A MICROFABRICATED IMPEDANCE SENSOR FOR IONIC TRANSPORT IN NANOPORES

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ABSTRACT

This paper reports on a multilayer micro-electrochemical impedance spectroscopic (μ -EIS) sensor with an integrated planar Ag/AgCl reference electrode that has been fabricated using MEMS technologies. The μ -EIS sensor is used to detect and characterize ionic transport across nanoporous membranes. The microfabricated multilayer μ -EIS system consists of integrated nanoporous membranes, working, counter, and reference electrodes. The μ -EIS sensor is tested for ionic flow through nuclear track-etched polycarbonate nanoporous membranes with pore diameters of 800, 220, 50, and 10 nm. For validation, the μ -EIS performance is compared to a macroscale 3-electrode electrochemical cell. The electrolyte is an aqueous solution of potassium phosphate (KH_2PO_4) of varying concentrations. Equivalent circuit modelling results are reported and these capture the trends displayed by the experimental results. Use of a Warburg impedance and the constant phase element (CPE) in modelling helps predict the mass transport limit for these sensors and accounts for the non-ideal capacitive behavior observed for these membranes.

INTRODUCTION

The ability to monitor ionic transport across nanopores is important for a variety of scientific and technological reasons, including the development of synthetic constructs mimicking ion-transport in biological channels [1], single molecule detection [2], and the development of molecular gates controlling separation of attomolar concentrations [3]. Macroscale electrochemical impedance spectroscopy (EIS) typically uses samples and electrodes with several cm^2 of area and cannot have electrodes placed near the nanopores. Thus, detecting and characterizing ionic transport across a few nanopores at a known transmembrane potential is difficult, often yielding extremely poor signal to noise (S/N) ratio for systems such as molecular gates [3]. In μ -EIS, the electrodes can be located relatively close to the nanoporous membrane. Also, with greatly reduced sensor size, small changes in ionic current can be detected with a reasonable S/N ratio. However, device integration challenges such as incorporating ideally polarized working and counter electrodes with an ideally non-polarized on-chip reference electrode must be addressed. Also, the relative location and dimensions of the electrodes must allow for accurate transmembrane potential measurements. Thus, a μ -EIS sensor needed to be developed that can provide rapid and direct characterization of translocating ionic species through nanoporous membranes without the need for amplification, chemical modification, surface adsorption, or binding agents. The μ -EIS impedance data gives magnitude and phase information along with I-V characteristics, thus also providing insight into the interaction between the translocating ions and the electric double layer (EDL) within nanopores due to the interplay between the surface zeta potential and the ionic charge of the electrolyte. Developing a system in which nanopore impedance can be measured accurately will help develop *in-situ* monitoring of nanopore electrokinetic flows.

EXPERIMENTAL DETAILS

A microfabricated multilayer μ -EIS system consisting of integrated nanoporous membranes, and working, counter, and reference electrodes is shown in Fig. 1. The schematic represents an assembled device. A 1000 Å thick sputtered Au layer, serving as the cell electrodes, is patterned on a 100 mm Si wafer, and a polyimide layer is spin-coated to serve the dual role of providing electrical isolation for electroplating the Ag layer and adhesion between the die stack. Double-sided photolithography and DRIE yields four 18 x 16 mm Si dies that are used to assemble the multilayer stack with the nanoporous membrane sandwiched in between. Device assembly requires several alignment and bonding steps. The various layers are bonded using a commercial adhesive and the process for applying and curing the adhesives has been reported previously [4]. The electrodes are located $\sim 500 \mu\text{m}$ from the membrane for accurate measurements of voltage drop across the membrane. A planar Ag/AgCl reference electrode [5] is incorporated to provide on-chip reference. The formation of the reference electrode with the appropriate chemical structure is verified by XPS (Fig. 2).

Figure 1: (A) Schematic of an assembled μ -EIS system showing the working, counter and reference electrodes, and the sandwiched nanoporous membrane. (B) An SEM image of the nanoporous membrane is shown along with digital photographs of individual dies in (A). (C-D) SEM images of Au and Ag/AgCl electrodes.

Figure 2: XPS spectra for the electroplated Ag/AgCl layer after treatment in FeCl_3 . The key peaks are shown in the spectra above including the characteristic double peak structure for Ag (3d) indicative of AgCl formation. The Ag/AgCl layer is used as the reference electrode.

RESULTS AND DISCUSSION

Impedance data is collected for varying salt concentrations of monobasic potassium dihydrogen phosphate (KH_2PO_4) in an aqueous solution. The thickness of the EDL can be estimated by using equation 1, which is valid for dilute solutions [6].

$$\lambda_D^{-1} = .39 \cdot 10^7 \cdot z \sqrt{c} \quad (1)$$

where, λ_D^{-1} is the inverse Debye length ($\sim$ the thickness of the EDL) predicted by the Gouy-Chapman model, z is the valence of the ion and c the bulk concentration of electrolyte solution. Equation (1) shows that with decreasing concentration the EDL thickness increases. For validation of the μ -EIS measurement, impedance measurements are conducted on a macroscale 3-electrode electrochemical cell with 800 nm pores in polycarbonate track etched (PCTE) membranes. Figure 3 shows the comparison between the macroscale EIS measurement and the μ -EIS system. It is seen from Fig. 3 that impedance data matches well from about 100 kHz to approximately 5 Hz. At low frequencies the magnitude of the measured impedance for the μ -EIS is about 3 times lower. The observed large differences seen at low frequencies can be possibly attributed to leakage current through the Si substrate. Figure 4 shows a comparative Nyquist plot for the 10 nm and the 800 nm pore diameter PCTE membranes at 100 mM salt

Figure 3: A Bode plot showing a comparison between the impedance data for the macroscale EIS measurement and the μ -EIS collected from 0.1 Hz to 100 kHz for a 800 nm PCTE membrane at 100 mM salt concentration.

Figure 4: A Nyquist plot showing comparison between impedance data for the μ -EIS collected from 0.1 Hz to 100 kHz for a 800 and 10 nm PCTE membrane at 100 mM salt concentration. The model used is shown as the inset.

concentration. The 10 nm pores display a mass transport limit indicated by the 45° line at low frequencies. At 1 mM salt with overlapping EDLs, the concentration impedance for the 10 nm pores increases by almost 2.4 times at low frequency (<1 Hz) and the imaginary part of impedance shows an increase of about 31% in comparison to the 100 mM case. Equivalent circuit modelling is carried out to estimate a possible electrical circuit that would better elucidate the physics of nanopore ionic transport. The presence of a Warburg impedance indicates that hindered ionic transport occurs in the 10 nm pore, and its absence till about 0.1 Hz for the 800 nm at 100 mM indicates normal electrokinetic flows without interacting EDL's.

This paper demonstrates the fabrication and preliminary testing results for a μ -EIS sensor, and that such a sensor can be used to evaluate electrokinetic ionic transport across nanopores.

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