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# Study on extraction of lithium from salt lake brine by membrane electrolysis

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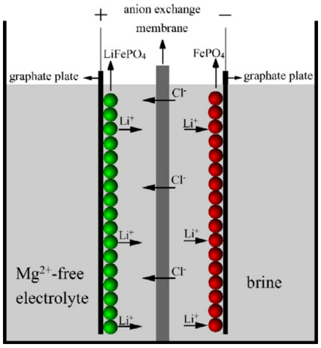
## HIGHLIGHTS

- Extracting lithium from brine by membrane electrolysis
- Studying the effect of operating parameters on $Li^+$ capacity and electrode stability
- Determining the suitable membrane electrolysis operating parameters
- Providing a reliable route for lithium extraction from brine

## GRAPHICAL ABSTRACT



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## ABSTRACT

Extraction of lithium from brine is becoming a focus of importance worldwide. Lithium was extracted from brine by membrane electrolysis in this paper, and the influences of operating parameters on $Li^+$ exchange capacity and stability of electrode are investigated. Various parameters including initial lithium concentration of anolyte, anode–cathode distance, electrolyte temperature, surface density of active substrate and electrolysis time are optimized. Under the optimal conditions, the electrode exhibits a remarkable $Li^+$ exchange capacity of 38.9 mg/g and the pH value of anolyte is less than 8. The results are beneficial for the extraction of lithium from brine by membrane electrolysis.

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## 1. Introduction

China is very rich in lithium resources in salt lake brine. There are more than 80 salt lakes located in Tibetan Plateau, and the reserve of lithium resources in these lakes reaches more than 5 million tons [1,2]. Unfortunately, the majority of salt lake brine is characterized with the high mass ratio of Mg/Li. The mass ratio of Mg/Li in most salt lake brine exceeds 40:1, and the highest even reaches an astonishing numerical value of 1837:1 [3–5]. Due to the similar chemical properties of $Li^+$ and $Mg^{2+}$, it's very difficult to separate Li from Mg in brine. Plenty of work has been done by many researchers, and many methods such as precipitation [6], solvent extraction [7,8], nanofiltration [9,10] and adsorption [11] have been developed to extract lithium from brine, but no effective method can be used to extract lithium effectively from high Mg/Li ratio salt lake brine.

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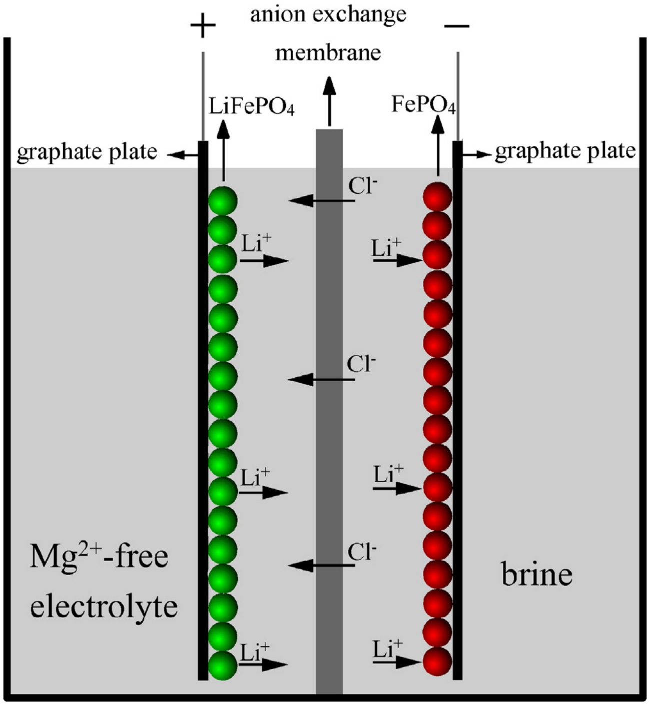

**Fig. 1.** The schematic diagram of electrolytic cell.

Recently, membrane electrolysis is widely used in the separation process, such as wastewater treatment and reclamation facilities [12–14]. In our research, a novel membrane electrolysis method was developed to extract lithium from high Mg/Li ratio salt lake brine [15,16]. It is well known that $LiFePO_4$ is recognized as a promising cathode material for lithium ion battery [17–19]. The reaction process is shown in the following formulas:

