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Development of recovering lithium from brines by selective-electrodialysis: Effect of coexisting cations on the migration of lithium

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ABSTRACT

The process for separating and purifying lithium in brines based on electrodialysis with monovalent selective ion exchange membranes was investigated in our previous work. The migration of coexisting cations in brines was competitive with lithium ions, especially monovalent cations (Na^+ and K^+). The aim of this study was to examine the influence of major coexisting cations in brines on lithium recovery in the selective-electrodialysis (S-ED) process. Considering the factors of coexisting cations, such as concentration and type, some migration laws of lithium ion were found as follows: the concentration of coexisting cations had negative effect on the migration of lithium ion; the influence order of coexisting cations on lithium migration was contrary to their hydrated radius sequence: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. In order to characterize the migration process of cations through monovalent selective cation exchange membrane in microcosmic theory, a partial dehydration conceptual model based on charge capillary column theory and ionic potential was proposed. And the model was used to characterize the ions migration process. Simultaneously, considering the hydration potential which indicates how strongly an ion would attract water molecules, the influence sequence of coexisting cations was explained legitimately. These observations might provide some theoretical basis and technological support for the relevant research of recovering lithium from brines.

1. Introduction

Lithium, the lightest metal in nature, is an essential chemical element in energy storage devices. It is with a lower density (0.534 g/cm^3) and a higher electrochemical standard potential (3.04 V) [1]. At present, lithium has been widely used as lithium-ion batteries (LIBs) material [2,3]. Several recent studies have estimated the lithium production could not be satisfied with an increasing demand, especially from the transport service, where LIBs are the most importantly component for electric vehicles [4–6]. The global lithium resource mostly derives from limited mineral in earlier years. And the extraction of lithium from ores or minerals, such as spodumene and lepidolite, using acid or alkaline process is chronically researched and developed [7]. But it is hardly to satisfy the demand of industry and the development of our society only relying on lithium extraction from ores and minerals. Furthermore, not only amount of energy will be consumed, but also lots of harmful gases released in the production process will impact on the surrounding environment [8,9]. On the other hand, more than 80% of lithium resource of global continent exists in salt lake brines [10]. And a wide range of salt lake brines containing lithium has been exploited by humanity in precipitation method. The chemical precipitation method [11,12] is an early technology for separating and recovering lithium from salt lake brines. As a simple recovery process, a large sum of precipitating agents will be used, and the loss rate of lithium will be high. Solvent extraction process is also used in recovering lithium from brines. Xiang et al. [13] achieved the extraction of lithium from salt lake brines containing borate anion and high concentration of magnesium. Other separation and purification technologies such as ion exchange [14], adsorption [15,16] and nanofiltration (NF) [17–20] have been attempted to recover lithium from brines. These methods have been developed to use in the extraction of lithium from brines, but no effective method can be used to extract lithium very effectively from

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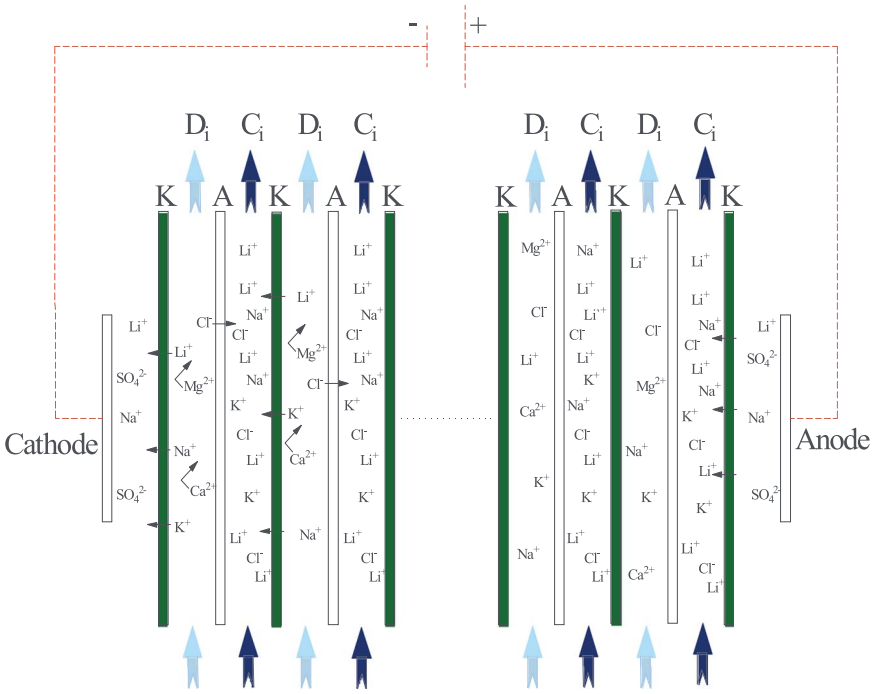

Fig. 1. The schematic principle of the S-ED stack (A, K, D_i and C_i represent the anion exchange membrane, cation exchange membrane, desalting compartment and concentrating compartment, respectively).

salt lake brines with high Mg^{2+}/Li^+ ratios [21]. So a potential technology of extraction and purification of lithium from brines should be developed and researched.

