Effect of Treating the Titanium Electrode of the Desalination Performance in Microfluidics System

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Abstract. The commercially applied macro desalination methods such as reverse osmosis, multi-stage flash distillation and multi-effect distillation suffer from several drawbacks such as high power consumption and low separation performance. It is believed that the micro-scaled structures will optimize the mixing efficiency of the micro-flow liquid and lead to higher desalination performance. Large surface-area-to-volume ratio in micro-scale promotes the fluids interaction since the laminar flow properties in the microfluidic device allowing the high-velocity gradients and dominant interfacial effects which is the manipulation of fluid streams [1]. The present work introduces a microfluidics chip for water desalination which fabricated using polydimethylsiloxane soft lithography method. Three layers of polydimethylsiloxane (PDMS) were fabricated using soft lithography method where PDMS liquid mixture was mixed and poured onto the designed wafer and heated to become solid. The solid PDMS was then peeled off from the wafer and hence assembled together with another PDMS by using surface plasma treatment process. The flow rate was set at 90 mL/h and the system was supplied with 9 V of potential difference. Aluminium and titanium were being used as the electrodes which achieved 65% and 15% of salt removal efficiency, respectively. Titanium was further treated by using the etching method and the performance was studied. The desalination efficiency was analyzed and evaluated with the flow rate of 90mL/h using capacitive deionization method. The result revealed that the performance of untreated titanium was better than the treated titanium which achieves 10% improvement in salt removal efficiency. The finding in this work show that the desalination efficiency was relied on the electrode surface property where the oxide layer inhibits the deionization from occurs.

1. Introduction

Desalination is the crucial technology and gaining more attention in order to solve the water scarcity problem by effectively utilize the abundant natural sourcing (sea water). The traditional and commercialized desalination methods such as multi-stage flash distillation (MSF) [2–4], multi-effect distillation (MED) [5–7], electrodialysis (ED) [8–11] and reverse osmosis (RO) [12–16] provide high productivity of potable water however, there are several drawbacks which reduce the overall efficiency such as high power consumption needed for RO due to the fouling problem faced in each membrane technologies and high thermal energy was needed for the distillation based techniques [14,15,17–19]. MSF and MED requires 27.25 and 21.35 kWh/m3 thermal energy respectively in order to vaporize the sea water [6]. According to Pilat (2001), the pumps consumed approximately 2.5
kWh/m³ of power in electrodialysis [20]. According to Reza and Sarim (2012), 4 to 10 kWh of electric energy is required by RO process to produce one cubic meter of fresh water [21].

Microfluidic technology has attracted the attention of researchers in science and engineering field [22–28] such as in the field of fluid flow for flow enhancement and drag reduction. The technology has also grabbed the interest from those who are extensively working in the desalination technology since it was given more opportunities for the researchers to overcome some drawbacks which faced in traditional and commercialized macro technologies. Among the microfluidic desalination technologies, capacitive deionization (CD) is emerging as an ion electrosorption technology which was demonstrated by using capacitive wire-based technology to remove the sodium and chloride ion with a pair of porous carbon coated electrode [29]. Recently, CD technology is widely explored for water desalination application due to its simplicity for the removal of charged ions which include sodium and chloride ions from aqueous salt solution [30–32]. The porous structure charged electrodes were used to attract and trap the ions when the potential difference was created. However, the ion removal efficiency decreased with time due to the effective surface area was reduced by the trapped ions. Hence, the desalination process was unable to be carried out in continuous mode and the overall processing time was increases since the rinsing process was needed to be carried out in batches to detach the trapped ions from the electrodes.

The most common type of electrodes in recent microfluidic desalination was silver/silver chloride and carbon electrode. Silver/silver chloride electrode was being used in electrochemical desalination together with the Nafion membrane based on the Faradaic reaction where the sodium was removed during the oxidation reaction [33]. Based on the research, 90% salt removal was reported with a maximum flow rate of 40 µL/min and initial salt solution concentration of 0.6 M NaCl. A supercapacitor was designed using capacitive deionization method where two porous activated carbon electrodes were placed facing each other and 1 V potential was applied. The sodium and chloride ions from the solution were moved towards the oppositely charged electrical double layer. It was reported that > 50% of charge efficiency was needed by the porous carbon electrode in order to achieve 70% desalination in this CD [34].

Aluminium is highly favourable and common to be used in various fields such as food and construction industries due to its highly against to weathering factor and fully resistant properties to rust. The oxidation property of aluminium causes it reacts spontaneously with water and air to become aluminium oxide which forms its corrosion protective layer. Despite its very high electrical conductivity ability, its short lifespan in the electrolyte that contains water make it seldom to be used as an electrode [35].

Titanium is normally to be used in electric power plant, naval ships, missiles, desalination plants aircraft and heat exchanger since it almost completely unaffected by the marine environment which showed a remarkable corrosion resistivity towards salt water [36–40]. Due to its corrosion resistivity property, titanium has been widely used in desalination fields such as magnetized titanium dioxide for sea water purification, titanium tubes in multi-stage flash (MSF) desalination and titanium oxide nanoparticles for enhancing nanofiltration desalination [4,36,41].

