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Electrochemical sodium ion impurity removal system for producing high purity KCl

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ABSTRACT

Potassium hydroxide (KOH) is widely used in various industrial fields, especially KOH used in electronic fields has a high economic value because it requires a high purity of 99% or more. At present, KOH is commercially mass-produced by an electrolysis process of potassium chloride (KCl), and thus, the purity of KOH produced is directly influenced by the purity of the raw KCl materials. In the case of industrial raw KCl materials, the impurities are removed by crystallization because they contain sodium ion impurities. However, crystallization has a problem in that a pretreatment process is required when the concentration of the sodium ion impurities is high. In this study, we propose an electrochemical system using sodium manganese oxide (NMO) and potassium iron hexacyanoferrate (KFeHCF) which can remove sodium ions selectively from the raw KCl material used in the industrial process for KOH production. As the main results of this study, the NMO/KFeHCF system selectively removed approximately 36% of the sodium ion impurities in the industrial raw KCl solution after 3 cycles of operation. We demonstrated that the purity of KCl could be increased to 99.8% or more; thus, it was possible to produce high purity KOH with high economic value.

1. Introduction

Potassium hydroxide (KOH) is widely used as a chemical reagent required in various industrial fields such as semiconductor processing and the manufacturing of potassium compounds, pharmaceuticals and synthetic resins. In particular, the economic value of KOH used for surface etching in the field of semiconductor processing has increased because the KOH used in this field requires a high purity of 99.8% or more. At present, KOH is commercially mass-produced through electrolysis of a potassium chloride (KCl) solution; thus, the purity of KOH is directly affected by the purity of the raw KCl materials. Because the raw KCl materials used for industrial purposes contain NaCl salts as the main impurities, it requires an additional process for the purity control of KOH such as a crystallization method. However, the crystallization method cannot function effectively in a KOH solution which contains sodium ion impurities of 200 mg/kg or more (Osakabe et al., 2009). Thus, a pretreatment process to remove the sodium ion impurities for highly purified KOH production is necessary.

Electrochemical systems using battery materials can be proposed as an alternative or the pretreatment process for the crystallization method. Recently, selective ion separation systems using battery materials have been actively studied as a next generation technology. A desalination battery system based on a mixing entropy battery system using salinity difference has emerged as an environmentally friendly and energy efficient desalination technology (La Mantia et al., 2011; Pasta et al., 2012b). The technology utilizing such electrochemical battery systems has been applied not only to desalination but also to resource recovery. As a representative example, a technique for selectively extracting and recovering lithium ions from the brine has been studied (Kim et al., 2015; Lee et al., 2013; Pasta et al., 2012a). Additionally, HCDI (hybrid capacitive deionization) systems have been studied with great potential as a desalination technology for brackish water because of its simple process and high energy efficiency (Kim et al., 2016; Lee et al., 2014b). In a HCDI system, cation selective battery materials are applied with a counter carbon electrode which can lead to better deionization performance compared to the conventional CDI system (Anderson et al., 2010). Na-ion desalination (NID) systems based on sodium ion intercalating electrodes have also been studied for desalination with simulated results (Smith and Dmello, 2016). Although these electrochemical systems with battery materials are expanding their applications based on their selective ion separation function, there are few studies on the purity control or on the selective

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removal of ion impurities. A selective ion separation system can be applied to the impurity removal process in a situation where specific ions become impurities. If sodium ion impurities are to be selectively removed, sodium ion battery materials which are known to selectively intercalate and deintercalate sodium ions can be used (Sauvage et al., 2007b).

When removing sodium ion impurities in the presence of potassium ions, Prussian blue analogues (PBAs), which have an open framework structure capable of capturing cations such as Na^+ and K^+, can be used as a counter electrode (Lee et al., 2014a; Lu et al., 2012; Wessells et al., 2011). Prussian blue is commonly used as a pigment or medicine to adsorb cesium; however, the application of PBAs has been extended to aqueous battery materials because of their low cost and stability in an aqueous system (Karyakin, 2001; Pasta et al., 2012c; Su et al., 2017; Trócoli et al., 2015). It has been studied for electrochemical desalination by rocking chair desalination battery (Lee et al., 2017) and cation intercalation desalination (CID) system (Porada et al., 2017; Smith, 2017) designed through the combination of PBAs electrode and ion exchange membrane. In this study, the principle of a rocking chair battery system was applied to a selective sodium ion removal process to improve the purity of a KCl solution (Scrosati, 1992). It is expected that the electrochemical system consisted of a sodium manganese oxide (NMO) electrode for capturing sodium ions and a potassium iron hexacyanoferrate (KFeHCF, a kind of PBAs) electrode for capturing potassium ions can selectively remove sodium ions.

This study demonstrated that an electrochemical system can be applied as an impurity removal technique in the manufacturing industry for potassium products as a simple, energy efficient and low cost method. Thus, this study investigated how the NMO/KFeHCF system works with a specific ion exchange behavior. The applicability to an actual industry was also tested using a raw material (~4 M KCl) that is used in the industrial process for KOH production.

