



Technical note

Selective lithium recovery from aqueous solution using a modified membrane capacitive deionization system



Dong-Hee Lee^{a,1}, Taegong Ryu^{b,1}, Junho Shin^b, Jae Chun Ryu^a, Kang-Sup Chung^{b,*}, Young Ho Kim^{a,*}

^a Department of Chemical Engineering and Applied Chemistry, Chungnam National University, Daejeon 34134, Republic of Korea

^b Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Republic of Korea

ARTICLE INFO

Keywords:

Lithium recovery
Lithium manganese oxide
Electrosorption
Electrodesorption
Membrane capacitive deionization (MCDI)

ABSTRACT

Selective lithium recovery from aqueous solutions containing various cations (Li^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) was tested using a modified membrane capacitive deionization system consisting of a lithium manganese oxide electrode for lithium ion capturing and a carbon electrode for anion capturing. The effect of cations and their concentrations on lithium ion selectivity was investigated. The results showed that the selectivity order found in the collected solutions was $\text{Li}^+ \gg \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$. This order indicates that the ionic radius and oxidation state affect the selectivity. Approximately $0.35 \mu\text{mol/g}_{\text{-adsorbent}}$ of lithium was recovered, which is 7 times higher than that from the physisorption process under the same experimental conditions. The required energy in the recovery process was calculated as 23.3 Wh/g of lithium. The results were reproducible, and no manganese dissolution was observed during 5 consecutive recovery cycles.

1. Introduction

Hydrogenated manganese oxide (HMO) derived from spinel type lithium manganese oxide (LMO) has been reported to have selective adsorption properties for lithium ions among various ions (Yanagase, et al., 1983; Ooi et al., 1991; Chitrakar, et al. 2000). The adsorbed lithium is recovered from the HMO through an acid treatment process, and the HMO can be reused. These properties imply the potential utility of HMO in the process of lithium recovery from aqueous solutions such as brine, groundwater, and seawater, which contain relatively small amounts of lithium compared to other cations (Yoshizuka et al., 2002; Chitrakar et al., 2001; Umeno et al., 2002). Over the past two decades, research has been conducted on recovering lithium from solutions using HMOs (Chitrakar et al., 2001; Umeno et al., 2002; Wang et al., 2009; Shi et al., 2011). Except for some studies that have reported the synthesis of adsorbents, most reports focus on the fabrication of composites by mixing powdered HMO with one or more polymeric binders (Sagara et al., 1989; Chitrakar et al., 2000; Chung et al., 2008; Umeno et al., 2002; Shi et al., 2011; Park et al., 2014; Nisola et al., 2015). This composite material has the advantage that it can easily be collected from the solution after the adsorption process. However, due to the use of the polymer binder, the access of lithium ions to the adsorption site is difficult and as a result, the adsorption efficiency is reduced. In

addition, manganese dissolution from HMO in the acid treatment process for the recovery of the adsorbed lithium remains a challenge for the practical application of HMO (Wang et al., 2009; Tian et al., 2010; Lawagon et al., 2016).

On the other hand, the capacitive deionization (CDI) process is an electrochemical desalination technique using the principle that ions are accumulated in an electric double layer (EDL) when a low adsorption potential is applied (Johnson and Newman, 1971; Farmer et al., 1996; Welgemoed and Schutte, 2005). Various carbons (activated carbon, carbon nanotubes, and graphene, etc.) with a high adsorption capacity and conductivity are normally used as electrode materials. These carbon materials have excellent electrochemical properties but little selectivity for specific ions. We have previously suggested an asymmetric HMO-activated electrode system in which one carbon electrode is replaced by an HMO for lithium recovery from a singular lithium-containing solution (LiOH and LiCl) by utilizing the principle of a CDI system (Ryu et al., 2013, 2015). From the results, the electro-based lithium recovery process showed an enhanced adsorption rate compared to the physisorption process. It was also found that the adsorbed lithium ions can be recovered under a reverse electrical potential without manganese dissolution.

