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Li extraction from high Mg/Li ratio brine with $LiFePO_4/FePO_4$ as electrode materials

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ABSTRACT

The challenge for lithium extraction from brine has been the separation of Mg and Li. Because they are located in diagonal positions within the periodic table, they exhibit many chemical similarities. But since Mg^{2+} has a high charge density and is easily hydrated, we explored a new separation method from an electrochemical perspective using $LiFePO_4/FePO_4$ as electrode materials. Through CV tests and technical experiments in a different electrolyte, this approach was verified. Our results show that lithium exhibits good reversibility in $LiFePO_4/FePO_4$ structures, and the redox peak separation is 0.592 V while that of Mg^{2+} is 1.403 V, indicating its more serious polarization. Technical studies using a voltage of 1.0 V show that, in pure lithium solution, the inserted capacity of lithium can reach $41.26\ mg \cdot (1\ g\ LiFePO_4)^{-1}$, which is 93.78% of its theoretical value (44 mg), and the subsequent extracted capacity can attain $38.93\ mg \cdot (1\ g\ LiFePO_4)^{-1}$, which is 94.3% of its inserted capacity. But the extracted capacity of Mg^{2+} from a solution containing magnesium is only $5.5\ mg \cdot (1\ g\ LiFePO_4)^{-1}$. Furthermore, the experimental data at different voltages prove that a lower voltage is beneficial for separating Mg and Li, and this method also works well in brine since the Mg/Li ratio can be reduced to 0.45 from 60. All these results indicate that this method, while simple, is quite promising for separating Mg and Li from a high Mg/Li ratio brine.

1. Introduction

Since the lithium rechargeable battery was commercialized by Sony in 1990, lithium has become more and more important in modern industry and has been regarded as a "future and strategic metal", widely used in various portable electronic devices due to its high energy density and long cycling ability. Consequently, lithium extraction has become a high priority.

Lithium resources exist naturally in two forms: as a mineral and as a liquid. The limited availability of lithium in minerals, along with its high extraction costs, has steered the industry towards its liquid state resources, which are estimated to contain more than 85% of the world's recoverable lithium (Harben and Edwards, 1997). The liquid state lithium mainly resides in salt lake and subsurface brine. Brine consists of chloride, sulfate or carbonate electrolyte with a variety of components such as lithium, sodium, potassium, magnesium, calcium, boron and other ions (Averill and Olson, 1978). Among them, magnesium presents a major challenge for lithium extraction because these two elements are located in diagonal positions within the periodic table, resulting in their many chemical similarities, such as: light ionic quality and small radius, as well as the corresponding carbonate and hydroxides which are insoluble in water (Cheng and Kenneth, 2001; Hamzaoui et al., 2003). The methods used for lithium extraction vary with the concentration of magnesium. When the Mg/Li ratio is less than 6, the precipitation technique can effectively separate Li and Mg. However, once the Mg/Li ratio exceeds 6, the precipitation technique appears so limited that effective lithium extraction becomes much more difficult. Unfortunately, a large majority of brine resources throughout the world are characterized by a high Mg/Li ratio.

Extracting lithium economically from brine with a high Mg/Li ratio has been a worldwide problem, seriously restricting its extraction and application. Researchers developed various methods to deal with this difficulty (Daniel et al., 2006; Hamzaoui et al., 2008; Jerome, 2003; Königsberger and Harris, 2008; Wen et al., 2006; Zeng et al., 2007; Zhong and Yin, 2003), but most of them were either complex, with ensuing high costs, equipment corrosion and other problems, or did not obtain satisfactory results. Hence, the need to develop effective methods for the separation of macro amounts of Mg and Li has become urgent.

Any technique used for the separation of similar elements must take advantage of any small differences between them. Mg^{2+} has a high charge density (twice the level of Li^{+} with about the same ionic radius) (Poul et al., 2003) and is easily hydrated, which inevitably can lead to its higher polarization. These subtle differences encouraged us to explore a new separation method from an electrochemical perspective.

In recent years, olivine $LiFePO_4$ has been used as the cathode material for lithium rechargeable batteries because of its good chemical stability, eco-friendliness and reversible performance. The excellent

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reversibility of the cells on repeated cycling is due to the striking similarity of the $LiFePO_4$ and $FePO_4$ structures (Padhi et al., 1997). The potential difference of this redox couple is quite small (Yamada et al., 2001). Moreover, the research with these batteries determined that $LiFePO_4$ is stable over a wide pH range in an aqueous solution and lithium exhibits a good reversible performance in it (Huang et al., 2007; Luo et al., 2010). To isolate the trouble caused by the organic electrolyte reacting with the electrodes, researchers substituted an aqueous inorganic salt electrolyte containing lithium, such as LiCl, $LiNO_3$, or Li_2SO_4 (similar to lithium salt in brine) for the organic electrolyte in order (Li et al., 1994).

As we know, the essence of deintercalated (or extracted) lithium from $LiFePO_4$ arises from the oxidized reaction of the transition metal. By imposing a positive potential, Fe^{2+} in $LiFePO_4$ is oxidized to $Fe^{3+}$to release one electron. This forces lithium ions to dissociate out from $LiFePO_4$, move towards the surface of the negative electrode (LiCs) through the electrolyte, and meet electrons from external circuit. It can be seen that the positive electrode ($LiFePO_4$) is lithium-saturated at the charged state, while the negative electrode is lithium-absent. So it gives us a new idea, namely, brine electrolyte could be used for lithium sources instead of the lithium from commonly used organic electrolyte ($LiPF_6$). By controlling the potential, lithium ions in brine would go into the negative electrode, and release in appropriate electrolyte. By this means lithium in brine could be separated from Mg^{2+} and then concentrated. Whether Mg^{2+} behaves differently from lithium is a key to lithium extraction from brine. Hence, it is required to verify the above assumption by experimental studies.

