



Lithium recovery system using electrostatic field assistance



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ABSTRACT

In this study, we suggested a novel recovery system for lithium using electrostatic field assistance (EFA) to improve the conventional adsorption method, which requires a long adsorption time. To verify our suggested concept, a lithium selective electrode was prepared using a lithium selective adsorbent and hydrophilic PVA binder, and a test set was fabricated by modifying the conventional membrane capacitive deionization (MCDI) system. The adsorption performance by EFA was compared to that of the conventional adsorption process. The results showed that the adsorption performance by EFA increased with increased cell potential up to 1.0 V and initial lithium concentrations. The adsorption performance for lithium by EFA was superior to that by physisorption in the range of initial lithium concentration tested. The adsorption time to reach an equilibrium state by EFA was reduced compared to that of physisorption, which showed the acceleration effect of EFA. The suggested system also showed good reproducibility and durability during the repeated adsorption/desorption cycles. This system could be an alternative recovery system for lithium from aqueous solution containing lithium ions.

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1. Introduction

Lithium is a crucial resource used in the raw materials of secondary batteries, light aircraft alloys, catalysts and fuel for nuclear fusion reactions (Dang and Steinberg, 1978; Epstein et al., 1981; Hartley et al., 1978). It is expected that the exhaustion of lithium resources due to the rapid increase in its demand will act as an obstacle for human civilization in the near future. There have been many efforts to develop recovery technology for lithium from various sources, such as ore, salt lake and seawater (Chitrakar et al., 2001). Of these, the recovery technology of lithium by the adsorption method from seawater has received much attention because seawater is a vast source containing approximately 2.5×10^{14} kg of lithium, although the average lithium concentration is low (0.17 mg/L) (Abe et al., 1985; Chitrakar et al., 2001; Miyai et al., 1988).

Inorganic adsorbents with high selectivity for lithium ions in aqueous solution have been investigated, of which spinel-type lithium manganese oxides, such as LiMn_2O_4 , $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$, and $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$, are considered to be promising lithium-selective adsorbents (Ammundsen et al., 1995; Feng et al., 1992; Ooi et al., 1990; Sagara et al., 1989; Wang et al., 2006). However, there are drawbacks to overcome for the practical use of the lithium recovery technology using these adsorbents because the recovery of the powder type adsorbent after the application is difficult and the adsorption process demands a long time, from a few

days to a few weeks, when the concentration of lithium is low. In addition, the use of toxic agents such as hydrochloric acid is inevitable in the desorption process. This may lead to environmental problems and a decrease in the recovery efficiency because the addition of a large amount of alkali-solution to adjust the pH in the following separation step of the lithium ions is required after the desorption process (Shi et al., 2011).

In our previous work (Ryu et al., 2013a), we suggested an alternative desorption process for lithium ions using EFA without acidic solution after the adsorption reaction of the lithium ions in which a modified MCDI technology with the adsorbent membrane was applied. Using EFA, the required time in the desorption process decreased, and the procedure was simplified. However, a drawback in this system with a conventional adsorption process by ion-exchange reaction remains due to the slow adsorption reaction. To accelerate this adsorption reaction, we also applied EFA in the adsorption process. In the proposed adsorption method, the adsorption reaction of lithium ions can be accelerated by the enrichment of lithium ions onto a lithium adsorbent layer due to EFA, as depicted in Fig. 1. Other ions that are not adsorbed onto the adsorbent layer are removed by flushing them with distilled water under no EFA. Finally, the concentrated lithium solution is obtained by desorption with EFA, as mentioned in our previous work (Ryu et al., 2013a).

The objective of this study is to verify the feasibility of the proposed concept. A spinel type of LiMn_2O_4 was chosen as the lithium-selective adsorbent. A test set was fabricated by modifying that of conventional MCDI system, in which, the modified test set consisted of the carbon electrode, adsorbent electrode, anion exchange membrane and a dielectric spacer. The effect of various experimental parameters such as the

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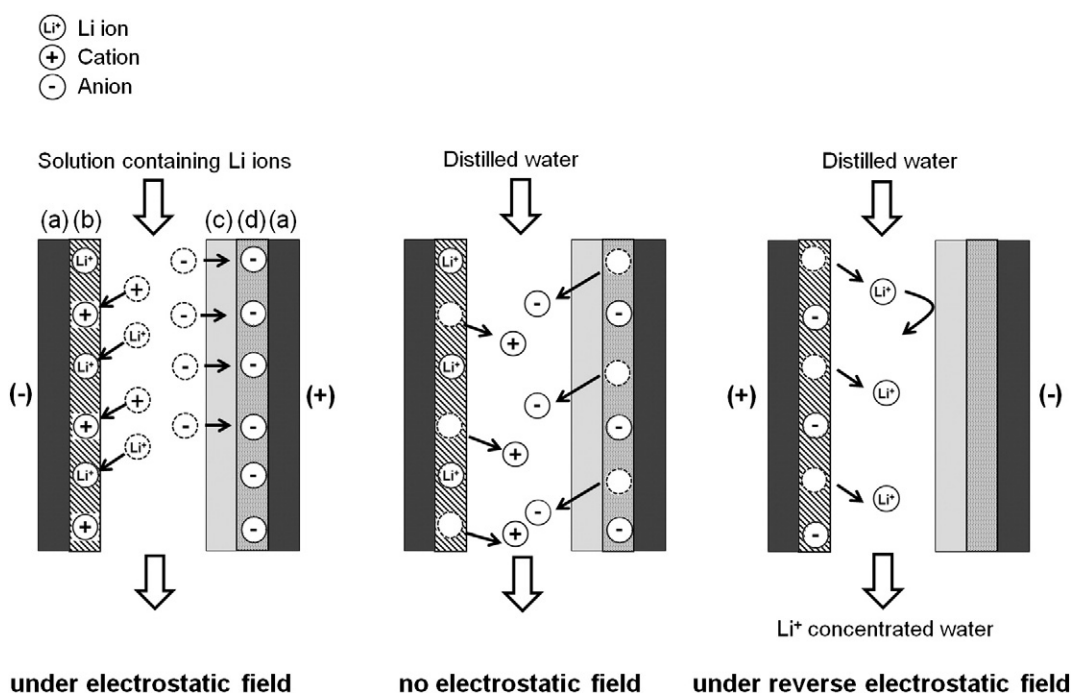


