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Direct numerical simulation of continuous lithium extraction from high Mg^{2+}/Li^{+} ratio brines using microfluidic channels with ion concentration polarization

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ABSTRACT

A novel ion concentration polarization-based microfluidic device is proposed for continuous extraction of Li^{+} from high Mg^{2+}/Li^{+} ratio brines. With simultaneous application of the cross-channel voltage that drives electroosmotic flow and the cross-membrane voltage that induces ion depletion, Li^{+} is concentrated much more significantly than other cations in front of the membrane in the microchannel. The application of external pressure produces a fluid flow that drags a portion of Li^{+} (and Na^{+}) to flow through the microchannel, while keeping most of Mg^{2+} (and K^{+}) blocked, thus implementing continuous Li^{+} extraction. Two-dimensional numerical simulation using a microchannel of 120 μm length and 4 μm height and a model, highly concentrated brine, shows that the system may produce a continuous flow rate of 1.72 mm/s, extracting 25.6% of Li^{+}, with a Li^{+}/Mg^{2+} flux ratio of 2.81×10^{3}, at an external pressure of 100 Pa and cross-membrane voltage of 100 times of thermal voltages (25.8 mV). Fundamental mechanisms of the system are elaborated and effects of the cross-membrane voltage and the external pressure are analyzed. These results and findings provide clear guidance for the understanding and designing of microfluidic devices not only for Li^{+} extraction, but also for other ionic or molecular separations.

1. Introduction

Lithium-ion batteries have been widely used in electronics and many other fields since their invention in the last century, due to their high open-circuit voltages, high energy densities, wide operating temperature ranges, etc. [1]. Because of their environmental friendliness, they are substituting the traditional pollution-prone gasoline in the automobile industry. Natural resources of lithium are mainly mineral rocks and lake brines. It has been estimated that about two-thirds of the lithium resources exist in brine of lakes, located in the central Andes and China [2]. Currently, the cost of extracting Li^{+} from brine is lower than that from mineral [3], making extraction of lithium from brines indispensable. One challenge of Li^{+} extraction from brines is the low concentrations of Li^{+}, which is generally less than 100 mM [4]. Another challenge comes from the high Mg^{2+}/Li^{+} ratio, which is generally greater than 40 in the salt lakes of China. Because Mg^{2+} and Li^{+} have similar chemical properties, extraction of lithium while simultaneously removing the more abundant magnesium remains technically difficult.

Currently, there are mainly two classes of lithium extraction technologies: chemical methods [5] and electro-dialysis [6]. Chemical methods extract Li^{+} from brines by precipitation [7,8], solvent extraction [9,10], adsorption [11–13], etc. Although these methods are playing dominant roles in the current Li^{+} extraction industry, they usually suffer from problems of long processing time, large consumption of chemical reagents, membrane fouling, and equipment erosion, etc. [14–17]. Electro-dialysis systems utilize nanofiltration membranes together with ion selective membranes to separate monovalent Li^{+} and Na^{+} from Mg^{2+} [18,19]. Despite the relatively low energy consumption [20] and the environment-friendliness [4], these systems generally suffer from membrane clogging and high cost. In addition, durability of the membranes needs to be enhanced before commercial applications [5]. Overall, the existing extraction techniques are inadequate for most lithium resources [21], and methods based on new mechanisms are of huge demand.

The main interest herein is to develop a novel method to extract lithium from brines of high Mg^{2+}/Li^{+} ratios, based on the ion

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concentration polarization (ICP) phenomenon using microfluidic channels. Fundamentally, ICP is induced by selective ion transport across nanochannels or ion-exchange membranes [22], or reactions at the electrode surfaces [23]. Accompanying the selective ion transfer, an ion depletion zone with extremely low ion concentrations and amplified electric fields is formed. Combination of ICP and fluid flow facilitates a series of novel applications, such as desalination [24–26], mixing [27,28], biomolecular preconcentration [29–32], and simultaneous separation [33–36]. Here, we use the ICP-induced electric field and the pressure-driven flow to realize flows of Li^+ and Na^+ through the microchannel, while keeping Mg^{2+} and K^+ blocked, thereby realizing continuous-flow extraction of Li^+ from the brine. As the typical three-dimensional (3D) channel size is in the order of tens of micrometers, and ion-exchange membranes in this new device is not responsible for the transport the fluid or Li^+, the system is free from the nanofilter's clogging and low permeability problems. The aim of this paper is to elaborate the fundamental mechanism of the proposed Li^+ extraction device by numerical simulation. Effects of key control parameters, more specifically the cross-membrane voltage and pressure, are clarified.