In this work, the possibility of the selective recovery of lithium ions from aqueous solutions containing various metal ions such as K^+ , Na^+ ,

* Corresponding authors.

E-mail addresses: ksc@kigam.re.kr (K.-S. Chung), yh_kim@cnu.ac.kr (Y.H. Kim).

¹ Dong-Hee Lee and Taegong Ryu contributed equally to this work.

Mg^{2+} , and Ca^{2+} was evaluated using the same HMO-ACP configuration. More specifically, the effect of cations and their concentrations on lithium ion selectivity was investigated. The physical and electrochemical properties of the HMO electrode after electrosorption and electrodesorption were also characterized by XRD, SEM, BET, Raman, and linear sweep voltammetry analyses to better understand the adsorption/desorption phenomena of lithium ions on the HMO structure under an electrical potential.

2. Materials and methods

2.1. Preparation of the electrodes and assembly of the test cell

Spinel-type lithium manganese oxide (LiMn_2O_4) was prepared through a solid-state reaction using Li_2CO_3 (99%, Aldrich) and MnCO_3 (99.9%, Aldrich) as the reactants. After being calcined at 500 °C for 4 h in air, the synthesized lithium manganese oxide powder was immersed in a 0.5 M HCl solution and stirred to extract the lithium ions through an H^+ - Li^+ exchange reaction, which yielded a lithium-selective adsorbent. After acid treatment, the resulting adsorbent obtained was the HMO. The adsorbent electrodes were prepared by mixing HMO (75% in dry weight), polyvinyl alcohol (PVA, molecular weight of 31,000–50,000, 98–99% hydrolyzed, Sigma-Aldrich) and glutaraldehyde (GA, 25 wt% solution in water, Samchun). The mixture was coated onto a graphite sheet (Sigaflex®, SGL Carbon). After drying, a HCl solution was sprayed over the electrode, dried in a vacuum oven at 60 °C and pressed. The amount of adsorbent loaded on the electrode (10×10 cm in size) was approximately 1.0 g per sheet.

The counter electrode was prepared by the following procedure. Activated carbon powder (ACP, specific surface area of 1260 m^2/g , Daedong AC) was mixed with polyvinylidene fluoride (PVdF, Sigma-Aldrich) dissolved in dimethylacetamide (DMAc, Sigma-Aldrich) and coated onto a graphite sheet. After coating, the electrode was dried in a vacuum oven at 50 °C overnight and pressed using a roll presser. The resulting carbon layer was approximately 200 μm thick, and the amount of activated carbon loaded on the graphite sheet (10×10 cm in size) was approximately 1.0 g per sheet. The resulting ACP content of the electrode was 85% in dry weight.

The cell was assembled between two Plexiglas plates in the following configuration: lower plate, ACP electrode, anion exchange membrane (AEM, Neosepta AMX, Tokuyama Soda Corp.), dielectric spacer (porous urethane foam, 200 μm thick), HMO electrode, and upper plate. The distance between the two electrodes was approximately 150 μm . The upper plate was designed with two inlet holes positioned at diagonally opposite corners and one outlet hole with an inner diameter of 2 mm at the center so that a solution could flow in and contact the inner sides of the electrodes.

2.2. Characterization

The crystal structure of the obtained adsorbent was determined by X-ray diffraction analysis (XRD, D/MAX 2200, Rigaku), and the morphology was examined by analytical scanning electron microscopy (SEM, S-4700, Hitachi). Analyses of the surface area and pore volume were performed using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods with a surface area and porosity analyzer (BELSORP-mini II, BEL Inc.). Raman spectroscopy was performed using a UniRAM (UniNanoTech) instrument under excitation by a 532 nm laser (MSL-III-532, single longitudinal mode laser, Changchun New Industries), and the laser power density was kept at 0.23 W/cm^2 to avoid damaging the HMO. The electrochemical characterization of the system was carried out by linear sweep voltammetry (LSV) using a Zive MP2 (WonATech Corp.) in the HMO and ACP electrode system.