2. Experimental

2.1. Preparation of $LiFePO_4/FePO_4$ electrodes

90 wt.% $LiFeO_4$/C (Liu and Zhao, 2010), 5 wt.% carbon black and 5 wt.% of polyvinylidene fluoride (PVDF) were mixed in N-methyl-2 pyrrolidone. The mixture was applied onto a base flat, and heated for 12 h at 120 °C under vacuum, before insulating its non-working surfaces with epoxy. The density of the prepared $LiFePO_4$ was around 20 $mg \cdot cm^{-2}$. The prepared $LiFePO_4$ electrode was cut to 6×7 cm^2 (to fit in the electrolytic cell) to serve as the cathode. Porous foam nickel (Changsha LYRUN, China) of the same size was chosen as the anode. An electrolytic cell filled with 600 mL 0.5 M NaCl aqueous solution (supporting electrolyte) was provided with a constant potential electrolysis of 1.0 V. The electrode distance between the porous foam nickel and the $LiFePO_4$ electrodes is typically 10 mm. The electrolysis runs for 10 h to ensure that the lithium ions can be completely extracted from $LiFePO_4$.

2.2. Preparation of the electrolyte

The synthetic brine was similar to the chemical compositions from West Taijnar Salt Lake in Qinghai of China, listed in Table 1. In technical experiments, the typical synthetic solution contained LiCl and $MgCl_2$. Lithium concentration was generally fixed at 220 $mg \cdot L^{-1}$, which was similar to its composition in brine, but the concentration of Mg^{2+} was varied. LiCl, $MgCl_6 \cdot 6H_2O$ and NaCl, respectively, were dissolved in distilled water to create the electrolyte. The concentration of Li^+ was determined by AAS (Atomic Absorption Spectrometry, Persee of Beijing, China), while that of Mg^{2+} by ICP-AES (IRIS intrepid XSP, Thermo Electron Corporation). All reagents used were of analytical grade.

Table 1
Chemical composition sampled from West Taijnar Salt Lake in Qinghai of China (unit: $mg \cdot L^{-1}$).

Element	Mg	K	Na	Li	Ca	SO_4^{2-}	Cl^-	B	Mg/Li	LiCl reserve
Content	13200	6900	82600	220	310	1140	16.2	180	60	1.78 MT

2.3. Electrochemical measurements

Cyclic voltammograms were obtained using a three-electrode cell with or without N_2 flow. The working electrode was square-shaped (1 cm^2 with 1 mm thickness) $LiFePO_4$. This square was electrically connected with Pt wire. The graphite and saturated calomel electrodes (SCE, 0.242 V versus NHE), respectively, served as counter and reference electrodes. The working electrode was cycled between −1.3 and 1.3 V or −1.0 and 1.0 V at a 0.2 $mV \cdot s^{-1}$ scan rate. On each occasion, the potential scan started at −1.3 V or −1.0 V, moving initially in the cathodic direction. All the cyclic voltammetry experiments were recorded via CHI660A (Chenhua, Shanghai) at an ambient temperature (25 ± 1 °C).

2.4. Preparation of the electrolytic cell for technical experiments

Fig. 1 shows a sketch of the rectangular PTEE electrolytic cell with dimensions of $(10 \times 8 \times 9.5)$ cm^3. The integrated electrolytic cell is divided in the middle by a permselective membrane (American IONAC) which allows anions to pass through, but blocks cations.

2.5. Electrolytic technical experiments

Each technical experiment includes two steps:

Step 1 Cathode: $LiFePO_4$; electrolyte: 600 mL 0.5MNaCl;
anode: $FePO_4$; electrolyte: 600 mL Li^+ or Mg^{2+} chloride solution or brine;
reaction time: 600 min.
Place the $LiFePO_4$ and $FePO_4$ electrodes (both have the same dimensions) into the electrolytic cell shown in Fig. 1. Each half-cells was filled with a different electrolyte as indicated and was equipped with magnetic stirring.

Step 2 Cathode: $MeFePO_4$ (the anode of step 1); electrolyte: 600 mL 0.5MNaCl; (Me: Li^+ or Mg^{2+});
anode: $FePO_4$; electrolyte: 600 mL Li^+ or Mg^{2+} chloride solution or brine;
reaction time: 600 min.

After running step 1 for 10 h, the electrodes are thoroughly flushed with 50–55 °C distilled water. The cathode electrode used in step 1 (lithium-eliminated) becomes the anode electrode in step 2; and the anode electrode from step 1 (lithium-saturated) becomes the cathode electrode in step 2, then voltage is applied for 10 h. Using this approach, lithium in brine or enriched lithium solution can be extracted and concentrated in the supporting electrolyte solution.

In each experiment, 1 mL sample was accurately withdrawn for analysis at different reaction time.

2.6. Data process

The inserted capacity or extracted capacity of Li^+ and Mg^{2+} was calculated as follows:inserted capacity:

$$Q = \frac{c_0 V_0 - c_s V_S}{We} = \mathrm{mg}(1\ \mathrm{g}\ \mathrm{LiFePO_4})^{-1}$$

extracted capacity:

$$T = \frac{c_s \cdot V_s}{We} = \mathrm{mg}(1\ \mathrm{g}\ \mathrm{LiFePO_4})^{-1}$$

where: Q — inserted capacity; T — extracted capacity; c_o — initial concentration of metal in solution [$mg \cdot L^{-1}$]; c_s — final concentration of