

Development of polymer lab-on-a-chip (LOC) for oxidation-reduction potential (ORP) measurement

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ABSTRACT

Reverse osmosis (RO) desalination has been recognized as a promising method to solve the water shortage problem. Nevertheless, since it is energy intensive and has many problems associated with biofouling/fouling of RO membranes in RO plants, its commercial acceptance is still slow. Especially, as high levels of oxidizing agents negatively affect RO membrane efficiency and life span. So, there is a need to develop sensitive, selective, portable and rapid methods to determine oxidation-reduction potential (ORP) in feed solution. For developing a polymer ORP lab-on-a-chip (LOC), a microchannel patterned on a polymer substrate was successfully filled with 800 nm diameter silica beads using self-assembly bead packing technology. The measured ORPs using the three kinds of redox potential solutions were typically slightly lower than those of the nominal redox potential. But, all of the measurements should be deemed acceptable. The ORP LOC has also a much shorter response time than the conventional potentiometric sensor.

Key words | ORP, polymer lab-on-a-chip, potentiometric sensor, self-assembly bead packing

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INTRODUCTION

The amount of potable water available for human use is very limited, due to the high population growth rate (Jones 1999), climate change probably caused by global warming (Vorosmarty *et al.* 2000; Afonso *et al.* 2004), and intensive anthropogenic activities, such as urbanization, industrialization, and agriculture. For solving global water shortage, so far, many countries have harvested rain water mainly by building water dams and ponds, but it cannot be both an ecologically and economically permanent solution. Groundwater can be also considered as the primary source of pure water available in the earth, but eventually, an important portion of this source may be depleted as a result of over-exploitation (Atikol & Aybar 2005), and can become contaminated in many ways. There is no doubt that once groundwater is contaminated, extremely costly operations are necessary to remove the contaminate. So, as a viable alternative for potable water production, seawater is preferably considered because it is cheap, inexhaustible, and relatively free from contaminants such as oil and colloidal matter (Al-Odwani *et al.* 2000; Praptowidodo & Khalik 2000). It has been already pointed out that

seawater desalination processes are one of the feasible technologies to solve the water shortage problem in many of the arid countries such as those in the Middle East, Asia and the Caribbean (Afonso *et al.* 2004).

Due to their capacity to efficiently remove ionic species and potential for removal of all classes of pathogens, reverse osmosis (RO) membrane filtration systems have been widely and successfully used for seawater desalination processes (Adham *et al.* 1998). With the rapid development of membrane fabrication techniques, a new generation of seawater reverse osmosis (SWRO) membrane can reduce the operating pressure and consumes less energy, which makes the processes much more economical and popular (Rvias & Paley 2006). However, SWRO membranes are still subject to a variety of problems including biofouling/fouling, scaling and chemical attack (Xu *et al.* 2007; Shon *et al.* 2009). Especially, the damage of thin-film composite membranes is most often attributed to oxidizing agents including chlorine, hydrogen peroxide, and ozone, which are commonly used in the field of seawater desalination (Iborra *et al.* 1997; Tessaro *et al.* 2005). High levels of these chemicals in feed water eventually

leads to an increase in the production rate of the permeate but a reduction in product quality due to SWRO membrane damage. Accordingly, if chemicals can be detected early, it is possible to increase the performance and life of the SWRO membrane by protecting from potential danger of membrane damage. Despite growing concern over the chemical attack of SWRO membrane, however, there is little information in the literature on monitoring techniques for SWRO membrane systems. It is feasible to use oxidation-reduction potential (ORP) monitoring as one of the important SWRO system parameters to identify possible problems early since solutions can be graded as oxidizing or reducing based on measurements of ORP value. For precise ORP measurement in the feed water, colorimetric or potentiometric methods can be generally used. Although colorimetric kits are relatively inexpensive, they are undesirable to monitor ORP because of some errors induced from the color of the water. Normally, most of the ORP monitoring systems have electrodes dipped into water containing chemicals, but monitoring systems with this type of sensor have had very low user satisfaction when operated under a continuous long-time mode because the electrode sensor become fouled or encrusted by bacteria, ions or other charged particles in the water. But, the polymer lab-on-a-chip (LOC) sensor developed in this study can be free of problems associated with fouling because it is disposable. Furthermore, since the Micro Electro Mechanical Systems (MEMS) fabrication technology usually enables not only the miniaturization but also batch-fabrication, inexpensive disposable sensors can be produced. With more development of the instrument, including a smart sipping system for automated sampling which prevents operators from frequently changing sensor chips, continuous ORP monitoring is also possible. Therefore, the objective of

this research was to develop miniaturized electrochemical ORP LOC sensor with planar microelectrodes and a self-assembled nanobead packed (nBP) column using both MEMS and self-assembly nanobeads packing technologies.

