Characterization of ionic transport at the nanoscale

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Abstract: This paper reports on the development of a multi-layer microscale impedance measurement system with integrated working, counter, and reference electrodes that can be used to probe transport at the nanoscale. System fabrication and testing are carried out to demonstrate the feasibility of such a system for characterizing transport through nanocapillary array membranes (NCAMs). Results indicate that transport through NCAMs is a complex phenomenon, and impedance does not scale linearly with either pore diameter or ionic concentration. Use of a microscale construct for probing ionic transport at the nanoscale appears to be a promising path forward with further development.

Keywords: nanopore, aqueous ionic transport, water, microscale, nanocapillaries, electrochemical impedance spectroscopy

1 INTRODUCTION

The thriving interest in developing cheaper, smaller, and faster integrated and hybrid micro/nano systems for micro-total analysis systems (μ-TAS) [1] or lab-on-a-chip (LOC) type applications has led to intense research in understanding water and ion transport at the micro- and nano-length scales [2]. Driven by progress towards the construction of artificial membranes mimicking biological ion-channels [3], single molecule detection studies [4], water purification [5], and hybrid micro/nano molecular gates controlling separations of attomolar concentrations [6], the characterization of aqueous ionic transport at the nanoscale has become an important area of active research.

Ionic transport at the nanoscale is complicated by difficulty in conducting accurate experiments that will help elucidate the role of various parameters, such as surface charge, critical dimensions, and wall properties, on translocation of species through confined nanoscale systems. Many numerical and a few experimental studies have evaluated transport in nanopores, nanotubes, nanocapillary array membranes (NCAMs), and nanochannels [7–13]. Previous investigations have focussed on several different aspects of nanoscale transport. For aqueous transport, the role of relative hydrophilicity of the nanopores has been investigated [14]. Due to the enormous surface-area-to-volume ratio at these length scales, the transport is greatly affected by the nature of walls. In a recent report, the role of surface currents due to transport of ions in the electric double layer (EDL) has been shown to be a significant factor that can affect ionic transport across nanopores [15]. The surface charge on the walls can be a key parameter that influences ionic transport at the nanoscale. Recent developments of surface-modified microchannels, nanofluidic transistors, and ion-current rectifiers have shown the importance of surface charge [16–19]. It was found that, for the case of EDL overlap, the ionic conductance of nanochannels reaches a plateau at low concentrations [16]. In a contrasting discovery [20], it was reported that EDL overlap may not be required to observe the plateau region for ionic conductance of the nanochannels at low ionic concentrations. Despite a growing body of literature on aqueous ionic

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transport, several questions with regard to transport at the nanoscale remain open, such as the role of surface charge, walls, charge-to-mass ratio of the translocating ionic species, and electric potentials within the nanopores or nanochannels. Thus, a system that can employ the advancements made at the microscale to probe the transport processes at the nanoscale can potentially be a useful construct; therefore, microfabrication methods naturally lend themselves to the development of a system that can be used to probe aqueous ionic transport at the nanoscale.

In this work, NCAMs are used as nearly 1D nanometer scale pipes with monodisperse diameters to study ionic transport. Like most porous membranes, ion permeation across these is generally characterized by observables, such as permeate flux, membrane conductance, current (I)–voltage (V) relationships, and membrane potentials [21]. Most methods, to date, for characterizing transport in these systems have relied on DC measurements. Inherent to DC measurements is the use of high voltage perturbations (for example, of the order of 1 V or higher) that can cause faradaic activity within the system of interest [22]. In addition, phenomena such as electrolytic transport within nanopores can be quite complicated due to the pore wall–ion interactions, and, thus, transport processes within NCAMs may require special attention [21]. AC measurements can give information about capacitive components, which are common in EDL interactions, related to ionic transport at the nanoscale. Electrochemical impedance spectroscopy (EIS) [23–27] provides a non-invasive method that can accurately provide an estimate of transport at the nanoscale. A multi-layer micro-electrochemical impedance spectroscopic (μ-EIS) system has been developed to characterize ionic transport across NCAMs. Use of small amplitude AC perturbations (of the order of 10 mV) over a relatively small DC bias (~0.1 V or less) reduces the role of faradaic components in the measured impedance and interrogates impedance components related to transport processes, such as diffusion and double layer interactions, as a function of frequency.

