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Numerical study on energy harvesting from concentration gradient by reverse electrodialysis in anodic alumina nanopores

Byeong Dong Kang, Hyun Jung Kim, Moon Gu Lee, Dong-Kwon Kim*

Department of Mechanical Engineering, Ajou University, Suwon 443-749, South Korea

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ABSTRACT

Energy harvesting from a concentration gradient by reverse electrodialysis in anodic alumina nanopores was numerically investigated. Power generation from the nanopores when they are placed between two reservoirs containing potassium chloride solutions with different concentrations was examined. The current–potential characteristics of the nanopores were calculated by solving the strongly coupled Poisson equation, the Nernst–Planck equation, and the Navier–Stokes equations. Alumina nanopore arrays were also investigated experimentally to obtain the proper values of the surface charge density for the numerical model. The effects of various engineering parameters, such as the pore length, pore radius, and concentration, on the power generation were investigated on the basis of the developed numerical model. Finally, it was shown that a power output density of 9.9 W/m^2 can be achieved using the alumina nanopores. This indicates that the alumina nanopores have the potential to be used as ion-selective membranes for microbatteries and micro power generators.

1. Introduction

Renewable energy sources, including solar, wind, biomass, geothermal, ocean thermal, wave, tidal, and hydro energies have received significant attention owing to the limited availability of and environmental issues associated with fossil fuels [1–4]. Salinity gradient energy, which is available from the difference in salt concentration between seawater and freshwater, is one such source of renewable energy. Sustainable power can potentially be generated by extracting the Gibbs free energy during the mixing of freshwater and seawater [5,6]. Theoretically, mixing 1 m^3 of freshwater with a large volume of seawater can generate 2.3 MJ of energy [7]. Therefore, as shown in Table 1 [8], the power density of salinity gradient energy is small compared to that of other electrical energy storage systems. However, the total volume flow rate of water in rivers worldwide is 1.1 $\times$ 10^6 m^3/s, and this flow could possibly generate 2.4 TW of power [9], which is comparable to the total electricity currently produced worldwide [10,11]. The techniques currently available for desalination can generate power from ion concentration gradients when operating in the reversed mode [12]. These techniques include pressure-retarded osmosis [13], vapor-pressure difference utilization [14–16], energy conversion in chemomechanical engines [17,18], and reverse electrodialysis [19]. Among these, reverse electrodialysis can harness the concentration gradient energy through ion-selective membranes. Since Pattle proposed the concept of reverse electrodialysis in 1954 [19], many researchers have focused on experimental studies of reverse electrodialysis using polymer ion-exchange membranes [20–25]. Recently, Vermaas et al. [9] reported a promising power density of 2.2 W/m^2, which is higher than the power densities obtained using polymer ion-exchange membranes to date. In addition, reverse electrodialysis can capture energy from waste heat by using salt solutions that could be continuously regenerated using waste heat [26–28]. Reverse electrodialysis can also be used to generate energy from organic matter in wastewater and biomass by placing ion-selective membranes between microbial fuel cell electrodes [29].

In recent years, solid-state nanofluidic channels, i.e., nanopores, have been demonstrated experimentally to serve as ion-selective membranes for small reverse electrodialysis systems. As shown in Fig. 1, when nanopores are filled with an aqueous (polar) solution, their surfaces acquire surface electric charges by ionization, ion adsorption, and ion dissolution [30]. These surface charges influence the concentration of nearby ions in the solution of the nanopores. Ions with a charge opposite to that of the surface (counterions) are attracted toward the surface, whereas ions of like charge

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

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Table 1
Specific energies and energy densities of electrical energy storage systems.

Systems	Specific energy (Wh/kg)	Energy density (Wh/L)
Salinity gradient power plant	0.6	0.6
Flow battery		
VRB	10–30	16–33
ZnBr	30–50	30–60
Battery		
Lead-acid	30–50	50–80
NiCd	50–75	60–150
NiS	150–240	150–250
ZEBRA	100–120	150–180
Li-ion	75–200	200–500
Fuel cell	800–10,000	500–3000
Metal-air battery	150–3000	500–10,000
Capacitor	0.05–5	2–10
Pumped hydroelectric storage	0.5–1.5	0.5–1.5
Compressed air energy storage	30–60	3–6
Solar fuels	800–100,000	500–10,000
Superconducting magnetic energy storage	0.5–5	0.2–2.5
Flywheel	10–30	20–80

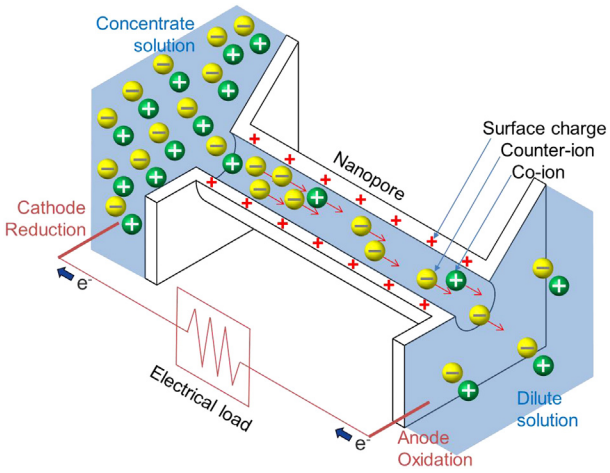

Fig. 1. Schematic of reverse electrodialysis in an ion-selective nanopore.