Despite the promising nature properties of aluminium and titanium as electrodes in several fields, there is still limited study in investigate the performance of these electrodes in microfluidic desalination. In this present study, the effect of both aluminium and titanium electrode on the dilute conductivity value was being studied in order to determine the salt removal efficiency by the microfluidic desalination chip. The surface morphology of both electrodes was also being observed under scanning electron microscope (SEM) while the weight percentage of the elements on the electrode surface was obtained from energy dispersive X-ray spectroscopy (EDX).
2. Material and methods

2.1. Chemical
Sodium chloride (NaCl) powder, ethylene glycol, ammonium fluoride, aluminium foil and 200 µm titanium sheets were purchased from Sigma-Aldrich (St. Louis, Missouri, USA), polydimethylsiloxane (PDMS) and the polymer curing agent from Dow Corning (Michigan, USA) and SU-8 (GM1060 for layers between 5 and 27 µm, GM1070 for layers between 15 and 200 µm) from Gersteltec (Pully, Switzerland).

2.2. Feed solution preparation
35 g/mL of NaCl solution which equivalent to 0.6 M NaCl was prepared by dilution method.

2.3. Electrode etching
The titanium surface was treated by anodization etching process with the presence of applied potential \[42,43\]. The 100 µm titanium sheets were cut with desired shape and pores size using cutting plotter (Graphtec, CE600060, USA). 90% by volume ethylene glycol and 10% by volume distilled water which equal to 180 mL and 20 mL respectively were measured and well mixed for 2 hours until homogeneous as etchant by using magnetic stirrer. 1 g of ammonium fluoride was measured and added into the mixture and stir until homogeneous. The ready cut titanium sheets were immersed into the well-mixed etchant and connected to the DC power supply with 60.0 V and 0.01 A for 3 hours. The DC power was switched off and the titanium sheets were removed from the etchant after 3 hours etching process. The titanium sheet was brought into the furnace for heating process at the rate of 5 °C /min until 500 °C and maintained the heat for 2 hours. The titanium sheets were ready to be used as electrodes after cooled to room temperature.

2.4. Desalination chip fabrication
Figure 1 showed the details of microfluidic desalination chip fabrication steps which conducted in the PDMS based microfluidic model system. 5 mL of SU-8 was pipetted onto a clean wafer and spin coat at 900 rpm for 1 minute in order to obtain the desired thickness of 100 µm. The wafer was pre-baked at 65 °C for 15 minutes and increase to 95 °C for 2 hours. After pre-bake, the wafer was exposed under micro-pattern generator (µPG) for the desired microchannel design. The microchannel design was generated by using AutoCAD software in order to obtain an accurate scale. Then, the wafer was post-bake at 65 °C for 15 minutes and increase to 95 °C for 40 minutes. The steps were repeated for the second layer coating and exposed. The PDMS was mixed with the polymer curing agent at the ratio of 10:1 using a planetary centrifugal mixer (model: Thinky, USA) and was poured onto the wafer in a petri dish. The PDMS was being degassed in a desiccator for 1 hour to remove all the air bubbles trapped inside and then heated for 2 hours in the oven.

After heating, the first part of PDMS was cut using a scalpel and peeled off from the wafer with tweezers. The electrode was brought to be placed onto the PDMS. The first part of PDMS and the second part of PDMS were brought to the plasma cleaner for surface treatment. Lastly, both treated PDMS were pasted together and pressed slightly. The steps were repeated to assemble the PDMS with the third part of PDMS. The desalination chip was fabricated by combining three layers of PDMS and two electrodes.
2.5. Experimental set up

Figure 3 showed the experimental set up where negative pressure-driven flow with 90 mL/h was generated by microfluidic flow sensor (Elveflow OB1 MK3, France) and the constant voltage was applied by a programmable DC power supply (Rigol Technologies Inc., USA). The desalination was conducted for 1 hour using both aluminium and titanium electrodes. The diluate outlet solution was collected and the conductivity was measured using conductivity meter (Eutech PCD650, SG).
Figure 3. Schematic diagram of experimental setup which consisted of (a) flow sensor, (b) computer, (c) feed reservoir, (d) pressure and vacuum controller, (e) desalination chip, (f) beaker for concentrated solution at anode side, (g) beaker for diluate and (h) beaker for concentrated solution at cathode side.

3. Result and discussion

3.1. Single factor analysis

Single factor analysis was conducted for aluminium electrode microfluidic desalination chip. Different voltage was manipulated with constant feed flow rate 90mL/h. Figure 4 shows the result of conductivity value at a different voltage with constant flow rate at 90 mL/h. The diluate conductivity decreased from 50.19 to 24.19 mS as the voltage increased from 1 V to 9 V. The voltage allowed the ions to be attracted to respective electrodes and the concentrated solution was removed from the substream. The conductivity slightly increased from 24.19 to 28.11 mS when the voltage increased from 9 V to 15 V. The conductivity did not have much change due to the limitation on effective surface area and hence limiting the charge efficiency of the electrode [44].