Fig. 1. The conceptual diagram of the proposed lithium recovery process using EFA: (a) current collector, (b) lithium-selective adsorbent layer, (c) anion exchange membrane, and (d) activated carbon layer.

initial concentrations of the lithium ions and the applied cell potentials were examined. The experimental results were compared to that of the conventional adsorption process without EFA under identical conditions.

2. Experimental methods

2.1. Preparation of the electrodes

A spinel-type lithium manganese oxide (LMO, LiMn_2O_4) was prepared by a conventional solid-state reaction using Li_2CO_3 and MnCO_3 as reactants (Ryu et al., 2013b). The resulting LMO powder was then immersed and stirred in a 0.5 mol/L HCl solution to extract the lithium ions by ion exchange reaction, which yielded the lithium-selective adsorbent. Polyvinyl alcohol (PVA, M_w 31,000–50,000, 98–99% hydrolyzed, Sigma-Aldrich) was chosen as a binder for the adsorbent powder because it is known as a typical hydrophilic polymer for facilitating the migration of ions onto the surface of electrodes in aqueous solution and because the cross-linked PVA polymer is not dissolved by water (Park and Choi, 2010; Yeom and Lee, 1996). PVA solution was prepared by dissolving PVA powder in deionized water. The adsorbent powder (particle size $<2\ \mu\text{m}$) was mixed with the PVA solution to give a total binder content of 15 wt.%. Glutaraldehyde (GA, 25 wt.% solution in water, Samchun Chemical), a cross-linking agent, was added into the mixture of adsorbent powder and PVA solution and was vigorously stirred at room temperature for 1 h to obtain a homogeneous slurry. The resulting slurry was then coated onto a graphite sheet (150 μm thickness, Dongbang Carbon Co.) of the adsorbent electrode with a thickness of 250 μm using a doctor blade equipped with an automatic speed controller and was then dried in a vacuum oven at 50 °C to remove the water. HCl solution was sprayed over the dried electrode to accelerate the esterification between PVA and GA. It was then uniformly pressed using a roll press. The resulting adsorbent layer was approximately 200 μm thick, and the loaded amount of adsorbent on the graphite sheet was approximately 1.0 g per 100 cm^2 (10 cm \times 10 cm in size). To prepare the carbon electrode having a high capacitance as a cathode of this system (Kim and Choi, 2010), the activated carbon powder (ACP, P-60, specific surface area = 1260 m^2/g , Daedong AC Corp.)

and poly(vinylidene fluoride) (PVdF, Sigma-Aldrich) dissolved in di-methylacetamide (DMAc, Sigma-Aldrich) were mixed to give a total binder content of 15 wt.% and coated onto the graphite sheet using a doctor blade. The coated electrode was dried in a vacuum oven at 50 °C overnight to remove the organic solvent. After heating the dried electrode at 90 °C, it was uniformly pressed using a roll press. The resulting carbon layer was approximately 200 μm thick, and the loaded amount of activated carbon on the graphite sheet was approximately 0.9 g per 100 cm^2 (10 cm \times 10 cm in size).

The crystalline forms of the obtained adsorbents were determined using an X-ray diffractometer (XRD, D/MAX 2200, Rigaku), and the morphology was examined using analytical scanning electron microscopy (SEM, S-4700, Hitachi).

2.2. Fabrication of the test cell

The test cell was fabricated by modifying the conventional MCDI cell that consists of carbon electrodes, an anion exchange membrane and a dielectric spacer (Biesheuvel and Van der Wal, 2010; Kim and Choi, 2010; Li et al., 2008). Fig. 2 shows a schematic diagram of the test cell and the experimental device. The test cell consisted of four parts, i.e., the carbon electrode, adsorbent electrode, anion exchange membrane (Neosepta AMX, Tokuyama Soda Corp.) and a dielectric spacer (porous urethane foam, 200 μm thick). Each part was assembled between two Plexiglas plates as follows: lower plate/carbon electrode/AEM/dielectric spacer/adsorbent electrode/upper plate. The resulting distance between the two electrodes was approximately 150 μm due to the flexibility of the dielectric spacer. The upper plate was designed to give two inlet holes positioned diagonally opposite at each corner and one outlet hole at the center of the plate with an inner diameter of 2 mm so that solution can flow in contact with the inner sides of the electrodes. The solution was supplied to the test cell using a peristaltic pump (Masterflex L/S, Cole-Parmer Co.). A cell potential was applied using a potentiostat device (Zive MP2, WonATech Corp.). The conductivity of the effluent solution was automatically measured at a time interval of 2 s using a conductivity meter (Vernier Software & Technology) with a data acquisition system. The ion concentration of the samples collected in

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