(co-ions) are repelled from the surface. As a result, the counter-ions are preferentially transported over the co-ions in the charged nanopores. Under a concentration 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 using the net diffusion current. Kim and Duan et al. [31] showed that silica nanochannels fabricated by standard semiconductor manufacturing processes can harvest energy by reverse electrodialysis. They achieved a power output of 2.89 pW using 10 nanochannels made by reactive ion etching. They obtained a power density of 0.77 mW/cm^2, which is nearly an order of magnitude higher than that obtained using a conventional ion-exchange membrane. Guo et al. [32] experimentally investigated single-ion-selective, track-etched nanopores embedded in polyimide membranes. They achieved a power output of 26 pW using a single nanopore device. They showed that if parallel nanopores with a pore density of 10^8 to 10^{10} nanopores/cm^2 are assumed, the power density can approach a value between 2 and 260 mW/cm^2. However, despite the improvement in the power density of nanofluidic channels and nanopores, the power generation reported in previous studies is not sufficient to drive microsystems such as low-power circuitry for wireless systems and biomedical implant devices [33,34]. This is because the conventional lithographic and track-etching processes used in previous studies have difficulty forming ion-selective structures with a high pore density on a large scale.

This difficulty can be overcome using an alumina nanopore array, which can be fabricated by anodic oxidation of aluminum in an acidic electrolyte [35]. It has columnar hexagonal cells with central, cylindrical, uniformly sized nanopores ranging from 4 to 200 nm in diameter [36]. The alumina nanopore array also has a high pore density (10^{11} pores/cm^2), which can be controlled according to the composition and temperature of the electrolyte solution, as well as the duration and applied voltage of the electrochemical process [37]. Recently, power generation by reverse electrodialysis using an alumina nanopore array was presented [38], and the highest measured power generated was 542 nW, which is several orders of magnitude higher than those measured in previous studies based on nanofluidic channels or nanopores.

However, to the best of the authors' knowledge, power generation from reverse electrodialysis in anodic alumina nanopores has yet to be studied thoroughly, although there have been several numerical studies focusing on reverse electrodialysis in solid-state nanofluidic channels and nanopores. Fair and Osterle analyzed the transport phenomena in long nanopores in reverse electrodialysis for the first time [39]. They obtained a one-dimensional model by integrating the Poisson–Nernst–Planck equations in the radial direction. They reported the operating characteristics of nanopores for various nanopore sizes, surface charge densities, and solutes. Kim suggested a two-dimensional model for slit nanochannels [40]. In this study, the Poisson–Nernst–Planck equations were solved numerically, and the effects of several engineering parameters on the power density were examined. Recently, Yeh et al. also proposed a two-dimensional model for conical nanopores and investigated the energy conversion efficiency for various concentration gradients, surface charge densities, and diffusion coefficients [41]. However, the models suggested in these previous studies cannot accurately predict the power generation capability of alumina nanopores in conjunction with reverse electrodialysis. This is because in the previous models, the surface charge density is assumed to be constant and independent of the concentration. However, in reality, the surface charge density is not constant, and there is experimental evidence indicating that the surface charge density of alumina increases as the concentration increases [42,43]. Therefore, it is highly desirable to develop an appropriate and accurate model based on realistic values of the surface charge density for analyzing reverse electrodialysis in alumina nanopores. To establish guidelines for the design of alumina nanopores, it is necessary to investigate the effects of various engineering parameters, such as the pore length, pore radius, and electrolyte concentration, on the power output density.

In this article, ion-selective alumina nanopores are numerically studied to investigate the power generation capability in conjunction with reverse electrodialysis. The generation of power from the nanopores when they are placed between two reservoirs containing potassium chloride solutions with different concentrations is investigated. The current–potential characteristics of the nanopores are calculated by solving the strongly coupled Poisson equation, Nernst–Planck equation, and Navier–Stokes equations. The alumina nanopore array is also investigated experimentally to obtain the proper values of the surface charge density for the numerical model. Finally, the effects of various engineering parameters on the power generation are investigated.

2. Numerical analysis

Let us consider a charged nanopore with length L and radius R connecting two identical reservoirs on either side, as shown in Fig. 2(a). The nanopore has a surface charge density σ. The left and