



Short communication

Dielectric properties of a single nanochannel investigated by high-frequency impedance spectroscopy



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ABSTRACT

High-frequency electric impedance spectroscopy is used to characterize the dielectric properties of a single nanochannel in a micro/nanofluidic device. The simulated electric impedance results lead to the determination of two conductance regimes, a non-ideal capacitance and its surface charge.

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1. Introduction

The understanding of the physics of ionic transport in biologic membranes, solid-state nanofluidic devices or porous material offers new perspectives from biology to energy storage domains. [1,2,3,4,5,6,7,8,9] In such systems characterized by at least one nanometer dimension, the role of the surface charge is exacerbated [10,11], and new phenomena such as surface charge-mediated transport and permselectivity occur. The unbalanced ionic transport between anionic and cationic species through nanofluidic structures initiates a polarization effect related to the concentration domain, which can be applied to focus and locally preconcentrate ionic species [12,13]. Compared to the classical microfluidic field, the nanometer dimension of the channel requires specific theoretical predictions and experimental discussions [14,15,16,17]. The conductance law through nanochannels depends on the ionic strength of the background electrolyte [18,19,20]. At high concentrations, in which the Debye length is much smaller than the channel height, conductance through the nanochannel follows the solution conductivity; at low concentration corresponding to a large Debye length

with respect to the channel height, the nanochannel conductance becomes concentration-independent and is fully governed by surface charge. Recently, Reed et al. [20] investigated the conductance change in an intermediate regime of ionic strength and have speculated about a surface charge inversion in divalent systems where ion–ion correlations exist. In this context, development of direct real-time measurement of conductance in nanofluidic channel is of great interest and necessitates new strategies for more accurate characterization.

In this letter, a new methodology to accurately determine the nanochannel electric properties in a micro/nano/microfluidic device using high-frequency (HF) electric impedance spectroscopy is presented. Indeed, the main limitation encountered with the use of traditional commercially available EIS instruments is the HF measurement accuracy. To overcome this limitation, we combined a HF EIS frequency analyzer with a dielectric interface apparatus dedicated to electric impedance measurements for high resistive materials [21,22,23].

2. Experimental

2.1. Chemicals and reagents

KCl and NaOH (from Sigma-Aldrich) were used as background electrolyte solution and as washing solution for the glass surface regeneration, respectively.

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2.2. Nanochannel and microchannel fabrication

The hybrid micro/nanofluidic device displayed in Fig. 1 was fabricated in borosilicate glass chip with a $1.47 \pm 0.01 \mu\text{m}$ height microchannel and a $170 \pm 10 \text{ nm}$ height nanochannel. Nanochannels were made using the following process. (1) First, 300 nm of amorphous silicon ($\alpha\text{-Si}$) was deposited by plasma-enhanced chemical vapor deposition on a $500 \mu\text{m}$ glass wafer. (2) Then, AZ-5214 reversible photoresist was spin-coated (5000 rpm, 30 s) on the $\alpha\text{-Si}$ glass substrate. (3) The microchannels were designed by UV lithography on a SUSS MicroTec MJB4 mask aligner. (4) In the regions that were not protected by the resin, the $\alpha\text{-Si}$ was etched by reactive-ion etching (RIE) with SF_6 . (5) The microchannels were then etched on $\alpha\text{-Si}$ not protected areas of the glass, using ammonium fluoride–hydrofluoric acid mixture (AF 875-125, etching mixture, Aldrich). (6–9) The nanochannel was made using the same method after a second spin-coating, lithography and RIE (SF_6) procedure. (10) The reservoirs, where solutions were injected, were drilled by sandblasting. (11) The remaining $\alpha\text{-Si}$ was removed using RIE (SF_6). (12) The glass chip and another $300 \mu\text{m}$ glass wafer were then carefully washed using, successively, trichloroethylene, acetone and isopropyl alcohol, the etching mixture for a few seconds, and deionized water. (13) The two wafers were bonded without any intermediate layer using a wafer bonder SB6 (SUSS MicroTec). During thermal bonding, wafers were put in contact for 2 h under vacuum at $550 \text{ }^\circ\text{C}$ with an applied pressure of 3–5 bars. (14) A 5 mm layer of polydimethylsiloxane (PDMS) with holes aligned with the reservoirs was bonded on the chip using air plasma for 70 s.

2.3. Instrumentation and measurement

Electric impedance measurements were performed with a frequency response analyser (FRA 1255B) coupled with a dielectric interface (DI 1296A), which extends the frequency range up to 20 MHz. The originality derives from the use of this latter instrument which contains a very high input impedance allowing the measurement of ultralow currents. [24,25] Impedance was measured between two Ag|AgCl junctions located in the microchannel reservoirs (Fig. 1). The frequency range was varied from 1 MHz to 0.1 Hz. The sinusoidal ac signal amplitude was set to 100 mV, and no dc bias was imposed in order to avoid any faradic reactions.

