core. The values of T_{DE2} show an average 72% reduction due to DND seeding. Fig. S3a, and S3b show the values of R_{DE2} and P_{DE2} , respectively, neither showing significant trend due to DND seeding at the IDEs. The values of R_{DE2} stayed within the same order of magnitude with an average 11% variations. Also the value of the exponent, U_{DE2} was consistently within 1 ±0.03; hence, to simplify the fitting process, we fixed U_{DE2} to 1, resembling the Cole-Davidson model. The values of the exponent, P_{DE2} could not be fixed to 1 without getting a bad fit, and it ranged between 0.82–0.95 with 5% variations during the fit as shown in Fig. S3b, which reflected no particular trend due to DND seeding.

The equivalent circuit model values were then used to calculate the diffusion coefficient (D_n) , the mobility of negative mobile charged species (μ_n) and the dielectric relaxation time (τ) of the





Fig. 6. Plot showing (a) the diffusion coefficient calculated from the values of T_{DE2} in Fig. 5a, (b) the mobility of negative charged species, μ_n using the electrical mobility equation and (c) the dielectric relaxation time, τ derived from the resistance, R_1 and the capacitance, C_1 in Fig. 5a and b respectively.

system. The diffusion coefficients, D_n calculated as,

$$D_n = \frac{2\lambda_d^2}{T_{DE2}} \tag{7}$$

are plotted in Fig. 6a, where λ_d is the Debye length (~680 nm) for pure water. Since D_n is inversely proportional to T_{DE2} , we find an incremental trend in D_n with the DND seeding over the gold IDEs. The mobility of negatively charged species, μ_n calculated using the electrical mobility equation as,

$$\mu_n = \frac{D_n e}{k_B T} \tag{8}$$

are shown in Fig. 6b. The values of the mobility of negatively charged species doubled for all eight sensors after DND-seeding. Dielectric relaxation time, τ calculated as,

$$\tau = R_1 C_1 \tag{9}$$

are shown in Fig. 6c, with an average 56% reduction after DNDseeding. The value for τ are not reflective those of bulk water (8.2 ps at 25 °C) [41], but more for surface bound water molecules similar to those in ice (2.4 µs extrapolated to 25 °C) [42]. This Table 1

Com	parison of PNI	A model	parameters re	ported	previously	/ for im	pedance s	spectroscop	v of	pure wa	ter and	out	data	using	IDEs
									-						

(F) corresponds to values fixed.

points towards the fact that the bulk water is not the major conduction medium but rather a denser layer than bulk water.

We compared the above-calculated values to those published in literature for water. Prior, Lenzi et al. and Duarte et al. have studied the electrical response of ultrapure water using two circular electrodes parallel to each other with a finite separation distance [43,44]. Lenzi et al. used a fractional diffusion model where the impedance data was segregated into low frequency regime (less than 1 kHz) and high frequency regime (greater than 1 kHz). With two mobile charged species having equal mobility and concentration, Lenzi et al. found anomalous diffusion to model the low frequency regime better while ordinary diffusion fit the high frequency regime. Duarte et al. used the Poisson-Nernst-Planck (PNP) model with two mobile situation with unequal motilities. Recently, Macdonald revaluated their data using the Chang-Jaffe Poisson-Nernst-Planck anomalous (CJPNPA) diffusion model (circuit H, LEVMW) with one mobile and two mobile charge cases [37]. Macdonald found that the one mobile model fit better than the two mobile situation with simple PNP/PNPA model. The values of the electrode separation distance in terms of total Debye layer thickness, total concentration of the dissociated charged species. PNP anomalous exponent, diffusion coefficient and mobility from these three studies are listed in Table 1 along with values obtained in our study.

From Table 1, we find that the values for N_o , and ψ obtained in this study are relatively lower compared to those previously reported, whereas the values for μ_n , and D_n are higher (~5.6 times) than those published by Lenzi et al., but lower than those published by JRM (\sim 10 times), and Duarte et al. (\sim 6 times). We believe that a direct comparison between the values is not suitable. (1) While the previously reported values originate from experiments with a set of parallel circular electrodes, and the charge conduction forced through the bulk of the water, the data obtained here is with a pair of IDEs, which have a higher surface area to volume ratio where the mobile charges may not even see the bulk medium. Also in the case of IDEs, the electric field is not perpendicular to the electrode surface, which will induce edge effects and a field strength distribution along the width of the electrodes, thus requires solving the PNP anamolous diffusion atleast in two-dimensions for a reasonable approximation. (2) Further the previous reports use experimental setups with values of M much greater than 1, while that for the present report are for M-value relatively closer to 1. Also the separation distance is comparable to the width of the electrodes. The value of ψ being low compared to 1 (which corresponds to PNP model for diffusion through bulk) also indicates a surface-bound pathway for motion of the charges.