The main question being addressed in this paper is the feasibility of developing a microscale construct for probing ionic transport at the nanoscale. This paper describes the fabrication and results of initial testing of a μ-EIS system with an integrated on-chip Ag/AgCl reference electrode to characterize ionic transport across nanopores [28, 29]. The objectives of developing a μ-EIS system are (i) to reduce the effect of concentration polarization in making accurate measurements of membrane potentials by locating the electrodes much closer to membranes and avoiding the common problems that occur in macroscale systems, such as probing outside the unstirred layers, and (ii) to evaluate the role of the EDL in ionic transport that cannot be obtained from DC measurements [26]. The purpose of this paper is to report on the development of a multi-layer microscale impedance measurement system that can be used to probe transport characteristics through NCAMs.

2 EXPERIMENTAL DETAILS

2.1 Multi-layer stack fabrication

The silicon-based, multi-layer μ-EIS system developed consists of (i) two cavity dies to accommodate an aqueous electrolyte solution and provide an opening for electrical contact, (ii) an electrode die with a counter electrode and an Ag/AgCl reference electrode, (iii) a polycarbonate nanoporous membrane (NCAM), and (iv) a second electrode die with two working electrodes. This μ-EIS system is fabricated using some of the previously developed microelectromechanical systems (MEMS) processes [28, 30, 31]. A schematic showing the fabrication sequence, briefly, and the assembled μ-EIS system is shown in Fig. 1, and the detailed fabrication procedure is described next.

The electrode and cavity dies are 18 × 16 mm and made from 100-mm n-doped double-side polished wafers (Silicon Quest, 400 μm thick, <100> oriented, 100 Ω·cm nominal resistivity), on which a 2000 Å thermal oxide is grown. To build the multi-layer stack, first on the front-side of the electrode die wafer 170 Å Cr and 1000 Å Au layers are deposited by DC magnetron sputtering (~10⁻² torr of Ar background pressure). Photolithography and lift-off delineate the Au electrode pattern. Next, a polyimide (PI) layer (PMDA-ODA PI2808, HD Microsystems) is spin-coated as an adhesion and electrical isolation layer. The PI layer is patterned and etched in reactive ion etching (RIE) to form the masking layer needed to etch the underlying silicon. Double-sided photolithography is used to align the front-side pattern to the etch pits on the back of the wafer. The underlying oxide layer is removed by a sacrificial etch carried out in a 50 per cent buffered HF solution. A 50-μm thick cantilever-like electrode structure is created using deep reactive ion etching (DRIE, Plasma-Therm SLR 770). The Au layer is selectively exposed by removing the PI layer by using a Si shadow mask and etching with oxygen plasma in an RIE system (Jupiter III, March Instruments). The exposed Au layer on the Si cantilever structures serve as dual working electrodes and a counter electrode. The remaining Au layer on the counter electrode side is further processed to form an on-chip reference electrode as described below. The cavity dies are fabricated by means of double-sided photolithography and DRIE.
Device assembly with the four Si dies and the polymeric NCAM requires several alignment and bonding steps. The various layers are aligned manually and bonded using a commercial adhesive. The process for applying and curing the adhesive layers has been reported previously [17, 28, 30]. Briefly, an epoxy-based adhesive (epoxy novolac-modified resin, Dow Corning) is contact printed from a poly(dimethyl siloxane), or PDMS, stamp onto the back-side of the cavity die, which is then bonded to the front (PI side) of the electrode die at 130°C for 10 minutes. The same bonding and alignment step is repeated for the second electrode–cavity die stack. The NCAM is sandwiched between these two Si stacks to yield the multi-layer system. The entire five-layered stack is then bonded to 1-mm thick PDMS sheets to seal and enclose the electrolyte chamber. In this μ-EIS system, the sensing electrodes are within ~ 400 μm of the NCAM. There are some advantages of making measurements in regions close to membranes as it is these regions that contain most information about transport affected by the nanoporous membranes such as NCAMs. Bringing the electrodes close to the membranes reduces the effect of measured impedance due to solution between the electrodes and the NCAMs, thereby providing more accurate measurements of potential drop across the NCAMs. In addition, an eventual goal of this work is to bring electrodes close enough to the membranes so that measurements can be made within the hydrodynamic boundary layers, i.e. within the unstirred layers near the membranes. These measurements will provide a more accurate picture of ionic transport across the nanoporous membranes. In this work, the distance between the electrodes and the membrane is almost an order of magnitude closer than the state-of-the-art macroscale EIS systems.