$$\text{Charge process}: LiFePO_4 \rightarrow Li^+ + FePO_4 + e \tag{1}$$

$$\text{Discharge process}: FePO_4 + Li^+ + e \rightarrow LiFePO_4. \tag{2}$$

Unlike the traditional application, $LiFePO_4$ and $FePO_4$ are used to extract lithium from brine in this work. As shown in Fig. 1, the electrolytic cell is divided into two slots by anion exchange membrane. One slot is filled with salt lake brine and the other with $Mg^{2+}$-free electrolyte. $FePO_4$ anode is placed into the brine and $LiFePO_4$ cathode into the $Mg^{2+}$-free electrolyte. Driven by the external potential, $Li^+$ in the brine is intercalated into $FePO_4$ to produce $LiFePO_4$, and $Li^+$ is released into the $Mg^{2+}$-free electrolyte from $LiFePO_4$ cathode to produce $FePO_4$ in the membrane electrolysis process. In other words, $FePO_4$ in brine reacts with $Li^+$ to produce $LiFePO_4$, and $LiFePO_4$ in $Mg^{2+}$-free electrolyte is decomposed into $Li^+$ and $FePO_4$. At the same time, the anions transfer from the brine to the $Mg^{2+}$-free electrolyte to maintain the charge balance because the cations cannot penetrate the anion exchange membrane. By this way, $Li^+$ can be extracted selectively from salt lake brine into the $Mg^{2+}$-free solution. The mass ratio of Mg/Li can be reduced to 0.3 from 493 by this method [20], indicating that it is efficient to separate magnesium and lithium from salt lake brine. Moreover, the effects of $Na^+$, $K^+$ and $Mg^{2+}$ on Li extraction were investigated in our previous work and the side-effects of $Na^+$, $K^+$ and $Mg^{2+}$ can be eliminated by controlling proper electrolytic voltage [15,20]. However, the $Li^+$ exchange capacity and stability of electrode, which is critical to meet the requirement of electrode cycling, has not been taken into account in previous work. If the $Li^+$ exchange capacity of electrode is higher, the needed weight of electrode will be reduced, which is beneficial for the decrease of cost. For the meantime, the stability of electrode is critical to the cycle times of electrode used in the membrane electrolysis process. In our previous research work, the results showed that the $FePO_4$ electrode will decompose if the pH of anolyte is more than 8 [21]. In that case, $Li^+$ in the solution cannot intercalate into $FePO_4$ electrode to form $LiFePO_4$. Finally, lithium in brine cannot be extracted by membrane electrolysis. Therefore, how to enhance the $Li^+$ exchange capacity of electrode and maintain the pH of solution in reasonable region are very important for the application of this novel method. Therefore, based on the previous research, the influence of other factors on $Li^+$ exchange capacity and stability of electrode during the membrane electrolysis was studied in this paper.

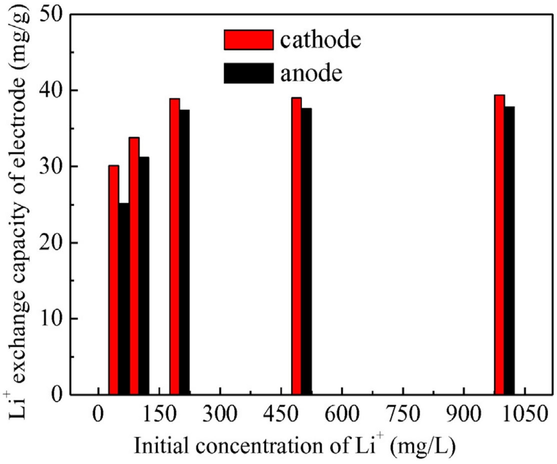

**Fig. 2.** Effect of $Li^+$ initial concentration of anolyte on exchange capacity of electrode.

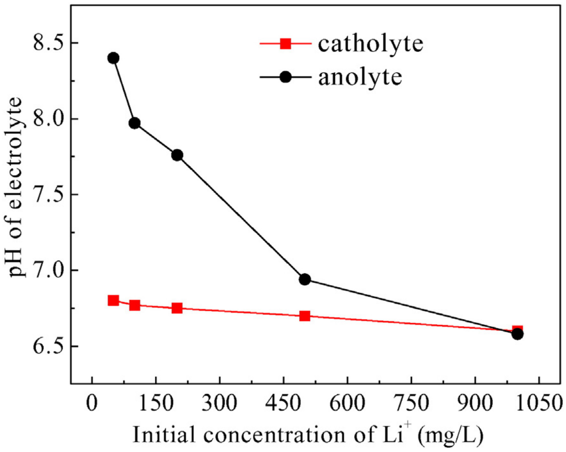

**Fig. 3.** Effect of $Li^+$ initial concentration of anolyte on pH of electrolyte.

## 2. Experimental

### 2.1. Electrode preparation

The $LiFePO_4$ electrode was obtained in the following procedure: 90 wt.% $LiFePO_4$ (active substrate), 5 wt.% acetylene black and 5 wt.% polyvinylidence fluoride(PVDF) binder were well mixed and then dispersed completely in N-methy1-2 Pyrolidone(NMP) to produce slurry. The slurry was overlaid onto the graphite plate with the size of $4 \times 4\ cm^2$ according to predesigned surface density and then dried in vacuum at 110 °C for 10 h.

$FePO_4$ anode was obtained by deintercalating lithium from $LiFePO_4$ cathode. The electrolytic cell was filled with 1 mol · $L^{-1}$ NaCl solution, and then $LiFePO_4$ cathode and nickel anode were put into the electrolytic cell. A constant electrolysis of 1.0 V was ended until the ultimate

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