Overall, our impedance spectroscopy and equivalent circuit modeling suggests that the highly disperse seeding of 5 nm average wide DNDs at IDEs results in (a) a significant drop in R₁, (b) a minor increase in C1, (c) a ψ -value significantly lower than 1, (d) a significant drop in dielectric relaxation time, and (e) a significant increase in diffusion coefficient and mobility of charge carriers, but (f) no drastic change in the charge carrier density. In consistency

with these findings, we propose that the DNDs enhance the motion of charged species between the two electrodes of the IDE pair through either (1) the water bulk, or (2) the diffuse layer as show in Fig. 7. Based on the diffusion coefficient values obtained, these ions may be sulfate ions (SO_4^{2-}) left over from piranha cleaning $(D = 1.06 \text{ cm}^2/\text{s})$, carbonate ions (CO_3^{2-}) , or bicarbonate ions (HCO_3^{1-}) from carbon dioxide dissolved from the atmosphere $(D=0.92 \text{ cm}^2/\text{s} \text{ and } 1.11 \text{ cm}^2/\text{s}, \text{ respectively})$ [45]. In mechanism (1), the negatively charged ions move across the two electrodes by diffusing into the water bulk. The addition of DNDs will not result in resistance change of such a pathway. In mechanism (2), due to the distance between the electrodes ($\sim 9 \,\mu m$) being comparable to the Debye length (~680 nm in pure water), and the co-planar orientation of the electrode surface, the charged ions within the diffuse layer are primarily responsible for electrical conduction. This is supported by the dielectric relaxation constant values found from equivalent circuit modeling. The Debye layer thickness stays constant with or without DNDs. However, the addition of the DNDs to the IDE surface reduces the effective surface potential (also the zeta potential) and thus the electrostatic force holding these mobile charged species in the diffuse layer, and increase the



Fig. 7. Proposed mechanism of mobility of charged species. General model of water structuring composing of the Helmholtz double layer, the diffuse layer and the bulk, here shown over the DND-seeded Au IDEs. The silicon wafer shown as the dark yellow layer, the white layer showing the thermal oxide over it, the bright yellow layer showing the gold IDEs, and the tiny diamond-shaped objects as the DNDs. Gold and oxide surface form a negatively charged surface in presence of water. The double layer is formed over the DND-surface with cations shown here as red circle with a positive sign followed by solvated anions. A diffuse layer composed of charged species but with lower density forms adjacent to the double layer. The proposed pathways for mobility of charges through bulk water, and arrow 2 indicates mobility through the diffuse layer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mobility of the charges in the diffuse layer. This could account for the higher diffusion coefficient, and lower R_I that we saw. Further, the addition of DNDs reduces the dielectric relaxation time (τ) as shown in Fig. 6c, indicating the water molecules in the bound state in mechanism (2) are more free compared to when without DNDs. The mobility of surface-adsorbed ions could be expected to be typically on the order of 10⁻⁴ cm²/V-s [46]. Hence we believe that mechanism 2 is dominating and explains the tuning of charge mobility at the IDEs due to DND seeding at the IDEs.

4. Conclusion

In summary, we have investigated the effects of DND seeding on a microfabricated IDE pair using impedance spectroscopy in pure water. The impedance data was modeled using LEVMW to fit a simple equivalent circuit accounting for the geometrical resistance of the cell in series with a distributed element for Havriliak-Negami dielectric relaxation model and in parallel with the geometrical capacitance of the cell, while simultaneously solving for the PNP model with anomalous diffusion of the charged species between two partially-blocking conducting electrodes. The PNPA Diffusion model does not predicts the sign of the charged species or whether it is a one-mobile or two-mobile case, however the overall density of charges is found to stay within the same order magnitude as 3.31×10^{13} per cm³. Equivalent circuit modeling shows that the Havriliak-Negami model reduces to Cole-Davidson model, seeding the DNDs with a positive zeta potential at the IDEs reduced the geometrical resistance by \sim 57%, and the time constant for the Havriliak-Negami distributed element by \sim 72%, while increased the geometrical capacitance by \sim 3.4%. This results in higher diffusion coefficients of the charged species, and higher charge mobility, and reduced dielectric relaxation time constant. The overall diffusion coefficients and mobility are higher at IDEs compared to those previously reported for conventional electrochemical cells. The high mobility at IDEs can be explained by the participation of the ions from the diffuse ion layer. We propose that seeding DNDs with a positive zeta potential reduces the surface potential of the gold, and the oxide surfaces, and thereby reduces the electrostatic force acting on the diffuse ion cloud and increases the mobility of the charge carriers within. We believe this understanding will further enable engineering better IDE-based sensors with DND seeding.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. electacta.2016.05.053.

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