3. Results and discussion

3.1. Electric impedance spectroscopy on micro nanodevice

To determine the nanochannel dielectric properties, the procedure described below was followed for various KCl concentrations. Solutions

were introduced by capillarity in the device and measurements started only after a stabilization time of 45 min in order to reach the steady state conditions for complete solution uptake through the nanochannel. The results are displayed according the Nyquist or Bode (modified as phase and log (imaginary) vs. log (f)) plot representations. As displayed in Fig. 2A–B for $3 \times 10^{-4} \text{ M}$ KCl concentration, characteristic frequencies are indicated on the plot to visualize the time constants of phenomena involved. Indeed, the semi-circle shape suggests a traditional $R//C$ electrical circuit with a characteristic frequency f_{RC} that can be also identified on the Z_j and phase Bode diagrams. This f_{RC} value, equal to 1168 Hz, corresponds to the maximum of Z_j , equal to $R/2$ (R , semi-circle diameter). Furthermore, the nanochannel resistance, R , can be estimated as the difference on the real axis between the asymptotic resistance limit at zero-frequency, R_{LF} , and that as frequency tends towards ∞ , R_{HF} , (Fig. 2A,B). As one can observe on real axis, R_{HF} is negligible, then R identifies itself with R_{LF} . It is observed that the nanochannel capacitance, C , obtained in the HF domain is not ideal ($\varphi \neq 90^\circ$) because the impedance phase tends towards a constant value equals to -88° (Fig. 2B). This experimental result is also confirmed since the α -slope value for Z_j with frequency on log-log scale indicated in Fig. 2B is equal to -0.98 ($\alpha = -88^\circ/90^\circ \approx -0.98$ thus different from the unit). In brief, it had been assumed that nanochannel capacity was a non-ideal capacity because it is not independent of frequency. Indeed, this analysis of the data showed that it decreased with increasing frequency. Consequently, the glass/nanochannel interface behaves as an RC filter where a non-ideal capacitor can be theoretically represented by a constant phase element (CPE). The changes on the effective CPE coefficient, Q , can be calculated from the obtained raw data of the imaginary part in the HF domain, as proposed by Orazem et al. [26] with Eq. (1) as follows:

$$Q = \sin\left(\frac{\alpha\pi}{2}\right) \frac{-1}{Z_j(f)(2\pi f)^\alpha} \quad (1)$$

with Q and α being the CPE element and the CPE exponent, respectively.

In Eq. (1), when $\alpha = 1$, the effective CPE coefficient, Q_{eff} , becomes an effective capacitance, C_{eff} . The change of Q was plotted by using α -slope numerical value previously determined ($\alpha = -0.98$) and the Z_j data at each frequency. As expected, an asymptotic value $Q_{\text{lim}} = 1.08 \times 10^{-12} \text{ F s}^{(\alpha-1)}$ was deduced by plotting the Q_{eff} variation that behaves as a CPE in the HF domain (Fig. 2C). At this stage, it can be assumed that the observed CPE behavior probably originates from the nanochannel geometry which induces a non-uniform current and potential distribution at the nanochannel entrance with a CPE exponent, α , taking into account the role of concentration polarization.

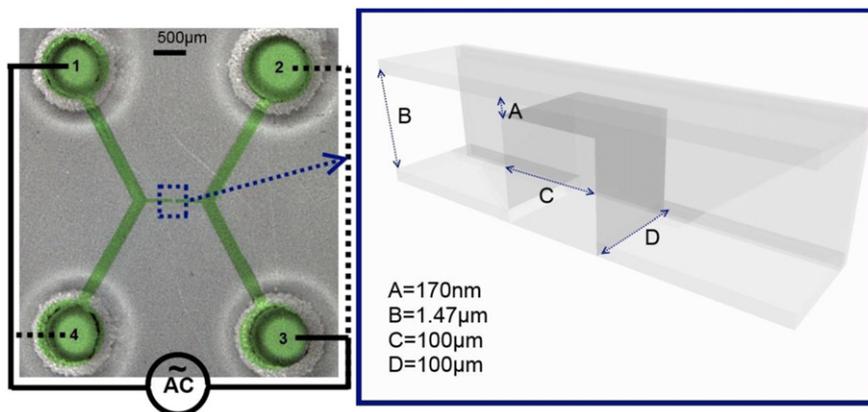


Fig. 1. Left: Global view of a microfluidic chip. At each corner, a hole is visible, where electrolyte is injected. Conductance changes between the two Ag|AgCl junctions are measured either between holes 1 and 3 or between 2 and 4. The nanochannel is in the middle, framed with blue solid line. Right: A schematic view of the micro/nano/micrometric geometry of the device in the middle. The microchannel is reduced to nanometric size on a short distance.

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