MATERIALS AND METHODS

Fabrication of a microfluidic chip

As shown in a left side of Figure 1(a), a cyclic olefin copolymer (COC, Topas 5013, Ticona, Summit, NJ, USA) plastic chip patterned with microfluidic channels was prepared by an injection molding technique using an electroplated nickel mold (Park et al. 2007). SU-8 2075 photoresist (Microchem Corp., Newton, MA, USA) was spin-coated on a 3-inch diameter nickel (Ni) disk to achieve a 100 μm thickness, followed by a pre-bake process. After the photoresist layer was exposed to a UV source (365 nm UV), it was baked again for cross-linking for about 5 h. After developing, Ni electroplating was performed in a Ni plating bath, using a two-electrodes system with a Ni anode and the patterned Ni disk cathode. Finally, a Ni mold with a 100 μm -thick plating Ni microstructure was obtained after removal of the residual SU-8. The microfluidic chip was then replicated from this mold in a COC substrate by a high-throughput injection molding machine (BOY 22A, BOY Machines Inc., Exton, PA, USA).

Silica nanobead packing in a microfluidic chip

Figure 1(b) shows the schematic procedure for the self-assembled nBP column in microfluidic chip. The patterned

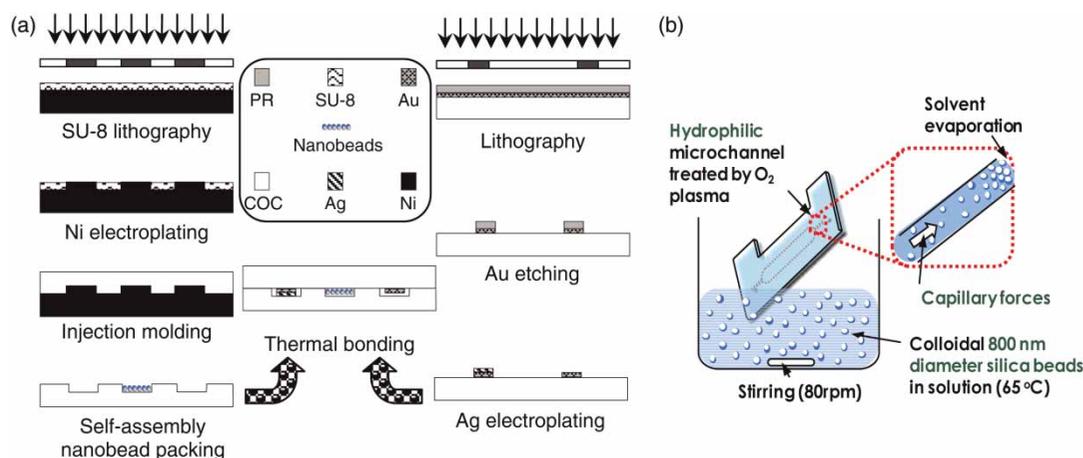


Figure 1 | (a) Schematic diagram of fabrication steps of a polymer chip sensor for ORP measurement and (b) the principle of self-assembly bead packing technology.

COC chip substrate was pretreated with O₂ plasma for 2 min to give high hydrophilicity to the microchannel surface (Park *et al.* 2007). The aqueous colloidal silica solution (800 nm, 0.1 wt%, Bang's Laboratories, Inc., Fishers, IN, USA) was heated to 65 °C in a beaker with gentle stirring (80 rpm) to prevent slow precipitation of the aggregated silica particles. Pretreated open microchannel allowed the aqueous colloidal silica solution to drive to the end of the channel by capillary action. Once the colloidal silica particles reached the end of the microchannel, spontaneous three-dimensional packing of the silica beads started from the end of the microchannels due to the slow evaporation of solvent. Subsequently, the self-assembled nanobead packing process continued toward the end of the empty microchannel at the bottom. The packed microfluidic chip was washed very gently and cautiously with plenty of deionized water to remove extra silica nanobeads at the dipped area and was dried completely at room temperature. The fabrication of the entire LOC including the self-assembled nanobead packing technology and microfabrication steps can be done within a day.

