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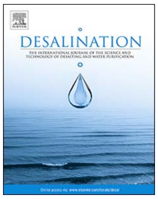

Electrodialytic concentrating lithium salt from primary resource

Yongming Zhou[b,c], Haiyang Yan[a], Xiaoli Wang[a,b], Liang Wu[a], Yaoming Wang[a,c,*], Tongwen Xu[a,*]

[a] Laboratory of Functional Membranes, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China
[b] Nano Science and technology Institute, University of Science and Technology of China, Suzhou, Jiangsu 215123, People's Republic of China
[c] Hefei ChemJoy Polymer Materials, Co., LTD, B-2, Liheng Industrial Square, Fanhua Road, Hefei, Anhui 230601, People's Republic of China

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ABSTRACT

Lithium and its related products are important materials in modern society. A large amount of energy is consumed for the extracting or concentrating lithium salts from primary resources. In this study, electrodialysis (ED) was introduced to concentrate Li_2SO_4 solution. Effects of ion exchange membrane type, applied voltage drop across the ED stack, and especially the operating mode were investigated. Results indicated that Neosepta AMX/CMX membranes were more preferable than FKS/FAS and CJMC/MA membranes for lithium salt concentrating at the voltage drop of 6 V. Additionally, it's found that the volume ratio of 1:3 was optimal choice for two-stage ED. The final Li_2SO_4 concentration could reach as high as 17.4 wt% with two-stage electrodialysis (V_c:V_d = 1:3); while the special energy demand could be as low as 30.9 kWh/m^3 in one-stage ED when the operate voltage was 4 V. From the viewpoint of energy consumption, "a high volume ratio concentrating" with volume ratio of 1:10 was more competitive than "two-stage concentrating". Naturally, electrodialysis is not only energy saving but also high-effective for lithium extraction and concentrating.

1. Introduction

The content of lithium in the earth's crust is at 0.002%–0.006 wt% and it's the 33rd most abundant element in nature [1]. Lithium and its compounds, as important materials, have a very significance role on the development of lithium-ion batteries [2–4], pharmaceuticals [5–7], nuclear power [8,9] and other industries [10–12]. According to the resources of lithium, extraction of lithium can be divided into primary resources and second resources. In primary resources, lithium extraction can be from minerals, clays, brines, sea water and bitterns. In secondary resources, extraction of lithium is mainly from lithium-ion batteries [13]. Lithium carbonate is a basic material for the production of secondary lithium and lithium metal and it's the most critical lithium industry product. Other industrial lithium products are almost lithium carbonate downstream products. Sulfuric acid method is a dominant method for the production of lithium carbonate from lithium ores. A schematic diagram for the production of lithium carbonate by sulfuric acid method is shown in Fig. 1. The common concentration of lithium sulfate is ~6 wt% after sulfuric acid roasting and leaching process. Saturated mass fraction of lithium sulfate is 20.5 wt% in 25 °C. It's necessary to concentrate Li_2SO_4 at first and thereafter lithium carbonate sediment can be obtained after adding sodium carbonate. Traditionally, thermal method is used for lithium salt concentrating, but it is high in energy consumption and labor intensity. For example, 0.4 tons of steams are needed to remove 1 ton water with a typical three-stage evaporator in practical case. It is necessary to develop more efficient concentrating technologies than the present evaporation method.

Electrodialysis (ED) is an electrochemical process for the desalination and concentrating of electrolyte solution under the influence of an electrical potential difference [14]. It's an energy-saving and environmentally friendly technology which has been widely used in water desalination, resource recycling, and environmental protection [15–18]. There are several trials for lithium salt extraction or recovery with ED or membrane electrolysis. Hoshino [19] has proposed a new method for Li recovery from seawater by electrodialysis using an ionic liquid. Nazila et al. [20] have investigated the recovery of lithium ions from sodium-contaminated lithium bromide solution by ED. The result showed that ED is a promising method to recover the polluted LiBr solution. But there is little research for lithium salt concentrating from sulfuric acid leaching method. Considering aqueous lithium salt solution is a strong electrolyte, it should be economic and feasible for ED technology to condense Li_2SO_4 solution from a low concentration to a high concentration.

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[*] Corresponding authors at: Laboratory of Functional Membranes, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China.

E-mail addresses: ymwong@ustc.edu.cn (Y. Wang), twxu@ustc.edu.cn (T. Xu).

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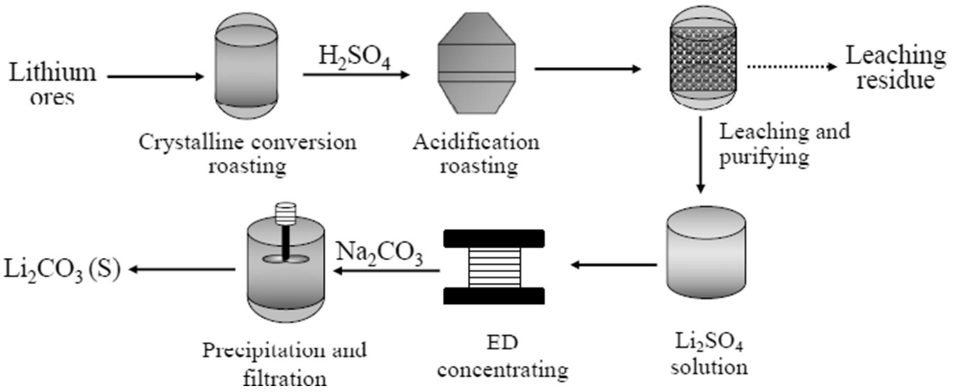

Fig. 1. A schematic diagram for lithium carbonate production by sulfuric acid method.

