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Research Article

Concentrating and Rejecting Lithium Ion Using Forward and Reverse Electro-nanofiltration

Nyoman Agus Budi Hanifan[1], Sutijan[1], Indra Perdana[1], Himawan Tri Bayu Murti Petrus[1,2], Yayat Iman Supriyatna[3], Agus Prasetya[1,2*]

[1] Department of Chemical Engineering (Sustainable Mineral Research Group), Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika No. 2 Kampus UGM Bulaksumur, D.I. Yogyakarta 55281, Indonesia

[2] Unconventional Georesources Research Group, Faculty of Engineering, Universitas Gadjah Mada, Jalan Grafika No. 2 Kampus UGM Bulaksumur, D.I. Yogyakarta 55281, Indonesia

[3] Research Center of Mining Technology, National Research and Innovation Agency (PRTPB-BRIN), Jln. Ir. Sutami km 15, Tanjung Bintang, South Lampung 35361, Indonesia.

*Corresponding Author: aguspras@ugm.ac.id

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Abstract: The demand for lithium for lithium-ion batteries (LIB) has increased due to the raised usage of electric cars (EVs) and hybrid electric vehicles (HEVs) to lower CO_2 emissions. The use of LIBs is not exclusively confined to EV and HEV applications. LIBs play a crucial role in capturing and storing energy generated from renewable sources, including solar and wind, highlighting their importance in advancing sustainable energy technologies. Therefore, effectively concentrating lithium (Li^+) containing lithium-ion is crucial for recovering Li^+ from brine or repurposing battery effluent to meet the demands for producing LIB. Electro-nanofiltration is one of the convincing methods because of its low energy consumption and cost compared to other filtration methods. In this paper, a low concentration of Li^+ (78 ppm) and a high concentration of Na^+ (2200 ppm) solution will be fed into the nanofiltration module. The nanofiltration membranes used are NF 1 and NF 2 from Membrane Technology (Beijing) Co., Ltd., with a forward electric field (EFs), reverse (EFs), and no electric field conditions. The experimental with 5 bar pressure findings show that a high concentration of Na^+ solution has a high rejection with NF 1 membrane without EF 40%, rate compared with a low concentration of Li^+ solution with NF 1 10% rejection. The presence of EFs significantly influences rejection rates, with NF 2 membrane in Forward EF configuration, Na^+ solution has a -327% rejection which has dramatic decrease than the normal filtration 40% rejection.

Keywords: Lithium-ion batteries, Li^+ solution, Membranes, Electro-nanofiltration, Rejection.

1. Introduction

Lithium-ion batteries (LIBs) are crucial to achieving the net zero emission target. They are the primary energy source of electric vehicles (EVs) and hybrid electric vehicles (HEVs) or energy storage from renewable sources[1]. LIBs are the best choice of energy sources and storage because of their advantages, such as long-life cycles (400-1200 cycles), high charge/discharge efficiency (80-90%), high energy density (250-693 Wh/L), and resistance to high temperatures [1–3]. LIBs mainly were used for personal computers (40%), mobile phones (35%), EVs (16%), HEVs (4%), E-bicycles (4%), and energy storage (1%) [4]. Technological advances continue to drive the production of more LIBs, and the International Energy Agency (IEA) predicts that 50% of cars made and sold in 2050 will be electric cars.

Current EVs require approximately 4 kg of lithium for a battery pack with a 20-kWh capacity, which costs 6,000 to 12,000 US$ [5].

The limited reserves of lithium worldwide are an issue because lithium is widely used in various fields, such as glass, pharmaceuticals, ceramics, lubricants, and waste treatment. According to the United States Geological Survey (USGS), lithium consumption is mainly used for batteries (87%), ceramics and glass (4%), lubricating grease (2%), air treatment (1%), medical (1%), continuous casting mold flux powders (1%), and others (4%) [6]. Lithium demand in the IEA scenario, in which an estimated 50% of vehicles produced in 2050 are EVs, has risen dramatically compared to the scenario with constant EV demand [5].

Lithium can be extracted from various sources, including mineral rocks, brine, seawater, claystone, and geothermal brines[7]. Due to continued exploration, lithium is increasingly being discovered. According to the latest report by the USGS, in 2024, the world's lithium reserves are around 105 million tons. The largest lithium reserves in the world are in Bolivia (23 million tons), Argentina (22 million tons), and the United States (14 million tons)[6]. Another source of lithium is from spent LIBs, the high demand for lithium for LIBs to achieve net zero emissions will also result in many disposable LIBs [8]. By 2030, there will be 2,140 kilotons of disposable LIBs from electronics using LIBs, EVs, and HEVs. [9]. LIBs recycling using the hydrometallurgy process still produces waste containing quite a lot of lithium, similar to the concentration in brines under 99 ppm[10, 11].