Fabrication of a microelectrode chip

The microelectrodes were also made by microfabrication technology illustrated on the right side of Figure 1(a). An Au layer of 100 nm was deposited on the 3-inch blank COC wafer using an e-beam metal evaporator (Temescal FC1800, BOC Edwards Temescal, Livermore, CA, USA). After Au deposition, the wafer was cleaned again by using acetone, methanol and DI water, sequentially. The working electrode was etched by Au etchant to form the designed electrode patterns. In order to obtain the designed electrode pattern, unprotected Au should be removed from wafer surface. The electrode was etched by Au etchant (TFA) to form the designed electrode structure. The TFA was made by adding 10 g I₂ and 40 g KI into 400 ml of deionized water. As the last step, liquid-liquid junction Ag/AgCl reference electrode was fabricated for potentiometric electrochemical LOC. For the liquid-liquid junction reference electrode, the silver (Ag) layer was deposited on the Au seed layer to make the Ag/AgCl reference electrode using electroplating method.

Bonding process for a polymer ORP LOC

After drilling holes for fluidic interconnection at inlets and outlets using a 0.8 mm-diameter micro drill bit, the microfluidic chip was bonded with the sensor chip using the

fusion bonding method to make the final ORP LOC. The patterned COC substrate was made of a resin having a high glass transition temperature ($T_g = 134$ °C). After packing with silica nanobeads, the packed substrate was covered with a plain COC plate having low T_g ($T_g = 78$ °C) and sealed using a homemade hot embossing machine (Park *et al.* 2007). To avoid the destruction of the silica packing by the pressure applied during press-bonding, the temperature of the chip in the hot embossing machine was maintained at 85 °C for 20 min without pressing and the cover plate was allowed to soften. The softened cover plate was squeezed from the top with the weight of the hot plate of the embossing machine for 30 min in order to bond it to the packed substrate. Then it was cooled down to room temperature without removing the weight. All electrodes were electrically connected to the potentiostats by gold spring-loaded pins (Mill-Max Mfg. Corp., Oyster Bay, NY, USA). Experiments were carried out at room temperature to eliminate any temperature effects.

Calibration of a polymer ORP LOC

Three calibration ORP solutions, including a commercial ORP calibration solution (Sensorex, Garden Grove, CA, USA), pH 4.0 and pH 7.0 buffer solutions of saturated quinhydrone (Sensorex, Garden Grove, CA, USA) was used. If the signal readings for the standard solutions showed them to be out of range (more than ±10 mV from the known potential values), the ORP LOCs made in our laboratory were discarded.

RESULTS AND DISCUSSION

Self-assembled nBP column in a microfluidic chip

The major principle of self-assembly bead packing method is that the aqueous colloidal silica solution can be initially injected into the microchannel by strong attractive capillary forces during the solvent evaporation. It was already pointed out that subsequently solvent evaporation from the already ordered arrays causes a convective particle flux towards the drying bead particles layer from the bulk of the colloidal suspension (Han 2006). So, for the ideal porous structure in a microchannel, the balance between capillary forces and convective particle flux during the solvent evaporation is essential. The fabrication of a self-assembled nBP column described in this study is relatively simple, but it provides a promising method for bio/chemical sensors and

membrane area due to the periodic porous structures. Figure 2(a) shows environmental scanning electron microscope (ESEM) image of crystalline assemblies that were self-assembly packed in a microchannel (50 μm width, 50 μm height, and 5 mm length) filled with 800 nm diameter silica beads. It took 20 min to fully self-assembly crystallize in such a micro-volume channel of 0.0125 mm³. At higher magnification ($\times 30$ k) of the top surface, as shown in Figure 2(b), hexagonal packing structure was clearly observed.

From this result, it could be assumed that colloidal nano particles were well self-assembly packed into a microchannel, meaning that it produced well controlled pore size and/or structure of a self-assembled nBP column. The self-assembled nBP column in this study was used for a nanopore membrane to filter particles in the liquid sample. Accordingly, without any conventional purification or degassing steps for solutions, ORP in raw sample could be directly measured by portable ORP chip sensor system at on-site.

For on-site measurements, all electrode elements must be integrated on a chip. However, in almost all cases the miniaturization was limited to the working electrode while a macroscopic reference electrode is used (Jang *et al.* 2005). The importance of the use of the right reference electrode, which must ideally be reversible and nonpolarizable, is undisputed in potentiometric measurements (Suzuki *et al.* 1999b; East & del Valle 2000; Kim *et al.* 2004; Liao & Chou 2006). The Ag/AgCl reference electrode, which maintains its equilibrium potential as a function of the aqueous chloride ion activity, was used in this study due to its simplicity, stability, and non-toxicity (Jang & Kim 2004). So, a thin-film Ag/AgCl reference electrode has been widely used for electrochemical measurements because it could eliminate the need of an internal-saturated chloride solution. However, the main problem was that the lifetime of a thin-film Ag/AgCl was very short. As mentioned previously, to achieve a high level of accuracy and to

maintain constant chloride-ion activity, it is quite promising to miniaturize a conventional liquid-junction reference electrode containing an internal filling solution. However, one of the most troublesome problems in the development of microelectrochemical sensors has been the unavailability of a miniature reference electrode with a liquid junction (Suzuki *et al.* 1999a). In this study, we similarly made liquid-junction reference electrode by means of nBP column. Nanobeads in a microcontainer with a through-hole for a liquid junction were used to impregnate the KCl electrolyte solution. There was the very low leak rate of the filling electrolyte from a through-hole, which permitted the necessary electrolytic contact with the working solution. The capability of providing a stable potential under service conditions is the most important specification of a reference electrode.