There are numerous studies for the concentration of inorganic salts (e.g. NaCl) or organic salts (e.g. ionic liquid) using ED technology [21–24].Generally, the operating mode of ED for salt concentrating can be classified to two types. One operating mode is called "a high volume ratio concentrating". The salt concentrating is achieved by a high volume ratio between dilute and concentrate chamber, such as the works by Jiang et al. and Yan et al. [21,22]. In this case, salt is continuously transported from the dilute chamber into concentrate chamber. Even though water is combined with salt molecules during the salt migration, the salt concentration in the concentrate chamber can be increased to several times of initial concentration due to a high volume ratio between dilute and concentrate chamber. The other operating mode is called as "multi-stage concentrating", such as the works by Turek [25] and Zhang et al. [26]. In this case, the salt is concentrated with a couple of stages. It is first concentrated to a moderate concentration and afterward raised to a high concentration. For example, for a 3 wt% NaCl solution, it is first concentrated to 9 wt% at first-stage, then be raised to 15 wt% at second-stage and finally be concentrated to 21 wt% at third-stage. Two advantages for multi-stage concentration are expected. First, it is feasible to concentrate salt to a high concentration even though the ion exchange membranes have relative poor performance for salt concentrating. Because there is a relative low salt concentration ratio between concentrate and dilute chamber with this kind of operating mode, the back diffusion of salt from concentrate chamber into dilute chamber is alleviated. Second, the capital cost for multi-stage shall be lower than that for one-stage. At the high stage ED stack, the salt concentration is high, so the limiting current density shall be very high. ED can be operated at a high current density in that case. As a consequence, less membrane area will be needed for a certain size of installation. The disadvantage for multi-stage concentrating is that it may lead to an increment in energy consumption. Nevertheless, it is still unknown which operating mode is more competitive for Li_2SO_4 concentrating. Therefore, the main objectives of this study are to test the usability of ED for Li_2SO_4 concentrating and to investigate the effects of membrane type, applied voltage drop, and especially the operating mode on process performance.

2. Set-up and experiments

2.1. Material

The membranes used in the experiment were FAS-PET-130 (anion-exchange membrane, AEM, FuMA-Tech *GmbH*, Germany), FKS-PET-130 (cation-exchange membrane, CEM, FuMA-Tech *GmbH*, Germany), Neosepta AMX (AEM, Tokuyama Co., Japan), Neosepta CMX (CEM, Tokuyama Co., Japan), CJMA (AEM, Hefei ChemJoy Polymer Materials Co. Ltd., China), CJMC (CEM, Hefei ChemJoy Polymer Materials Co. Ltd., China). The main properties of the membranes were listed in Table 1. Li_2SO_4 (mass fraction 6 wt%) was provided by BYD electronic Co., Ltd. China. Deionized water was used throughout the experiment.

Table 1
Types of membrane and their properties.

Membrane type	Thickness (μm)	Ion exchange capacity (IEC) (meq/g)	Water uptake (%)	Area resistance (Ω cm^2)	Transport number (%)
FAS-PET-130[a]	125 (wet)	1.07	19.7	2.9	95
FKS-PET-130[a]	127 (wet)	0.74	19	3.7	99
CJAM[b]	200	1.05	20	2.8	> 98
CJCM[b]	145	1.2	22	3.5	> 98
Neosepta AMX[a]	134	1.25	16	2.35	91
Neosepta CMX[a]	164	1.62	18	2.91	98

[a] The data were collected from the Ref [22].
[b] The data were collected from the product brochure provided by manufacturers.

2.2. Setup

Schematic diagram of the ED experimental set-up was illustrated in Fig. 2. Specially, this laboratory-scale experimental setup was comprised of (1) a cathode and an anode, which were made of titanium coated with ruthenium; (2) alternatively arranged anion-exchange membranes (AEM) and cation-exchange membranes (CEM) and with four repeat units. An additional AEM was placed adjacent to electrode to block the transport of Li^+ to cathode compartment since electrode rinse solution was Na_2SO_4 (0.3 mol/L). The effective area of each membrane was 189 cm^2. The neighboring membranes were separated by a silicone partition net (thickness = 0.8 mm) with the flow channels. These membranes were arranged between anode and cathode. Two electrodes were connected with a direct current power supply (WYL1703, Hangzhou Siling Electrical Instrument Ltd.). The experiment was operated at constant voltage condition; the current across the stack was directly read from indicators on the power supply. The stack has three chambers, named concentrate chamber, dilute chamber and electrode chamber. Peristaltic pumps (BT-100 L, Baoding Lead Fluid Technology Co., Ltd.) were used to circulate the solution with the maximal flow rate of 420 mL/min during the experiments. The brix of solution was measured by a digital hand-held "Pocket" refractometer (PAL-1, ATAGO Co., Ltd.) at intervals. In the concentrating experiments, two operating modes were carried out, one is "A high volume ratio concentrating" (HVRC) and the other one is "Multi-stage concentrating" (MSC). More detailed descriptions of these two modes were provided in the Results and Discussion part.

2.3. Determination of concentrated and diluted lithium's concentration

The concentration of total dissolved salt is determined by the brix of solution. Initially, a standard line of brix-predetermined concentration was tested and plotted. A linear relation was regressed as Eq. (1) with regression coefficients of 0.9991. Then the final concentration of