Nanofiltration (NF) membranes are excellent methods for sifting out divalent or multivalent ions while allowing monovalent ions to pass through the membrane pores at low pressure and high permeability[12]. In general, the separation mechanisms in NFs only rely on routine separation actions, such as pore filtration (ionic convection) and electrostatic repulsion (electromigration), resulting in less efficient separation. Electric field (EF) assisted NF is an innovative separation method that increases the electrostatic repulsion in the system[13].

This research investigates the separation performance of a lithium and sodium salt solution using an NF with and without the presence of EF. The ion composition used in this research is based on the composition of lithium ferro-phosphate (LFP) battery waste from the hydrometallurgical process.

2. Materials and Methods

2.1. Reagents and materials

The feed solution used LiOH 98% and Na2SO4 99% analytical grade produced by Merck & Co, Inc. reagents, and 1 M HCl was used as a pH adjuster. NF 1 and NF 2 membranes was purchased from RisingSun Membrane Technology (Beijing) Co., Ltd., Titanium Ir-Ru electrode mesh from Suzhou Shuer Tai Industrial Technology Co., Ltd., and demineralized water.

2.2 *Preparation of membranes and feed*

To achieve a stable flux, the membrane will be soaked in demineralized water for 24 hours before the experiment. The feed solution used for this experiment uses synthetic LFP battery wastewater from the hydrometallurgy process. Each salt is dissolved in demineralized water to prepare the feed solution in a single salt solution system.

Table 1. Cation concentration in LFP battery wastewater.

Component	Concentration (ppm)
Li^+	78
Na^+	2200

2.3 *Electro-nanofiltration system*

The electro-nanofiltration configuration used a continuous crossflow system, as depicted in Figure 1. The crossflow system's advantages over dead-end systems, such as higher stabilized flux levels, better solute rejection, better removal efficiency, low chance of fouling, and lower energy consumption, led to its selection for this experiment [14, 15]. Three different configurations used in this experiment are filtration without an electric field and filtration with forward and reverse EF. The forward electric field configuration is prepared by connecting the current source to the cathode on the permeate side, while the positive side of the current source is connected to the anode on the feed side. In contrast, the reverse

electric field is vice-versa, as shown in Figure 2. The separation process is conducted by flowing the feed solution through the membrane module at a system pressure of 5 bar with room temperature conditions (30°C). Ion separation is carried out with variations in electrical voltage of 0V and 6V of forward and reverse EF on two types of membranes, NF 1 and NF 2. When the permeate flows steadily, the DC power supply is activated to apply electric fields (EF) to the nanofiltration (NF) module under a constant voltage. The ion concentrations within the feed and permeate solution were determined through conductivity measurements using the Eutech pH 700 conductivity meter manufactured by Thermo Scientific.

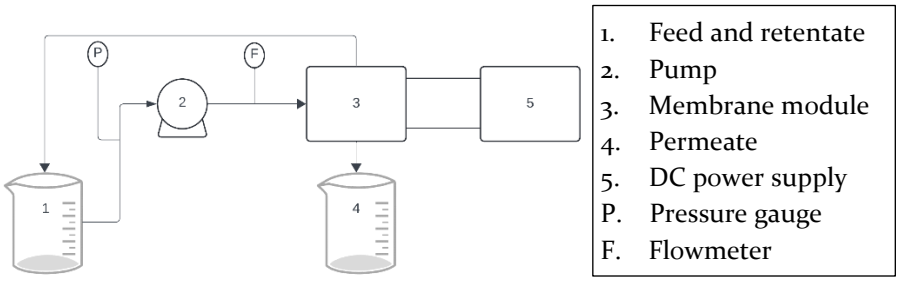
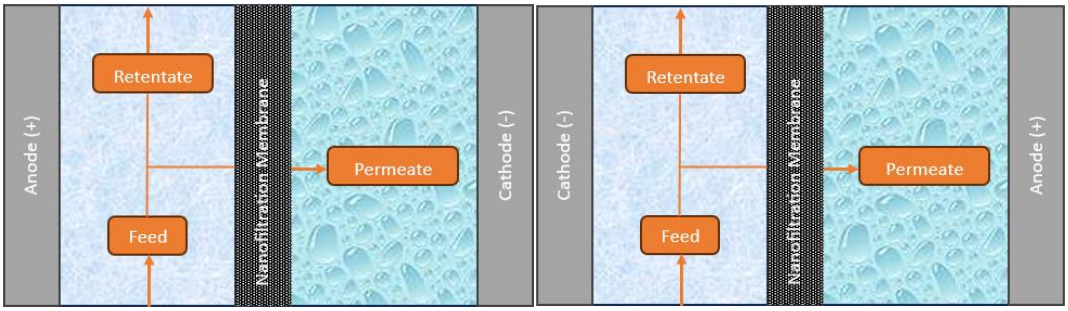


