Supporting Information

1. Development of a pressure sensor

A measurement setup was developed in order to allow the in situ measurement of layer-by-layer deposition in the membrane. This would ideally be measured with a real time output to monitor the layer as it was deposited, then recorded for further data analysis. For ease of calibration purposes, the sensor PX26-001DV from Omega Engineering was used. This same sensor was also used in the Savarir et al. paper on molecular discrimination inside of nanotubules.\[^{51}\] This calibration would be done using a 70 cm high water column, providing an easy method of measuring and calibrating the sensor with each set of measurements. For ease of calculation, the effect on pressure due to altitude was neglected. This sensor has been used as well for the use of hydraulic measurements in soil science using a commercial data logger and a INA125 instrumentation amplifier setup.\[^{52}\] The circuit was developed prior to knowledge of this publication.

The overall setup was envisioned as such: a syringe pump would provide a constant and adjustable flow of water to the membrane holder, connected to the pressure transducer through a T-piece. The pressure transducer would be connected to the amplification/data collection box via the provided connector (Omega Engineering). The scale would provide flow rate data through a serial cable, connected to the amplification/data collection box, which would then provide output data to the computer, which would act as a data logger (Figure S1). A photo of the actual setup is also provided in Figure S1. This provided a basic setup for low-cost membrane measurements with easy calibration and as little introduction of new variables as possible. The major development performed was in the construction of the instrumentation amplifier/data collection box, which will be described further in this chapter.

2. Amplification data collection box development

This section describes the development and layout of the amplification and data collection box used to gather membrane pressure data from the PX26-001DV sensor. The circuit board layout can be found in Figure S2, and the electrical schematic can be found in the appendix.

2.1. Power supply and stabilization circuitry

An external supply with 9-12 volts was fed to linear regulator (7805), which furnishes a stabilized 5 V for the digital electronics. For the sensor, instrumentation amplifier and op-amp (operational amplifier), higher positive and negative supply voltages are needed. For this purpose a Traco Power TMA0512D Dual output +/- 12 V DC/DC converter was used. The voltages are stabilized with LC (inductance-capacity) low pass filters (L1-C14 for +12 V and L2-C15 for -12 V) with a cutoff frequency of about 5.9 kHz ($F_{\text{c}}=1/(2\pi\sqrt{L*C})$). This reduces noise in the output signal. As the output voltage of the unloaded DC-DC-converter is higher than 12 V, it is then limited to +/- 12 V over two Zener-Diodes (D3 and D4).

2.2. Microcontroller and support circuitry

An Atmel ATmega1284p was chosen as microcontroller (MCU) to control the circuitry, interface to the scale, provide the reference voltage and digitize the sensor output signal. The ATmega1284p was chosen for the following reasons:

- It is easily programmable with the Arduino (www.arduino.cc) environment.
- It has a second serial port that can be used to interface with a

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Figure S1. Schematic (top) and picture (bottom) of the sensor and filter-holder setup.

Figure S2. Layout of data collection box circuit board.
scale, the first serial port is used for interfacing with the computer via a UART-USB converter.

- It is available reasonably cheaply in single quantities (about 9.25 CHF)

The programming of the bootloader requires a 6-pin ISP (In System Programming) interface.

Clock generation for the MCU is provided via a 16 MHz crystal and two 22 pF load capacitors. Jumper JP4 interfaces to two buttons (with 2 10 kOhm pullup resistors R16 and R17) and two LEDs via 2270Ohm current limiting resistors (R14 and R15) to prevent the LEDs from pulling too much current and burning up.

There are two I2C interfaces provided on the board. One is used by the 2*16 character HD44780 display via a PCF8574 port expander; the second one is for possible additional peripherals but was not needed in this case. A reset switch with its 10 kOhm pullup resistor is provided. All power supply pins are connected to the 5V VCC rail via 100 nF bypass capacitors. These stabilize the rail for transient load and "short circuit" noise to ground, which serve to stabilize the supply network.

