Energy 51 (2013) 413–421

Contents lists available at SciVerse ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Energy harvesting from salinity gradient by reverse electrodialysis with anodic alumina nanopores

Juwan Kim [a], Sung Jin Kim [a], Dong-Kwon Kim [b,*]

[a] School of Mechanical, Aerospace, and Systems Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, South Korea
[b] Department of Mechanical Engineering, Ajou University, Suwon 443-749, South Korea

ARTICLE INFO

Article history:
Received 28 September 2012
Received in revised form
27 December 2012
Accepted 5 January 2013
Available online 8 February 2013

Keywords:
Salinity gradient
Reverse elctrodialysis
Nanopore array

ABSTRACT

Power generation by reverse electrodialysis from anodic alumina nanopores is experimentally investigated by placing an alumina nanopore array with a nominal pore radius of 10 nm between two sodium chloride solutions with various combinations of concentrations. Both bare and silica-coated alumina nanopore arrays are used in the present study. The current–potential characteristics are measured for various electrolyte concentration levels, and the transference number and the electrical conductance of the nanopore arrays are obtained from these characteristics. The transference numbers of the bare and silica-coated alumina nanopore arrays are 0.30 and 0.72, respectively; these values are nearly independent of the concentration of the sodium chloride solutions when it is less than 200 mM. Therefore, the bare and silica-coated alumina arrays can be used as anion selective and cation selective membranes, respectively, for micro batteries and micro power generators. Finally, power generation by reverse electrodialysis using an alumina nanopore array is presented. The highest power generation measured is 542 nW, which is several orders of magnitude higher than those measured in previous studies based on nanofluidic channels or nanopores.

1. Introduction

Renewable energy sources have received significant attention due to limited fossil fuel sources and global warming [1,2]. In particular, the oceans offer a number of energy flows that could be tapped as sources of energy [3]. They include salinity gradient energy, ocean thermal energy, and waves and tidal power. The salinity gradient energy is available from the difference in the salt concentration between seawater and fresh water, and is represented by the osmotic pressure difference between fresh water and salt water [4]. Experiments indicate that the equivalent pressure head between 0.5 M seawater and fresh water is about 24 atm. This has the potential to generate sustainable power by extracting the Gibbs free energy during the mixing of fresh water and seawater [5]. According to Spiegler [6], the mixing of 1 m^3 of fresh water per second with a large volume of seawater can generate 2.25 MW of power. Theoretically, the total river flow of the world is 1.08×10^6 m^3/s, which can produce 2.43×10^{12} W of power [7,8].

It is possible that current techniques available for desalination could generate electric power from salinity gradients when operated in the reversed mode [9,10]. Several techniques for energy conversion of the salinity gradient have been previously proposed: pressure-retarded osmosis [11], vapor-pressure difference utilization [12,13], energy conversion in chemomechanical engines [14], and reverse electrodialysis [15]. Among these, the pressure-retarded osmosis uses induced fluid flow when two solutions of different concentrations are placed in contact through a barrier that is permeable to the solvent, but impermeable to solutes (ions) [16–18]. In contrast, the reverse electrodialysis uses induced ion flow when the ions in seawater with fresh water are mixed through ion-selective membranes. Since the proposal of reverse electrodialysis by Pattle [15] in 1954, many investigators have concentrated on reverse electrodialysis with polymer ion-exchange membranes [19–24]. Recently, Veerman et al. [25] reported a promising power density of 0.093 mW/cm^2, which is higher than the power densities from polymer ion-exchange membranes reported so far.

In recent years, solid-state nanofluidic channels or nanopores have been proposed to serve as an alternative of polymer ion-selective membranes. When nanopores are filled with an aqueous solution, surface ionization, ion adsorption, and ion dissolution charge the surface of the nanopores [26]. These surface charges draw counter-ions toward the surface and repel co-ions away; consequently, the counter-ions are preferentially transported over the co-ions in the charged nanopores. Under a concentration

---

* Corresponding author. Tel.: +82 31 219 3660; fax: +82 31 219 1611.
E-mail address: dkim@ajou.ac.kr (D.-K. Kim).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.01.019

gradient, the ions diffuse spontaneously across the nanopores, and a portion of the Gibbs free energy of mixing can be harvested continuously from the nanopores by means of the net diffusion current (Fig. 1) [27]. Kim et al. [28] have shown that silica nanochannels fabricated by a standard semiconductor manufacturing processes can harvest energy by reverse electrodialysis. They experimentally investigated the power generation from nanochannels with heights of 4, 26, and 80 nm placed between two potassium chloride solutions with various combinations of concentrations. The highest power density measured was 2.89 pW. Guo et al. [27] conducted a proof-of-concept experiment with single ion-selective, track-etched nanopores embedded in polyimide membranes. They achieved 26 pW of power output with a single nanopore device. Solid-state nanofluidic channels or nanopores are suitable for use in micro power generators and micro batteries where they promise more reliable operation, because they do not generally shrink and swell in response to their environment [29]. However, the power generation reported in previous studies is not sufficient to drive micro systems such as low-power circuitry for wireless systems and biomedical implant devices [30,31]. It is because the conventional lithographic processes and track-etching processes used in the previous studies have difficulty forming ion-selective structures with high pore density in large-scale.

