

Recovery of Li from salt lake brine using electrically switched ion exchange process with

MnO₂ electrode

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Highlights

- Electrically switched ion exchange was innovatively used to extract Li⁺ from brine
- The electrochemical behavior of Li⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺ was first investigated.
- The ESIX process with MnO₂ electrode is prospective in industrial application.

1. Introduction

As the rapid development of electric vehicle, the consumption of lithium ion batteries (LIBs) increased year by year. The consumption of LIBs account for 19% of that of all batteries in 2006, and this value increased to 39% by 2016^[1]. Currently, the research focus of lithium recovery is shifting from minerals to brine because of its abundant reserves and low cost. Therefore, it is significant to develop efficient technologies for the recovery of Li from brine to meet the demand of lithium product.

Electrically switched ion exchange (ESIX), which combines ion exchange and electrochemistry process, is a selective and reversible separation technique. It has been widely used to remove harmful ions from the waste effluents. However, the application of this technology in the field of lithium recovery from brine has rarely been reported.

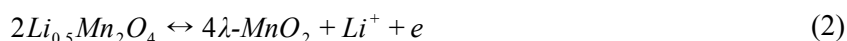
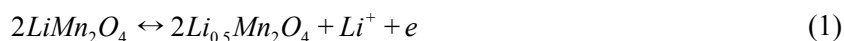
In this study, we report a newly developed ESIX technology with MnO₂ electrode for the efficient extraction of Li from brine. Compared to traditional technologies, the advantages of this method include the absence of drug consumption and waste solution discharge. The electrochemical behavior of Li⁺, Na⁺, K⁺, Ca²⁺ and Mg²⁺ in MnO₂ electrode was first investigated, and the cyclic stability of the MnO₂ electrode was tested for 50 cycles.

2. Methods

The electrochemical performance was tested in a three-electrode configuration. An Ag flake was employed as the counter, and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetry (CV) curves of the electrode were recorded on the electrochemical workstation. The metal concentrations were determined by ICP-OES. The structures, element valences, and morphology of the materials were studied by XRD, XPS and SEM, respectively.

3. Results and discussion

The CV curves of λ-MnO₂ electrode in LiCl solution at various scan rates are shown in Figure 1(a). These curves display two couples of reversible redox peaks, which are readily indexed to the two-step Li⁺ insertion/desertion from LiMn₂O₄, as shown in Eqs. (1–2). Moreover, the positions of redox reactions are locate in range of 0–1 V at low scan rates, indicating the ESIX process has low energy consumption.



The CV curves of λ-MnO₂ electrode in 1 M LiCl, NaCl, and LiCl+NaCl aqueous solutions at 1 mV·s⁻¹ are shown in Figure 1 (b). There is no redox peaks between 0.3 to 1.2 V in single NaCl solution, and the position

of redox peaks in single LiCl solution are similar to that in LiCl and NaCl mixture solution. These results indicate that Na^+ cannot interact with the MnO_2 electrode under the experiment conditions. This is because that the diameter of Na^+ is much larger than that of Li^+ ; therefore, Na^+ cannot enter the inside structure of $\lambda\text{-MnO}_2$.

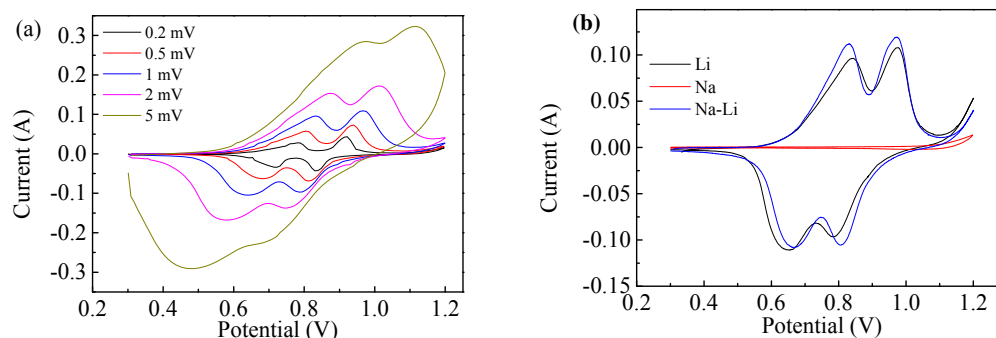


Figure 1. CV curves of a $\lambda\text{-MnO}_2$ electrode in different aqueous solution at various scan rates.