### 2.3. USB interface

Once the bootloader is written to the microcontroller via an external programmer, the ATmega1284p can be easily programmed via its' built in serial port. Also, once in operation, a way to get the data from the microcontroller to the computer is needed, and conveniently provided by the same port. In order to interface this port to a computer a USB to serial converter is required.

This interface is provided by a FTDI FT231X USB-UART converter in a TSSOP-20 package, a USB-to-serial interface. Circuitry follows the data sheet for a FT231X in Self Powered Configuration. Another possibility would have been to forgo the external supply and use the power supplied via USB from the computer but that would have necessitated more stabilization circuitry.

The FT231X connects to the ATmega1284P via the serial input (RXDO) and output (TXDO) pins as well as to the reset pin via capacitor C.

### 2.4. Scale interface

In lieu of a dedicated flowmeter, a Mettler Toledo DeltaRange PG4002-S was used. The scale provides a RS-232 serial interface through which the current weight on its load cell can be exported. As the RS-232 protocol sends the strings of bits (0 or 1) by alternating between logic 0: [3..15 V RS-232] and logic 1: [-15..-3 V RS-232] and the serial interface of the MCU works with 0 and 5 V for logic 0 and 1 respectively, a converter chip was needed, provided in form of a STMicroelectronics ST232C with four external capacitors for the charge pumps. On the PCB a 3-pole header is provided which is connected to a DB9 connector at the back of the interface. The ST232 is connected to the second serial port (RX1/TX1 on the MCU).

### 2.5. Sensor interface

In order to measure the pressure at the membrane, a differential pressure sensor Omega PX26-001DV was used. One port is connected to the water circuit, the other port is left open to the atmospheric air pressure. The sensor outputs a differential voltage rFW between MOUTSENS and POUTSENS proportional to the applied pressure (0: 0 V, 1 Psi: 16.7 mV) for an input voltage of 10.0 volts. As the sensor is ratiometric, its output is also proportional to the applied supply voltage; a fact that we could turn to our advantage by producing the supply voltage from the ADC reference voltage. Any fluctuation of the full-scale reference would thus be the same for the sensor and the ADC and cancel out.

The ADC of the ATmega1284p can either be supplied with an external analog reference voltage, use the 5 V supply voltage or generate "Selectable 2.56 V or 1.1 V ADC Reference Voltage" via bandgap references. In the case that the internal references are used, they are provided at the AREF-pin (analog Reference) of the MCU.

It was decided to use the 2.56 V reference from the MCU and multiply it by four to 10.24 V using a STMicroelectronics LM324 Op-Amp (operational amplifier) in non-inverting voltage amplifier configuration.

The LM324 is a quad Op-Amp (contains four individual op amps). IC2C is used for the multiplexor. The multiplication factor is set as 4 by two 0.1% tolerance precision resistors R22 (10 kOhm) and R23 (30 kOhm). The amplification is calculated via the following equation:

\[
\text{Amp} = \frac{(R22+R23)}{R22} \times \text{R22}
\]

The op-amp serves the purpose of having a high input impedance which prevents a voltage drop of the source that may have become problematic. The 10.24 Volt from the op-amp are then provided:

- As supply voltage for the pressure sensor.

- To the zero reference input for the instrumentation amplifier via a 10 kOhm precision resistor and a 200 Ohm trimmer so the zero output can be adjusted from 0 to about 200 mV (200 Ω* 10.24 V/10200 Ω) via a second Op Amp in voltage follower configuration. For digitalization of the signal with the ADC it is advantageous that the zero point be set slightly above (the noise at) 0 V.

The signal from the pressure amplifier is directly fed into the differential inputs of the instrumentation amplifier (U3, Texas Instruments INA126), which is "basically" constructed from two operational amplifiers and precision trimmed resistors that determine the voltage gain with the external resistor Rg following this relation:

\[
G = 5 + \left( \frac{80 \text{kΩ}}{R_g} \right)
\]

In our case we use a 0.1% tolerance 680 Ohm resistor, resulting in an amplification factor of 122.647.

