Available online at www.sciencedirect.com
ScienceDirect
Electrochemistry Communications 8 (2006) 1796–1800
electrochemistry communications
www.elsevier.com/locate/elecom

Theoretical study on the efficiency of nanofluidic batteries

Hirofumi Daiguji *, Yukiko Oka, Takuma Adachi, Katsuhiro Shirono

Institute of Environmental Studies, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa-shi, Chiba 277-8563, Japan

Received 10 July 2006; accepted 2 August 2006
Available online 7 September 2006

Abstract

A pressure-gradient-driven flow inside nanofluidic channels that have a surface charge can be used to generate streaming current and potential. This process forms the basis for electro-chemo-mechanical energy conversion in nanofluidic batteries. Here, the efficiency of such batteries was calculated using continuum dynamics. Results showed that (a) the bulk ion concentration to yield maximum efficiency depends on the channel height and surface charge density and (b) the efficiency can be expressed by two-dimensionless parameters when the flow is fully developed and the channel is a unipolar solution of counter ions.

Keywords: Nanofluidic battery; Electrical double layer; Streaming current; Efficiency

1. Introduction

When an external pressure gradient generates flow in an aqueous solution in a channel that has a surface charge on its walls, a streaming current (an electrical current generated by a pressure-driven liquid flow) and a potential are produced [1]. This phenomenon depends critically on the surface charge. In membrane science, the streaming potential is measured to determine the ζ-potential of a surface, which is an important and reliable indicator of the surface charge, and its knowledge is essential for design and operation of membrane processes [2–4].

Recently, Yang et al. [5] proposed the concept of a battery that uses streaming current and streaming potential, and reported results of a theoretical model and related experiments. They used a porous glass filter, 20 mm in diameter with pore sizes from 10 to 16 μm, and obtained a current of 1–2 μA from a 30 cm hydrostatic pressure drop. The maximum efficiency was estimated to be about 0.01%. van der Heyden et al. [6] measured the streaming current in individual rectangular silica nanochannels down to 70 nm in height. Their experimental results showed that the streaming current is proportional to the pressure gradient and that changing the sign of the surface charge reverses the streaming current. They also found that the maximum energy conversion efficiency is obtained in the regime of overlap of the electrical double layers. Previously, we [7] theoretically investigated the ion transport inside a nanochannel of 30 nm high and 5 μm long containing a surface charge on its wall (the surface charge density $\sigma = -1$ and $-5\ \mathrm{mC/m^2}$) and calculated the efficiency of such a battery as a function of the ion concentration. Because the streaming current in this battery is generated within the electrical double layer [8–10], the channel height should be reduced to the order of the Debye length, λ_D, which characterizes the size of the layer, to improve the efficiency of the battery. However, the calculated maximum efficiency of the model battery was only about 4% at $\sigma = -5\ \mathrm{mC/m^2}$. The objective of this study was to clarify theoretically the effect of channel height, surface charge density, ion concentration and physical properties of solution on the battery efficiency and to design a high performance nanofluidic battery.

* Corresponding author. Tel.: +81 4 7136 4658; fax: +81 4 7136 4659.
E-mail address: daiguji@k.u-tokyo.ac.jp (H. Daiguji).

1388-2481/$ - see front matter
doi:10.1016/j.elecom.2006.08.003

2. Governing equations

Fig. 1a shows the schematic of a nanofluidic battery consisting of a nanochannel with reservoirs on either side. In the analysis of ion transport in nanofluidic channels, the governing equations were the Poisson equation, the drift–diffusion equation [11,12] (also called the Nernst–Planck equations [13,14]), and the Navier–Stokes equations [7]

$$\nabla^2\phi = -\frac{1}{\varepsilon_0\varepsilon}\sum_{\mathrm{a}} z_{\mathrm{a}} e n_{\mathrm{a}}, \tag{1}$$

$$\nabla\cdot(n_{\mathrm{a}}\boldsymbol{u} + \boldsymbol{J}_{\mathrm{a}}) = 0, \tag{2}$$

$$\nabla\cdot\boldsymbol{u} = 0, \tag{3}$$

$$\boldsymbol{u}\cdot\nabla\boldsymbol{u} = \frac{1}{\rho}\left\{-\nabla p + \mu\nabla^2\boldsymbol{u} - \left(\sum_{\mathrm{a}} z_{\mathrm{a}} e n_{\mathrm{a}}\right)\nabla\phi\right\}, \tag{4}$$

where ϕ is the electrostatic potential, n_{a} is the concentration of ion species a, p is pressure, and $\boldsymbol{u}$ is a velocity vector. $\boldsymbol{J}_{\mathrm{a}}$ is the particle flux of ion species a due to a concentration gradient and electric potential gradient, and is expressed as $\boldsymbol{J}_{\mathrm{a}} = -D_{\mathrm{a}}\left(\nabla n_{\mathrm{a}} + \frac{z_{\mathrm{a}} e n_{\mathrm{a}}}{kT}\nabla\phi\right)$, where D_{a} and z_{a} are the diffusivity and valence of ion species a, k is the Boltzmann constant, T is the temperature. ε_0 is the permittivity of vacuum, ε is the dielectric constant of the medium, ρ is the fluid density, and μ is the fluid viscosity. The calculation region was inside a channel and reservoirs, i.e. the region enclosed by the dotted line in Fig. 1a. The boundary conditions at the channel walls, the reservoir walls, and the ends of the reservoirs are as follows:

$$\nabla_\perp\phi = -\frac{\sigma}{\varepsilon_0\varepsilon}, \quad J_{\mathrm{a}\perp} = 0,$$