(a) In 1M LiCl solution at various scan rates; (b) In 1 M LiCl, NaCl and LiCl+NaCl solutions at $1 \text{ mV}\cdot\text{s}^{-1}$.

The concentrations of Li^+ and Na^+ in adsorption and desorption solution from 1 to 5 cycles are shown in Figure 2(a). The concentrations of Li^+ in adsorption solution decreased with increasing cycle number. Simultaneously, the concentrations of Na^+ showed almost no change. Therefore, $\lambda\text{-MnO}_2$ has a high selectivity towards Li^+ , which is consistently with the CV results. Based on the experimental results, Li^+ adsorption capacity was determined as about $2 \text{ mmol}\cdot\text{g}^{-1}$, and the selectivity coefficients of Li^+ towards Na^+ , K^+ , Ca^{2+} and Mg^{2+} are 60.14, 42.16, 53.13 and 153.4, respectively. Repeated use of the same set of electrodes ($I = 20 \text{ mA}\cdot\text{g}^{-1}$) were performed 50 times to demonstrate the reversibility and applicability of $\lambda\text{-MnO}_2$ electrode for Li^+ recovery (Figure 2(b)). The Li^+ adsorption capacity remained 82.9% of initial value after 50 cycles.

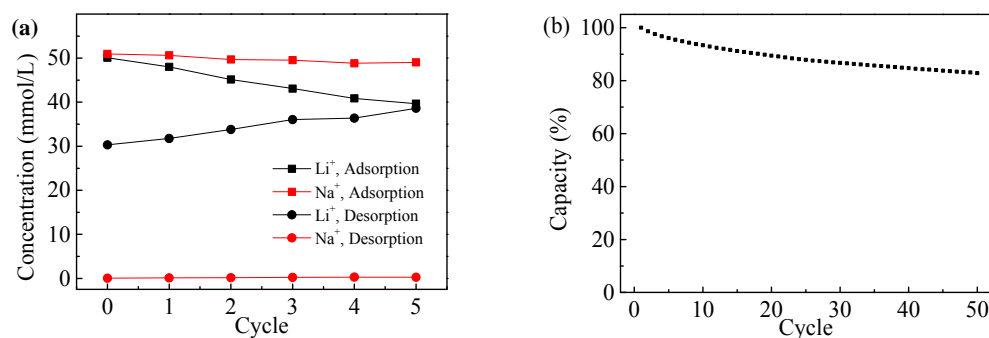


Figure 2. Electrochemical properties of $\lambda\text{-MnO}_2$ electrode.

(a) Concentrations of Li^+ and Na^+ during 5 ESIX cycles.; (b) Capacities of $\lambda\text{-MnO}_2$ electrode under 50 cycles.

4. Conclusions

CV experimental results indicate that $\lambda\text{-MnO}_2$ is a promising electrode for the recovery of Li from salt lake brine. The existence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} in brine has no significant effect on the Li^+ adsorption performance, and the selectivity coefficients of Li^+ towards Na^+ , K^+ , Ca^{2+} and Mg^{2+} are 60.14, 42.16, 53.13 and 153.4, respectively. Li^+ adsorption capacity of the MnO_2 electrode after 50 cycles is 82.9% of the initial value, indicating that the $\lambda\text{-MnO}_2$ electrode has great potential for industrial application.

References

[1] S Jewell, S.M. Kimball, U.S. Geological Survey. 2017: 100-101.

Keywords

Lithium recovery; Electrically switched ion exchange; MnO_2 ; Ion-sieve