This difficulty can be overcome by using anodic porous alumina, which is prepared by the anodic oxidation of aluminum in an acidic electrolyte. Anodic porous alumina has a packed array of columnar hexagonal cells with central, cylindrical, uniformly sized nanopores ranging from 4 to 200 nm in diameter [32]. Anodic porous alumina is a promising material for large-scale, ion-selective structures because nanopores can form simultaneously in electrochemical processes. Anodic porous alumina also has high pore density (10^{11} pores/cm^2) [33], and its nanopore dimensions can be controlled by the composition and temperature of the electrolyte solution, and by both duration and the applied voltage of the electrochemical process [34]. However, energy harvesting by reverse electrodialysis with anodic alumina nanopores has not yet been experimentally demonstrated. Therefore, we find it desirable to investigate the potential of anodic alumina nanopores for the use in reverse electrodialysis systems.

In this study, power generation from anodic alumina nanopores is experimentally investigated by placing an alumina nanopore array between two sodium chloride solutions with various combinations of concentrations. Both bare and silica-coated anodic alumina nanopores are used in the present study. The current–potential characteristics are measured, and the transference number and the electrical conductance of the alumina nanopore array are obtained from these characteristics. Finally, power generation by reverse electrodialysis with anodic alumina nanopores is presented.

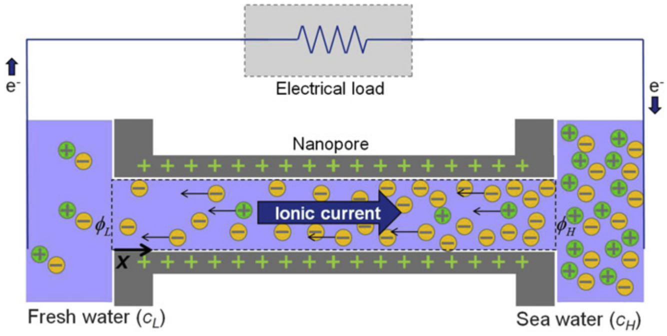

Fig. 1. Schematic illustration of the reverse electrodialysis in a nanopore.

2. Materials and methods

We constructed a reverse-electrodialytic cell as shown in Fig. 2, which consists of an alumina nanopore array and microchannel plates. We used an alumina nanopore array (Anodisc 47, Whatman Inc.) with diameter of 47 mm and thickness of 60 μm for the present study. Fig. 3 shows the top view and cross-sectional view of the SEM pictures of the alumina nanopore array. The nominal pore radius is 10 nm and the nominal pore density is 1.18×10^{11} cm^{-2}. Concentrated and dilute solutions flow through polycarbonate microchannel plates, which sandwich the alumina nanopore array. The thickness of the microchannel plates is 1 mm. Thin channels minimize the electrical resistance of the dilute solution in the microchannels. The cross-sectional area of the microchannels is 82 mm^2. Two Ag/AgCl electrodes are located at both ends of the cell. The electrodes are made by coating a silver mesh (05-1806-02, 40935, Nilaco Co.) with Ag/AgCl ink for reference electrode (011464, ALS Co.).

Concentrated and diluted NaCl solutions are supplied to the cell to establish a salinity gradient. The concentration of the dilute solution (c_L) increases from 0.1 mM to 10 mM while that of the concentrated solution (c_H) increases from 1 mM to 100 mM. The concentration ratio between the two solutions (c_L/c_H) is fixed at 10. The pH of the solutions was 5.4 ± 0.2. The syringe pump (KDS220, KD Scientific Inc.) is used as a pumping device to provide a constant flow rate. The source meter (Keithley 6430) recorded the current outputs, I_{cell}, from the cell for various applied voltages, E_{app}. We conducted each experiment six times.

In addition to the experiment on bare alumina nanopores, we also coated the silica layer on the alumina nanopores, as described in Kovtyukhova et al. [36]. In the first step, $SiCl_4$ molecules are absorbed on the hydrated surface of the alumina nanopores. Subsequent washing with CCl_4 removes the unbound adsorbate molecules from the pores. In the second step, the adsorbed $SiCl_4$ is

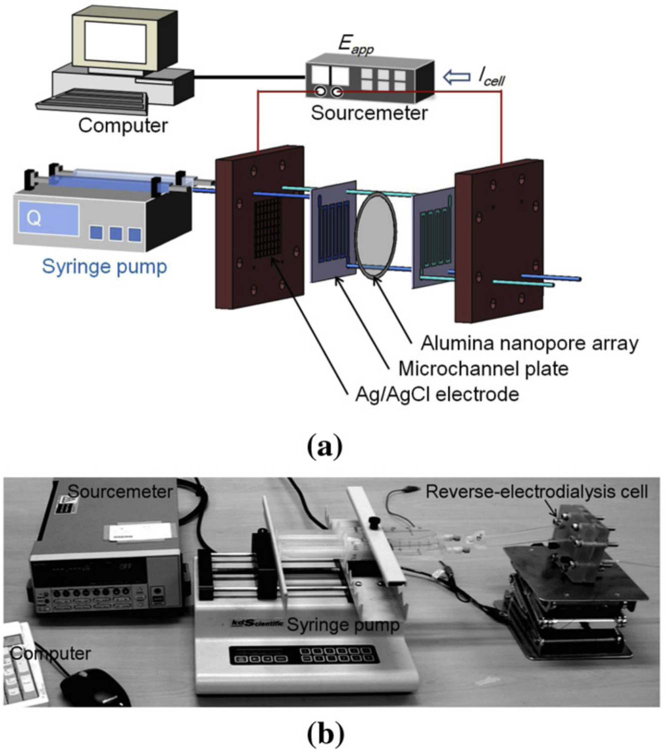

Fig. 2. Experimental setup for energy harvesting from a reverse electrodialysis cell (a) schematic diagram of the experimental setup (b) photograph of the experimental setup.