Electrodialysis (ED) is an electric ion exchange membrane technology that has some significant superiority in seawater desalination, extraction of metal resources in salt lake brines, and treatment of industrial effluents, and so on [22–24]. Due to its superior desalination performance and high-efficient enrichment of high concentration of salt solution, ED as a potential effective method is used in concentrated brines [25]. ED is based on the transport of ions through ion exchange membranes under an electrical potential difference as the driving force of mass transfer. When the conventional ion exchange membranes are replaced by monovalent selective ones partially, a new type of electrodialysis, called selectrodialysis (SED), is formed [26]. However, the configuration of membrane stack in this manuscript is that all of the standard anion- and cation exchange membranes are replaced with the monovalent selective anion- and cation exchange membranes. In order to differentiate, the membrane stack with above configuration was renamed as “selective-electrodialysis (S-ED)” in this work. The principle of the S-ED stack is shown in Fig. 1.

Monovalent selective cation exchange membranes and monovalent selective anion exchange membranes are placed alternately in S-ED stack. When a voltage is applied between the cathode and the anode, cations migrate toward the cathode side and anions toward anode side. So the monovalent cations (Li^+, Na^+, K^+) migrate through cation exchange membranes which have negative fixed groups, and are retained by the anion exchange membranes which have positive active groups. And the divalent cations (Ca^{2+}, Mg^{2+}) are blocked by monovalent selective cation exchange membranes and stranded in desalting compartment. This migration process causes an increase of the monovalent ion concentration in concentrating compartments and a decrease in the desalting compartments.

Nowadays, there is little information about recovering lithium from brines by ED using monovalent selective ion exchange membrane. Nie et al. [27] investigated the fractionation of lithium ions from magnesium ions by electrodialysis, and the results illustrated that ED exhibited superiority both technically and economically for the fractionation of Li^+/Mg^{2+} compared to NF. Lithium recovery from high Mg^{2+}/Li^+ brines by S-ED process was also investigated preliminarily in our previous work, and the separation of Mg^{2+} and Li^+ was partly solved [28]. But, the coexisting cations should be a certain negative influence on the migration and purification of lithium in theory. And those coexisting monovalent cations (Na^+ and K^+) would generate obvious competitive permeation along with Li^+ migration in ED process. This is also the reason why the current efficiency in the process of recovering lithium from brines by S-ED technology usually is lower. Furthermore, although the monovalent selectivity cation exchange membrane has lower selectivity for magnesium and calcium, and the separation effect of lithium and magnesium/calcium by S-ED process is obvious prior to nanofiltration (NF) process, the separation efficiency of lithium and magnesium/calcium should still be further improved. Also, those coexisting divalent cations (Ca^{2+} and Mg^{2+}) still have a certain impact on the migration of Li^+. Thus, the influence of coexisting cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in brines on lithium migration by batch S-ED process was studied in this work, in hoping of providing technical support for the comprehensive utilization of lithium resource in salt lake brines, seawater and bittern.

2. Materials and methods

2.1. Experimental set-up and operation conditions

The batch S-ED set-up schematized in Fig. 2 was provided by Beijing Huanyulida Environmental Products Ltd, China. The desalting, concentrating and electrolyte circulate solutions were in three closed loop, respectively. The experimental S-ED apparatus mainly contained the following parts: (1) a direct current (DC) power supply (JS3020D, Wuxi ANS Electronic Technology Ltd., China); (2) a cathode and an anode, which were made of titanium coated with ruthenium; (3) S-ED membrane stack (30 cm × 10 cm); (4) three solution storage tanks (desalting solution tank, concentrating solution tank and electrolyte solution tank); (5) three magnetic pumps (DP-100, Shanghai Xinxishan Industrial Ltd., China).

The internal structure of S-ED membrane stack is shown in Fig. 3. The S-ED stack is comprised of fixation plate, anode plate, monovalent cation exchange membrane (effective size, 21 cm × 6.7 cm), concentrate cell spacer, monovalent anion exchange membrane, dilute cell spacer and cathode plate. Diagonal nets spacers are incorporated into