2.2 On-chip reference electrode fabrication and characterization

A planar Ag/AgCl reference electrode is incorporated to provide an on-chip reference by implementing a previously reported scheme [32] with a few modifications. First, selective electroplating of an approximately 5-μm thick Ag layer [32] is accomplished only on the Au layer designated as the reference electrode in the μ-EIS system. The plating bath consists of 0.3 M AgNO₃ in 1 M NH₄OH with an Ag foil as the counter electrode. Prior to plating, an oxidative pre-treatment at +1 V is applied for 5 s for cleaning
the seed layer and better adhesion. Actual plating is performed at \( V_{\text{O}1} \) for 5 minutes. The plated electrode has a geometrical area of 4 mm\(^2\) and exhibits micron-size crystallites, as shown in Fig. 1(c). To form the Ag/AgCl electrode, the electroplated silver surface is treated with a 50 mM solution of FeCl\(_3\) for 1 minute at room temperature. The chemical formation of the fabricated Ag/AgCl reference electrode is verified by X-ray photoelectron spectroscopy (XPS). The XPS spectrum (Kratos Axis ULTRA, Al K\(\alpha\) radiation, 15 kV, 225 W) in Fig. 2(a) shows the characteristic double-peak structure for Ag (3d) indicative of AgCl formation. Comparisons of the behaviour of the microfabricated electrode with respect to the redox couple is similar to that of a commercial reference electrode.

2.3 Device characterization

The \( \mu \)-EIS system is tested to verify the operation of the system for characterizing ionic transport across NCAMs. The multi-layer system is connected to a Gamry FAS2 potentiostat (Gamry Instruments, PA) with the counter and reference electrodes on one side of the NCAM and the working electrode on the other side. Frequencies are scanned from 0.1 Hz to 100 kHz for a variety of pore sizes and ionic salt concentrations. Nominal pore diameters of 800 and 10 nm are used at salt concentrations of 100 mM and 1 mM potassium dihydrogen phosphate (KH\(_2\)PO\(_4\)). All solutions are prepared in de-ionized (DI) water. These experimental conditions are chosen to evaluate the operation of the \( \mu \)-EIS system for characterizing ionic transport across nanocapillaries.

3 RESULTS AND DISCUSSION

For validation of the \( \mu \)-EIS system, impedance data from the microscale system is first compared to that for a traditional three-electrode macroscale EIS system [23, 24]. Results indicate that after normalization to account for the differences in membrane and electrode area, the trends predicted for ionic transport by the \( \mu \)-EIS sensor are similar to those predicted by the macroscale system. Figure 3 shows the Nyquist plot comparing the impedance spectra between macro- and micro-scale systems for 800-nm diameter pore NCAMs. These NCAMs show similar trends for the measured impedance. The \( \mu \)-EIS system cell constant (represented by the radius of the semi-circle) is observed to be higher than that for the macroscale system, in agreement with previously reported results [34]. Equation (1) [34] highlights the role of the electrochemical cell...
constant, $\kappa$, for the $\mu$-EIS sensor that is proportional to the impedance, $z = V/i$, we have

$$\kappa = \frac{l_{\text{eff}}}{A} \quad \therefore \kappa = \frac{1}{l_c}$$

where $l_{\text{eff}}$ is the effective path length for current flow, $A$ is the area over which the desired electrochemical process occurs, and $l_c$ is the characteristic length for the system that experiences a complex electrical potential, $V$, and current, $i$, across it. It can be seen from equation (1) that by reducing the size, and thus $l_c$ of the impedance sensor, the cell constant increases and manifests itself in the Nyquist plot as a semi-circle with a larger radius, as seen in Fig. 3. With a higher cell constant, small changes in ionic transport across the NCAM will cause a larger change in the measured $V/i$ of the system.

Once the cell constant is determined for the $\mu$-EIS system, this system can then be used to characterize ionic transport across NCAMs. Two different salt concentrations and two different pore diameters are tested to demonstrate the feasibility of using a microscale construct to analyze and characterize transport at the nanoscale. These experimental conditions can help determine the effect that the pore size and the EDL thickness within the pore have on ionic transport. The EDL thickness is related inversely to the square root of concentration $[11]$. Hence, by lowering the concentrations, the EDL thickness increases. To extract some physical meaning from the impedance data, equivalent circuit modelling is employed. Figure 4 shows the two models that are used for data analysis. Model A in Fig. 4 is an ideal RC circuit typically used to model porous membranes $[24]$. Model B adds a mass transfer, or Warburg impedance, to the RC model. Figure 5 shows the Bode plot for the 100 mM KH$_2$PO$_4$ concentration. Solid squares, 10 nm modulus; solid diamonds, 800 nm modulus; open triangles, 800 nm phase; solid triangles, 10 nm phase; Solid lines, equivalent circuit model A fit to the experimental data. Impedance spectra are collected from 0.1 Hz to 100 kHz.