Polymer ORP LOC

For the fabrication of final polymer ORP LOC, adhesive bonding technique for COC substrate could be used to seal the microchannel of ORP LOC using an intermediate layer of SU-8 photoresist, but it caused some problems such as clogging for narrow microfluidic channels. It was reported that it was attributed mainly to the low viscosity of SU-8 photoresist and capillary effects during bonding (Bilenberg *et al.* 2004). Instead, in this study, fusion bonding technique was used for bonding two polymer chips, a microfluidic chip with self-assembled nBP columns and a microelectrode chip. The reasons why we used two chip parts having different T_g were to prevent the pressure-induced destruction of nBP structure and to obtain a softened cover plate (low T_g) that was compressed from the top of the nBP columns with pressure. Figure 3 shows the final microfabricated ORP LOC with self-assembled nBP columns. The potential of an electrochemical cell is

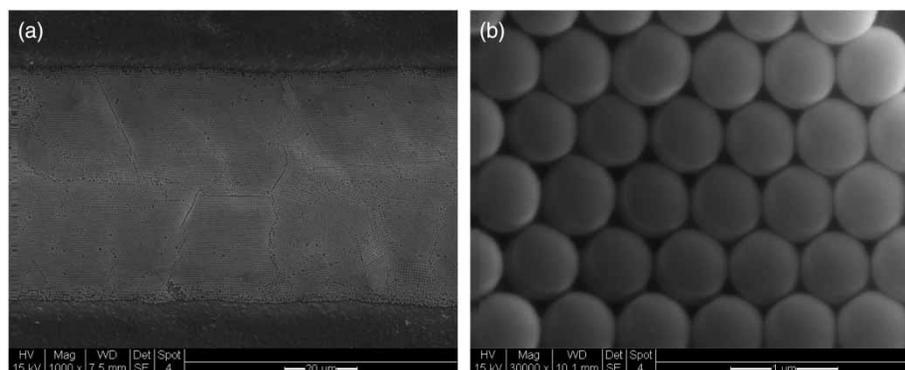


Figure 2 | ESEM images of crystalline assemblies of 800 nm silica beads in a microchannel ((a) $\times 1$ k and (b) $\times 30$ k).

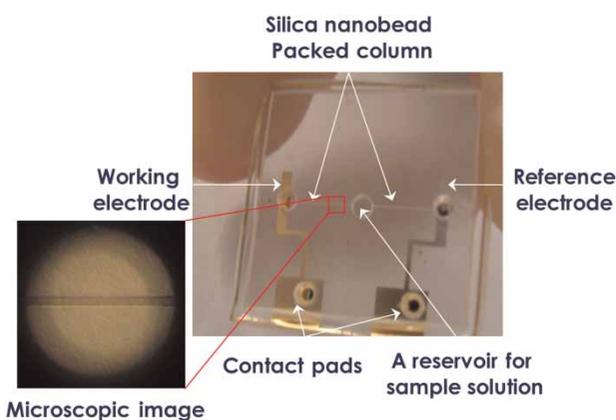


Figure 3 | Microfabricated ORP LOC with self-assembly nBP columns.

established when a working electrode and a reference electrode are both in contact with the sample solution. Thus, the two electrodes were connected intimately to a sampling hole to directly measure the ORP. The size of a chip sensor was 4 cm^2 ($2 \text{ cm} \times 2 \text{ cm}$). The contact pads were covered with evaporated gold (100 nm thick). Compared to the conventional electrode, the chip sensor described in this study required only a tiny volume of sample solution, which is one of the inherent advantages of MEMS technology. Another distinct advantage with using the LOC includes lower cost due to reduced use of reagents and labor, and the mass production ability of MEMS technology. The low unit cost could easily permit use of a single-use disposable chip sensor with high accuracy and reliability to monitor ORP at on-site. Figure 4 shows images taken from video clips of the self-conditioning process recorded at a