Figure 4. Conductivity of diluate as a function of different voltage.
3.2. Desalination efficiency

The first part of the experiment was conducted with two different electrodes which are aluminium and titanium. The desalination efficiency for both aluminium and titanium electrode microfluidic desalination chips were obtained by measure the conductivity at the diluate outlet solution. The result versus time was plotted as shown in Figure 5. The trend and performance of salt removal efficiency by the microfluidic desalination chips were observed for 1 hour. Both aluminium and titanium desalination chips took approximately 20 minutes to achieve the maximum salt removal efficiency of 65% and 15%, respectively. Since it was a continuous system, it takes time for more sodium and chloride ions to move towards the respective electrodes. Some of the sodium and chloride ions will retain on the electrode surface while some will be channelled out through the side channel. The titanium electrode desalination chip maintains almost constant salt removal efficiency since its surface slowly forms a thin film of oxide layer in salt water [36–40]. Aluminium electrode desalination chip achieved higher salt removal efficiency as compared to titanium however, it encountered a rapid drop in salt removal efficiency after 20 minutes due to the oxidation of its surface in salt water.

The stable performance of titanium was gaining attention and was further treated by using the etching process in order to increase the effective surface area of the electrode. Based on Figure 6, the non-treated titanium gives 15% salt removal efficiency which was three-fold higher than the treated titanium which only gives 5% efficiency. The etching process produced titanium dioxide where an oxide layer was formed on the electrode surface which increases the electrode resistivity [45]. The treated aluminium shows a very low electrical conductivity as well as the potential of attracting sodium and chloride ions.

![Figure 5. Salt removal efficiency for different electrodes.](image_url1)

![Figure 6. Salt removal efficiency for non-treated and treated titanium.](image_url2)
3.3. SEM-EDX analysis
The SEM analysis was performed to observe the surface morphology of both aluminium and titanium electrodes. The surface morphology of both electrodes was observed before and after the desalination as shown in Figure 7 while the EDX spectra was showed in Figure 8. Before the desalination experiment, the aluminium showed a very smooth surface as compared to the SEM image after the experiment where a rough surface was observed since oxidation happened and the oxide layer was formed. The oxidation of aluminium electrode after experiment was also observed from the EDX spectra where 43.347% oxygen was noticed as compared to 1.853% oxygen before experiment. The surface morphology of titanium before and after the desalination experiment was shown in Figure 7 (c) and (d). A smooth surface was observed from the titanium before experiment while a rough and coarse surface was observed after desalination since anodization happened at the electrode during electrolysis reaction. During anodization, an oxide layer was formed at the titanium surface. The oxide layer was further confirmed by EDX spectra where the percentage of oxygen was 44.514% after desalination as compared to the 11.146% of oxygen which was before desalination. Table 1 showed the weight percentage of each element for different electrode

Figure 7. Surface morphology of (a) aluminium, (b) aluminium at 30 minutes, (c) non-treated titanium and (d) non-treated titanium at 30 minutes.
Figure 8. EDX spectra of (a) aluminium, (b) aluminium at 30 minutes, (c) non-treated titanium and (d) non-treated titanium at 30 minutes.
Table 1. Weight percentage of each element for different electrode

| Element          | Weight percentage of each element (%) | A    | B    | C    | D    |
|------------------|---------------------------------------|------|------|------|------|
| Titanium         |                                       | -    | -    | 88.854 | 49.133 |
| Oxygen           |                                       | 1.853 | 43.347 | 11.146 | 44.514 |
| Carbon           |                                       | 15.799 | 12.343 | -    | 4.607 |
| Silicon          |                                       | 0.455 | 1.771 | -    | 0.725 |
| Chlorine         |                                       | -    | -    | -    | 0.586 |
| Iron             |                                       | -    | -    | -    | 0.436 |
| Aluminium        |                                       | 81.893 | 41.944 | -    | -    |
| Sodium           |                                       | -    | -    | -    | -    |
| Potassium        |                                       | -    | -    | -    | -    |

A – Aluminium
B – Aluminium at 30 minutes
C – Non-treated titanium
D – Non-treated titanium at 30 minutes

4. Conclusion

In this work, the capacitive deionization microfluidic desalination was conducted by using aluminium and titanium as the electrode. The operating condition was set at 90mL/h flow rate with 9 V potential difference. The microfluidic desalination efficiency via capacitive deionization method was related to the surface oxidizing property of both of the titanium and aluminium electrodes. From the first part of the experiment, it was noticed that the aluminium was high potential to be used as the electrode for desalination due to its high conductivity behavior however the oxidizing property causes the desalination efficiency dropped rapidly after 20 minutes. The titanium showed a relatively stable performance after 20 minutes as compared to aluminium. The etching process increases the titanium oxide layer which gave lower salt removal efficiency as compared to the non-treated titanium. Based on the results, the aluminium showed 65% salt removal efficiency which was a better performance as compared to the titanium which only 15%.

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