$$\nabla_\perp p = \mu\nabla_\perp^2 u - \left(\sum_{\mathrm{a}} z_{\mathrm{a}} e n_{\mathrm{a}}\right)\nabla_\perp\phi, \quad \boldsymbol{u} = 0 \text{ (at channel walls)}, \tag{5}$$

$$\nabla_\perp\phi = 0, \quad \nabla_\perp n_{\mathrm{a}} = 0,$$

$$\nabla_\perp p = 0, \quad \boldsymbol{u} = 0 \text{ (at reservoir walls)}, \tag{6}$$

$$\phi = \phi_{\mathrm{bulk}} \quad \text{or} \quad \nabla_\perp\phi = 0, \quad n_{\mathrm{a}} = n_{\mathrm{bulk}},$$

$$p = p_{\mathrm{bulk}}, \quad \nabla_\perp u = 0 \text{ (at ends of reservoirs)}, \tag{7}$$

where $\perp$ and bulk denote the wall-normal component and bulk value, respectively, and σ is the surface charge density. Eqs. (1)–(4) were solved under boundary conditions (5)–(7) using a finite difference algorithm, yielding ϕ, n_{a}, p and $\boldsymbol{u}$ in the battery. If these parameters are known, then the current density of ion species a can be obtained using the following equation:

$$\boldsymbol{i}_{\mathrm{a}} = \boldsymbol{i}_{\mathrm{a,adv}} + \boldsymbol{i}_{\mathrm{a,dif}} = z_{\mathrm{a}} e(n_{\mathrm{a}}\boldsymbol{u} + \boldsymbol{J}_{\mathrm{a}}). \tag{8}$$

The input power P_{in}, the output power P_{out}, and the efficiency η of the battery were given by the following equations:

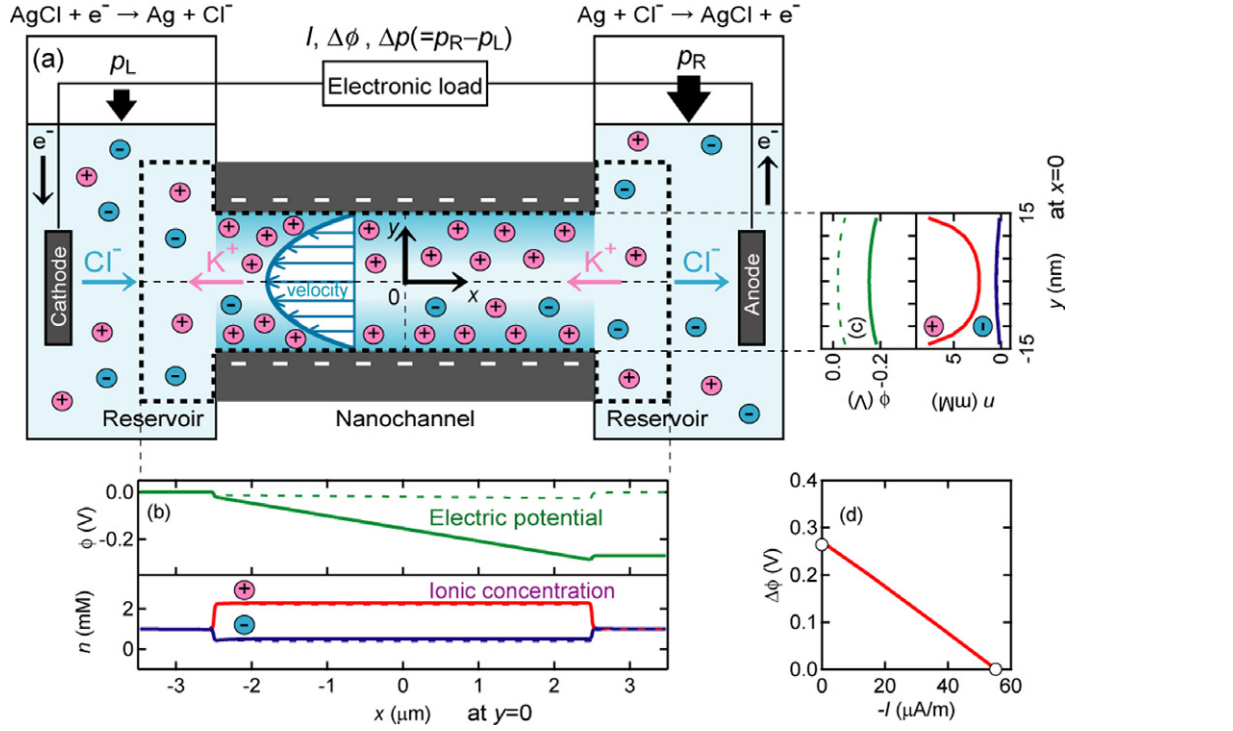

Fig. 1. (a) Schematic of a nanofluidic battery consisting of a nanochannel with reservoirs on either side, and the electric potential and ionic concentration profiles, (b) along the channel at $y = 0$ (along the x-axis) and (c) across the channel at $x = 0$ (along the y-axis) for $I = 0$ μA/m (solid lines) and for $\Delta\phi = 0$ V (dashed lines). (d) Current–potential bias (I–$\Delta\phi$) curves. Here, $L_x = 5$ μm, $L_y = 30$ nm and 1×1 μm^2 reservoirs are located on either side of the channel. $\sigma = -5 \times 10^{-3}$ C/m^2, $n_{\mathrm{bulk}} = 10^{-3}$ M and $\Delta p = 0.5$ MPa. The schematic is not the same scale in the x and y directions.