The maximum output voltage from the sensor at 1 psi is calculated as follows:

\[
10.24 \text{V} \times 16.7 \text{mV} / 10.0 \text{V} = 17.1008 \text{mV}
\]

while the maximum output voltage after instrumentation amplifier INA126 is:

\[
17.1 \text{mV} \times 122.647 = 2097.3628 \text{mV}
\]
The output voltage from the INA126 is fed into the ADC via a 4.7 kOhm resistor and a diode from ground both of which serve to protect the ADC input. We are using the 2.56 V internal reference of the microcontroller as the full scale comparison voltage for the ADC.

3. Software

A program running on the microcontroller serves to interface with the computer by outputting the data via serial interface on the microcontroller, which is output to the computer via a USB to serial interface. The program runs through its initialization routine where the interface to the scale and to the computer are set up, the display is initialized, the analog reference voltage for the ADC (2.56 V) is set up. Simultaneously, the timer function is started.

The user is then asked if he wants to calibrate the sensor with 2 water pressures (0 and 70 cm) and if the scale should be tared to 0. Otherwise, the measuring mode is started and runs forever in a loop.

In the measurement mode, the function runacqdisp is run at an interval of one second (triggered by an interrupt). That function outputs a counter value, the weight from the scale, the raw sensor data, and the calculated pressure (from raw data using the calibration values) to the serial port and starts a function displaying the weight and the raw sensor data on the display. After that, the function runmeasure is called which gets the measurements for the next cycle. The current weight is polled off the scale and 256 measurements of the sensor data are called every 2 ms. The calibration routine asks for the application of 0 pressure (no water level above the sensor input) and for the application of 703 mm H2O (corresponding to the full measurement scale of the sensor). These values are measured and stored to the EEPROM (nonvolatile memory in the microcontroller).

4. Sensor testing and calibration

The sensor was tested and calibrated using a 1 m high water column made of PVC tubing. A buret was not used due to problems with air bubbles. Water levels of 10 cm difference were recorded; the output can be found in Figure S3.

As can be seen in the graph, there is no visible noise while pressure is being recorded, and the pressure measurements can be taken over long periods of time without change (200 minutes total for the graph shown). The major unavoidable source of noise was the syringe pump, which contains a stepper motor that produces a periodic noise seen in Figure S4. While this did produce a relatively large noise spectrum, it could be averaged out and did not significantly increase the standard deviation of the results.

4.1. Flux calculation at low flow rates

Membrane flux is defined as the volume of liquid through a membrane divided by the time and the area:

\[ J = \frac{Q}{S} \]

where \( J \) is the filtrate flux (L/h*m²) where L is liters, h is hours, and m is meters, \( Q \) is the filtrate flow (L/h), and \( S \) is the membrane surface area. When pressure is factored in, the instantaneous specific flux is found by the equation:

\[ J_s = \frac{J}{\Delta P} \]

where \( J_s \) is the instantaneous specific flux (L*h⁻¹*m⁻²*bar⁻¹) and \( \Delta P \) is the transmembrane pressure (TMP, bar).

In general, membrane flux calculations are carried out using commercial equipment at high pressures (1 bar or more). However, due to the limitations of the sensor (a maximum pressure of 1 psi (0.069 bar)), all of the experiments and flux calculations were performed at a much lower flow rate and pressure. It was verified that the pressure within the range of the sensor was linear with the flow rate (Figure S5). With this knowledge, the
pressure could be scaled from one flow rate to another for easy comparison when the pressure exceeded the limitations of the pressure sensor. The exception to this was at very low flow rates and very low pressure, <0.01471 bar, where the pressure essentially leveled off. At higher pressures, the flow rate maintained the proper ratio with pressure.