2. Methods

2.1. System setup

Fig. 1(a) shows the diagram of a two-dimensional (2D) dual-channel ICP-based device for Li^+ extraction. Two horizontal microchannels with positively charged walls are bridged by an anion-exchange membrane (AEM). A cross-membrane upward electric field $\mathbf{E_2}$ is applied to produce the selective transport of anions through the AEM, and generate an ion depletion zone near the AEM in the upper microchannel. The leftward electric field $\mathbf{E_1}$ (facilitating the electroosmotic flow, EOF) and the external pressure P_0 (producing the pressure-driven flow) act together to drive the rightward fluid flow that drags all the charged species into the microchannel. The amplified electric field at the front of the ion depletion zone exerts strong electrophoretic forces on cations and hinders their migrations. For different cation species, balances between the leftward electrophoretic force (proportional to the valence), and the rightward fluid drag force (inverse proportional to the diffusion coefficient) are different, thus their chances of passing through the electric field barrier are different. By calculating the fluxes of different cations under varied electric fields and external pressure, we will demonstrate that Li^+/Mg^{2+} separation may be achieved by permitting only a portion of Li^+ and Na^+ to pass through the microchannel while keeping most Mg^{2+} and K^+ blocked.

Fig. 1(b) shows the schematic computational model for the above system. The key component is a microchannel of length L and height H, with AEM of length L_m embedded in the middle of both the upper and lower walls. The walls of the microchannel are positively charged with a surface charge density σ_+, and AEMs are assumed to permit the passage of anions only. Two wider compartments with length L_1 and height H_1 are connected to left and right ends of the microchannel, representing part of the reservoirs. The channel is filled with the mixed solution of Li^+, Na^+, K^+, Mg^{2+} and Cl^-, simulating the brine. The concentration of Cl^- in the membrane is C_m, which is determined by the requirement to balance the fixed charge density in AEM. Voltages V_L and V_R ($V_L < V_R$) are applied to generate a leftward electric field ($\mathbf{E_1}$ in Fig. 1(a)), which induces an rightward EOF (of the first kind, EOF1). In this sense, the left reservoir is referred to as the inlet reservoir, and the right one as the outlet reservoir. A voltage V_m is applied on the membranes to generate a cross-membrane voltage $V_{cm} = V_m\text{-}(V_L + V_R)/2$ ($V_{cm} > 0$, simulating $\mathbf{E_2}$ in Fig. 1(a)). Larger V_{cm} drives more anions out of the microchannel in unit time and induces stronger ion depletion inside it. Pressures at the left boundary and the right boundary are set to P_0 and 0, respectively.

2.2. Governing equations

The governing equations for incompressible fluid flow, transport of ions, and electric potential are the Navier-Stokes, Nernst-Plank, and Poisson equations [37,38], respectively,

$$\rho(\partial \mathbf{U}/\partial t + (\mathbf{U}\cdot\nabla)\mathbf{U}) = -\nabla P + \eta\nabla\cdot\nabla\mathbf{U} - \rho_e\nabla\Phi, \tag{1}$$

$$\nabla\cdot\mathbf{U} = 0, \tag{2}$$

$$\frac{\partial C_i}{\partial t} = -\nabla\cdot\ \mathbf{J}_i, \tag{3}$$

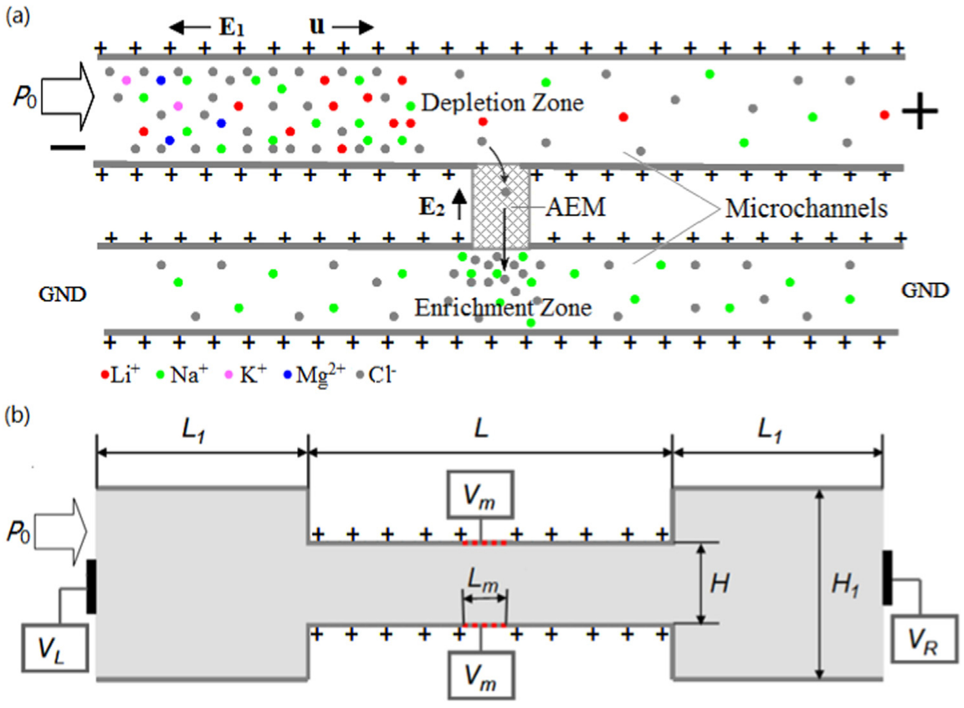

Fig. 1. (a) System setup of a dual-channel device for ICP-based Li^+ extraction. (b) The simulation model.