**Fig. 3** Nyquist plot comparing the macroscale and $\mu$-EIS sensor. The data has been normalized to account for differences in area as discussed in the text. The different cell constants between the macroscale and the microscale systems are seen in the plot.

**Fig. 4** Equivalent circuit models used in Figs 5 and 6. Model A represents an ideal RC circuit typically used to model ionic transport in porous membranes. Model B represents an RC circuit modified with Warburg impedance, which accounts for a mass transport limit for the system.

**Fig. 5** Bode plot for the 800 and 10 nm pores at 100 mM KH$_2$PO$_4$ concentration. Solid squares, 10 nm modulus; solid diamonds, 800 nm modulus; open triangles, 800 nm phase; solid triangles, 10 nm phase; Solid lines, equivalent circuit model A fit to the experimental data. Impedance spectra are collected from 0.1 Hz to 100 kHz.
Figure 6 evaluates the transport for the 10-nm pores in greater detail. Two different concentrations are investigated. At 100 mM, the EDL thickness is \( \sim 1 \text{ nm} \), and, at 1 mM salt concentration, the EDL thickness increases to \( \sim 10 \text{ nm} \). For the low salt concentration case, it is expected that the EDL within the 10-nm nanopores are interacting. The Nyquist plot from Fig. 6 shows that, at 100 mM concentration, there is a small semi-circle at high frequency and a line with a 45 degrees slope. This line confirms the earlier observation of the mass transport limit at a low frequency and is characteristic of the Warburg impedance. Model B is used to fit the experimental data and is found to predict the experimental trends. For the case of interacting EDL, a much more pronounced semi-circle is seen at higher frequencies. This is indicative of a larger RC time constant at lower concentrations. At low frequencies, the

![Nyquist plot showing the effect of concentration on ionic transport. Triangles represents the 1 mM case and the squares represents the 100 mM case. The experiments were conducted on a 10 nm NCAM.](image)

**Fig. 6** Nyquist plot showing the effect of concentration on ionic transport. Triangles represents the 1 mM case and the squares represents the 100 mM case. The experiments were conducted on a 10 nm NCAM. Impedance spectra are collected from 0.1 Hz to 100 kHz.

![Fabrication sequence.](image)

**Fig. 7** Nanopore with buried metal electrode for measuring local potential within the nanopore. (A) Fabrication sequence. (B) An SEM image showing the top view of the nanopore. (C) An SEM image showing cross-section view with the buried metal layer and nanopore.
Warburg impedance is still observed. In addition, Model B under-predicts the value of measured impedance at low frequencies. The capacitance of the double layer is related to the square root of the concentration [35]. Thus

\[
\left| z_{\text{meas}} \right| \propto \sqrt{1 + \frac{\text{concentration}}{\text{concentration}}} \tag{2}
\]

For the two concentrations used for Fig. 6, and using equation (2), it is seen that the impedance at 1 mM salt concentration should be at least 10 times greater than that at 100 mM salt concentration. However, for frequencies less than about 1 Hz, it is seen from Fig. 6 that the impedance of the 10-nm pores is higher by almost 30 per cent in comparison to the case when the EDLs do not interact. A possible reason for this deviation from expected behaviour is in line with the results of Fulinski et al. [15], where they showed that there are some surface currents that flow along the pore walls leading to deviations in pore conductance as compared to the case of no EDL overlap. Thus, the presence of surface currents would cause lower measured impedance than expected.

4 CONCLUSIONS AND FUTURE OUTLOOK

A μ-EIS system has been developed with electrodes measuring potential and current characteristics within 400 μm from the nanocapillaries. This microscale system has been shown to be a possible platform that can be used to characterize ionic transport at the nanoscale. Impedance data indicate that measured impedance does not scale as expected with both pore size and ionic concentration. Data also suggests that the phenomenon of ionic transport through NCAMs is a complex subject and will require further investigation as several open questions remain. One of the open questions relates to the electric potential distribution within the nanopores. Local potential measurements can help determine the effect, if any, of surface charge and surface currents on ionic transport across nanopores. In addition, if these measurements can be conducted within the fluid boundary layers, the effect of concentration polarization within the unstirred layers on these measurements can be minimized. Toward this goal, an embedded metal (Ni) electrode, separate from the working, counter, and reference electrodes in the μ-EIS system, but within a nanopore, has been fabricated (Fig. 7). Such a system can be employed to measure local potentials within the fluidic boundary layers along with collecting impedance data for transport across the nanopores. This system can be also integrated with the μ-EIS system for probing local potentials within a single nanopore and, thus, shed some more light on the physics of ionic transport at the nanoscale.

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