4.2. Poly(acrylic acid) deposition and pore characterization through pressure measurements

Deposition of the PAA layer at low flow rates showed little increase in pressure. This was expected, as pore diameter vs. area does not change in a linear fashion because the pore is circular. This can be modeled through the Hagen-Poiseuille equation, which is used in fluid dynamics to describe a fluid as it passes through a cylindrical pipe:

\[ J = \frac{\pi \Delta P r_p^4 m_p}{8 \eta \Delta x} \]

where \( J \) is the solvent flux (not the specific flux, which involves pressure, but the filtrate flux involving flow rate and surface area), \( \Delta P \) is the pressure, \( r_p \) is the pore radius, \( \tau \) is the tortuosity factor, \( \Delta x \) is the membrane thickness, and \( \eta \) is the viscosity of the solution.\(^{35}\) It has been noted in the literature that very few membranes follow this equation closely due to their structure.\(^{35}\) However, using it as a basic model for the expected increase in pressure, and assuming that all of the other factors are a constant \( k \), we can plot

\[ \Delta P = k \frac{1}{r_p} \]

to get a general idea of what the pressure data should look like as a pore closes. We would expect to see a very slow increase in pressure up to a point, and then a rapid increase as the pore becomes progressively narrow.

Unfortunately, this also becomes problematic when attempting to reach very small pore sizes. Using the average pore size of 40.6 nm as a starting number, it is possible to roughly determine pore size using flux data calculated from the pressure data. Rearranging the Hagen-Poiseuille equation once more and making the factors that are constant into a constant \( k \), where \( d_p \) is the diameter of the pore:

\[ \frac{J}{\Delta P} = k \frac{d_p^4}{\frac{\Delta P}{J}} \]

so that when comparing two pore sizes, this rearranges again to the equation:

\[ d_{p1} = \left( \frac{J_2 + \Delta P_2 + \Delta P_1}{\Delta P_2 + J_1} \right)^{1/4} \]

and from this it is possible to gain a rough determination of the final pore size. Since \( J/\Delta P \) is the definition of the specific flux, this is basically comparing the two specific flux measurements to get a pore size estimate.

\[ d_{p1} = \left( \frac{\text{flux}_1}{\text{flux}_2} \right)^{1/4} \]

This is a rough estimate because the tortuosity of the pore most
likely changes during layer deposition, the surface properties of the pore differ due to more or less hydrophilic polymers on the surface, and the fact that as the pores become more and more closed the smallest of the pores in the distribution found in Figure S6 may be blocked entirely. A disclaimer must be made here, that since neither the flow rate or the pressure is held constant for the entire experiment, and just the ratios compared, that it would be extremely difficult to determine additional information from the calculations here, for example to examine the other parameters of the Hagen-Poiseuille equation.

4.3. Pore polydispersity

As a beginning measure for characterization of the membrane, it was important to understand the membrane structure and quantify the “isoporous” nature of the pores. If the pores would then be slowly closed, then the dispersity of the pores would become increasingly important as the smallest pores would be blocked completely before larger pores. A crude calculation of the pore polydispersity could be obtained using Matlab, which is capable of image processing. A SEM picture containing a 2×2 μm area of the polymer membrane surface was used for the calculation (Figure S6). The average pore size was found to be 40.6 nm with a standard deviation of 6.72 nm and a PDI of 1.03.
Figure S12. Polyelectrolyte buildup on surface of membranes after 0.5 (left, no surface buildup), 1 (middle), and 1.5 (right) layer-pairs deposited at pH 7.4 for PSS and pH 6 for PEI.

Figure S13. GPC curve of the initial feed mixture (pink), and the three membrane tests. Membrane 1 has an approximate pore size of 24 nm (black), membrane 2 has an approximate pore size of 35 nm (blue), and membrane 3 is unmodified (approx. 40 nm pore size) (red). Approximate pore sizes are calculated from pressure data.

References

(S2) J. A. G. Gnechi, Self. 4.7.0, 11-2 (2011).
(S5) B. S. Lalia, V. Kochkodan, R. Hashaikeh, and N. Hilal, Desalination, 326, 77 (2013).