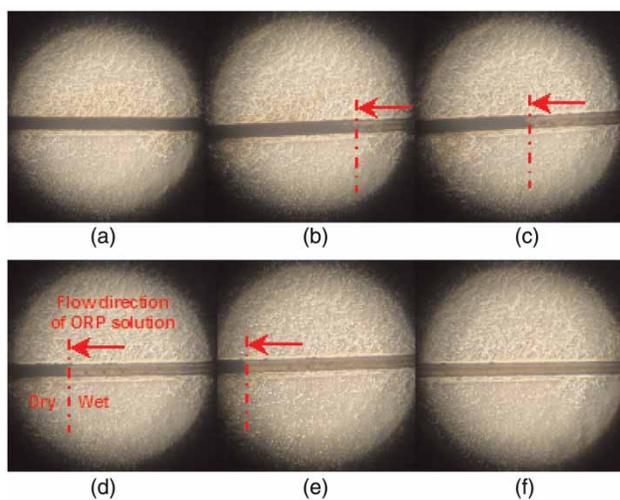


Figure 4 | Images taken from video clips of self-conditioning process, where the ORP standard solution is filling the nBP column by capillary force; (a) $t = 0$, (b) $t = 3 \text{ s}$, (c) $t = 7 \text{ s}$, (d) $t = 11 \text{ s}$, (e) $t = 16 \text{ s}$, (f) $t = 20 \text{ s}$.

position 1 mm from the center reservoir of the ORP LOC. After dehydrated by stepwise transfer into aqueous solutions of ethanol (10% increment, from 10 to 90% ethanol), the self-assembled nBP column was completely filled with ORP standard solution by only the capillary force without air bubbles. It took 20 s to fully fill a self-assembled nBP column with ORP standard solution. In order to calculate the mean pore solution flow velocity, nBP column was repeatedly filled with ORP solution. It can be seen that a mean pore velocity was at 0.045 mm/s.

Measurement of ORP using LOC

In potentiometry the potential difference of ion selective electrodes, such as pH, K^+ , NH_4^+ , NO_2^- and NO_3^- , is generally determined by selectively transferring the ion to be measured from the sample solution to the liquid ion exchange (LIX) membrane. The potential difference developed across the LIX membrane is directly proportional to the logarithm of the ionic concentration in the sample solution. Thus, in order to determine the ionic concentration of an unknown solution, it is only necessary to measure the potential difference in standard solutions, construct a straight-line calibration graph by plotting millivolts versus the logarithm of the ionic concentration, and then read off the unknown ionic concentration from the measured voltage. On the other hand, instead of LIX membrane of ion selective electrodes, a noble metal (platinum or gold) is used as a solid-state membrane in ORP electrodes. The redox potential generated at the solid-state membrane varies as the chemicals in the solution change. When coupled with an Ag/AgCl reference electrode, redox potentials for the pH 7 and pH 4 reference solutions, as recommended by the American Society for Testing and Materials (ASTM), should be 92 and 268 mV, respectively, at 20°C ; 86 and 263 mV, respectively, at 25°C (Jang et al. 2005). As shown in Table 1, the measured ORPs using the three kinds of redox potential solutions were typically slightly

Table 1 | Response time to stabilization and measured redox potential by the ORP LOC with a liquid-junction Ag/AgCl (1 M KCl) reference microelectrode (number of measurements, $n = 10$)

Redox standard or reference solution	Response time to stabilization (s)	Measured redox potential (mV)
ORP calibration solution	5.20 ± 0.63	220.84 ± 1.49
pH 4 ^a	7.30 ± 0.82	261.54 ± 1.39
pH 7 ^b	6.80 ± 0.63	82.690 ± 1.29

^apH 4 quinhydrone reference solution.

^bpH 7 quinhydrone reference solution.

lower than those of the nominal redox potential. However, ASTM suggests that the measured redox potentials should be within 10 mV of the nominal redox potentials for a good redox electrode. Thus, all of the measurements should be deemed acceptable. Additionally, the response times (seconds) to stabilization of the ORP LOC to reach 90% of the final stable reading were only a few seconds.

CONCLUSIONS

The determination of ORP in a variety of matrices, especially, in RO plants, is of great importance since solutions can be graded as oxidizing or reducing based on measurements of ORP value. The rapid development of microdevices for chemical analysis has been greatly promoted by the progress of MEMS techniques, and such microfabricated sensing platforms have attracted much attention of scientists and engineers since their simple measuring principles and portability make them suitable for on-site analysis. Clearly, such a LOC platform has paved the way for new and improved environmental monitoring devices, which apply ORP as one of the online control parameters in various RO plants. We believe this study is a good first step in developing a multi-analyte lab chip sensor for environmental field research where much more development of monitoring technologies should be required.

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