2. Materials and methods

2.1. Material synthesis

The sodium manganese oxide ($Na_{0.44}MnO_2$, NMO) powder used in this study was synthesized by a solid-state reaction (Lee et al., 2014b). Na_2CO_3 (Sigma-Aldrich) and $MnCO_3$ (Sigma-Aldrich) were mixed well at a 0.242:1 M ratio. The precursor of the solid reaction was heated in an electric furnace (MF-12GH, JEIO Tech) at 500 °C for 5 h under atmospheric condition. The mixing process was repeated one more time and then heated at 900 °C for 12 h under atmospheric condition. The obtained material was ball-milled and filtered to obtain the NMO powder. The NMO powder was analyzed by X-ray powder diffraction (XRD, D8 Discover) and scanning electron microscopy (SEM, FESEM, JEOL JSM 6700 F).

Potassium iron hexacyanoferrate ($K_xFe(Fe(CN)_6)$, KFeHCF) powder used in this study was synthesized by a controlled crystallization reaction. 100 ml of a mixed solution of $FeCl_2{\cdot}4H_2O$ (0.05 M, Sigma-Aldrich) and potassium citrate (0.4 M, Sigma-Aldrich) and 100 ml of potassium hexacyanoferrate (II) (0.05 M, Sigma-Aldrich) were slowly dropped at the same time and stirred for 24 h. The temperature was kept at 25 °C, and KFeHCF powder was obtained by filtering the submerged blue material. The composition of synthesized powder was analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AES, VARIAN 730ES). The K/Fe molar ratio of KFeHCF was analyzed to be 1.73/1, indicating that the synthesized material has a 'Potassium-rich' form. The physical characterization of the KFeHCF powder was analyzed by XRD and SEM methods.

2.2. Electrode fabrication

The NMO electrode was prepared with the following procedures. $Na_{0.44}MnO_2$ active material, carbon black (Timcal) and a binder (polytetrafluoroethylene, PTFE, Sigma-Aldrich) were mixed at a mass ratio of 86:7:7. The sample was placed in a roll-presser to produce a sheet-type electrode with a 250 μm thickness. The electrode was placed in a vacuum oven and dried at 80 °C for 12 h to evaporate the remaining solvent.

The KFeHCF electrode was also fabricated with the following procedures. KFeHCF active material, carbon black (Timcal) and a binder (polytetrafluoroethylene, PTFE, Sigma-Aldrich) were mixed at a mass ratio of 7:1:2. The method for manufacturing the sheet-type electrode was the same as described above.

2.3. Electrochemical analysis

The Cyclic voltammetry (CV) and galvanostatic charging/discharging were performed to investigate electrochemical characteristics of the NMO and KFeHCF electrodes. The CV was measured by a potentiostat/galvanostat (PARSTAT 2273, Princeton Applied Research) device using a three electrode cell with a working electrode (NMO or KFeHCF), counter electrode (Ag/AgCl) and a reference electrode (Ag/AgCl electrode, sat'd KCl). A glass microfiber filter (Whatman) was used as a separator and the scan rate was 1 mV/s in a 1 M NaCl and 1 M KCl solution.

The galvanostatic charging/discharging was done with a battery cycler (WBCS3000, WonA Tech Co.) using a three electrode cell with a working electrode (NMO or KFeHCF), counter electrode (Ag/AgCl) and a reference electrode (Ag/AgCl electrode, sat'd KCl). A glass microfiber filter (Whatman) was used as a separator and the current density was 0.01 A/g in a 1 M NaCl solution (In case of NMO electrode) and 0.1 A/g in a 1 M KCl solution (in the case of the KFeHCF electrode).

2.4. Sodium ion removal performance test

The NMO and KFeHCF electrodes were cut into a 2.5 × 3.5 cm shape and attached to a titanium plate as a current collector with a carbon adhesive. The NMO electrode was charged to 0.9 V (vs. Ag/AgCl, sat'd KCl) to remove the sodiums ion in the electrode. Fig. 1 schematically shows the NMO/KFeHCF system used in this study. The operation process of the system consists of four steps. The main steps are the sodium ion removal step (1st step) and electrode regeneration step (3rd step). The 2nd and 4th steps are the process of replacing the solution. The system was operated in a three electrode mode using NMO as a working electrode, KFeHCF as a counter electrode and Ag/AgCl (sat'd KCl) as a reference electrode.

During the sodium ion removal step (1st step), sodium ions in the target KCl solution were removed in a current condition of 2.625 mA ($0.3\ mA/cm^2$) by connecting the NMO electrode without sodium ions and the KFeHCF electrode containing potassium ions. As a target KCl solution, 20 ml of a mixed solution (20 mM NaCl and 40 mM KCl) and the industrial KCl solution (~4 M KCl) containing 20 mM NaCl as impurities were used. The industrial KCl solution is an actual raw material used in the KOH production process (provided by UNID company, Republic of Korea) and NaCl is the largest impurity component of it. In the 2nd step, the target solution was replaced with the reservoir solution (20 mM KCl solution). In the electrode regeneration step (3rd step), a current of 2.625 mA ($0.3\ mA/cm^2$) was applied in the opposite direction to that of 1st step, so that the sodium ions inserted into the NMO electrode were released, and the potassium ions were inserted into the KFeHCF electrode. Steps 1 to 4 represent 1 cycle, and several cycles can be operated continuously to remove sodium ions repeatedly. For the system operation, a battery cycler (WBCS3000, WonATech Co.) was used and the cation concentration was measured by ion chromatography (IC, DX-120, DIONEX).

The coulombic efficiency is calculated according to the following equation;