2.3. Selectivity test

Batch-mode experiments were conducted to study the effect of the type of cation on the Li^+ selectivity. LiCl, NaCl, KCl, MgCl_2 , and CaCl_2 were purchased from Samchun Pure Chemical and used without further purification. The pH of the feed solution was adjusted to approximately 7.5 by adding hydrochloric acid or a hydroxide solution of the metal to eliminate the influence of pH during electrosorption.

The lithium selectivity from binary mixture solutions of lithium ion and another cation was tested as follows. First, the solution from the influent reservoir was supplied to the test cell for 40 min at a constant flow rate of 20 mL/min using a peristaltic pump (Masterflex L/S, Cole-Parmer Co.). The electrosorption time was confirmed by the conductivity and current changes during the electrosorption process (see Fig. S1). At the same time, a cell potential of -1.0 V was applied using a potentiostat device (Zive MP2) so that the adsorbent electrode was negatively charged and the carbon electrode was positively charged. After the electrosorption process, deionized water was supplied to the test cell without applying the cell potential, thus removing the residual ions from the electrode. Finally, under flowing deionized water, a cell potential of 3.5 V was applied inversely so that the adsorbent electrode was positively charged and the carbon electrode was negatively charged. The concentrations of the ions in the effluent solution were determined using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Optima 7300D, PerkinElmer Inc.). The amount of desorbed lithium and other cations after the adsorption/electrosorption and washing processes was calculated as follows:

$$Q = CV/m \quad (1)$$

where Q is the amount of metal ions desorbed ($\text{mmol}/\text{g}_{\text{adsorbent}}$), C is the concentration of metal ions (mmol/L) released into the deionized water in the electrodesorption step, V is the volume of the collected solution, and m is the mass of the adsorbent in the electrode. All experiments were repeated 3 times, and the concentration of ions contained in the electrodesorption process was calculated as an average value.

The effect of various cations in solution on the Li^+ ion selectivity was also determined. The concentrations of Li^+ , Na^+ , K^+ , Mg^{2+} , and Ca^{2+} in the brine were 2.1×10^2 , 3.3×10^5 , 4.6×10^2 , 4.0×10^2 , and 7.75 mmol/L , respectively, which is the same cation concentration as at Salar de Atacama in Chile (Lee et al., 2013).

3. Results and discussion

3.1. Characterization of the HMO electrode after electrosorption and electrodesorption processes

Fig. 1 shows the XRD pattern of the HMO electrode after electrosorption and electrodesorption. The three major peaks at 2θ corresponding to the (111), (311) and (400) crystal planes of the spinel structure of LiMn_2O_4 (JCPDS no. 35-0782) are 18.66, 36.52 and 44.41°. After electrosorption, the 2θ values were shifted to 18.51, 36.14, and 44.06°. According to the literature (Ooi et al., 1989), after inserting lithium into λ - MnO_2 , 2θ shifts to lower values with increasing lithium uptake ratio. Interestingly, the 2θ values after electrodesorption were again shifted to 18.64, 36.32, and 44.26°. These values indicate the insertion of lithium ion into HMO structure and its removal by the application of electrical potentials. However, the peaks observed after electrodesorption were not completely returned to their original position. These results indicate that the adsorbed lithium ion was not completely desorbed in this electrodesorption condition. We previously reported that the adsorbed lithium ions in the adsorbent electrode desorbed by applying the electrodesorption potential, although the desorbed amount was approximately 45% less than that obtained by acid based desorption process (Ryu et al., 2013). The low desorption efficiency is presumably due to the low conductivity of the deionized

Download English Version:

<https://daneshyari.com/en/article/6476799>

Download Persian Version:

<https://daneshyari.com/article/6476799>

[Daneshyari.com](https://daneshyari.com)