Figure 1. Schematic diagram of Electro-nanofiltration device.



(**a**) (**b**)

Figure 2. Schematic diagram inside of NF membrane module (**a**) Forward EF configuration; (**b**) Reverse EF configuration.

2.4 *Mathematical model*

Ion rejection (R, %), which measures the proportion of ions that the nanofiltration membrane rejects or retains, is a metric that shows the selectivity of ion separation across the membrane[16]. The following equation was used to determine the salt rejection (R, %)[17]:

$$R\ (\%) = \frac{(C_f - C_p)}{C_f} \times 100\% \qquad (1)$$

3. Results and Discussion

3.1. Separation efficacy of lithium-ions

Cations and water molecules will interact after the lithium-ion salt is dissolved in water. Water molecules surrounding the cation are called hydration shells, leading to the hydration of the cations [18]. Hydrated cations subsequently release water molecules when subjected to an applied electric field. Each ion has a different size when hydrated, and the tendency to release its shell is guided by its hydration-free energy. The hydration-free energy of lithium and sodium ions is shown in Table 2.

Table 2. Thermodynamic and physical data of lithium and sodium ion [19].

Ion	Molecular Weight (Da)	Ionic radius (nm)	Hydration radius (nm)	Hydration-free energy $\left({}^{kJ}/_{mol}\right)$
Li^+	6.9	0.078	0.382	515
Na^+	40	0.098	0.276	365

The presence of an electric field in the nanofiltration system significantly affects lithium rejection, as shown in Figure 3. A nanofiltration system assisted by an electric field has lower rejection in both forward and reverse EFs, primarily due to the removal of lithium hydration shells, which decreases lithium-ion size [18]. The forward electric field system exhibits the lowest rejection (-63%) in the NF2 membrane, enabling the effective concentration of lithium ions facilitated by the system's applied pressure and the electrostatic attraction from the cathode. Changes in the electric field configuration affect significant rejection, where the reversed electric field produces relatively low for both NF 1 and NF 2 (5%). This result differs from previous studies because the pressure in the system (5 bar) is more significant than the electrostatic attraction of dehydrated ions, resulting in lower rejection than conventional filtration [12].

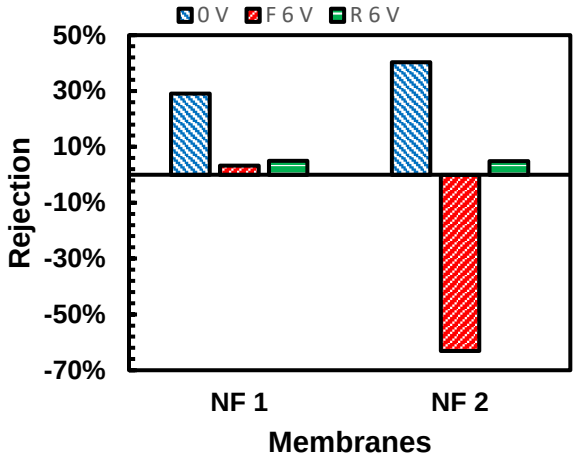


Figure 3. Lithium-ion rejection with a variation of EF on NF 1 and NF 2.

An analysis of the rejection characteristics of the two membranes reveals notable differences in their selectivity for lithium ions during filtration in the absence of an EF. Specifically, membrane NF 2 demonstrates a higher rejection rate for lithium ions compared to membrane NF 1. The presence of a forward electric field causes the rejection of NF 2 to decrease dramatically compared to NF 1. In contrast, the reverse electric field shows no significant difference between NF 1 and NF 2. The applied electric field can induce polarization of the functional groups within the membrane surface. This polarization effect significantly affects the ion separation mechanism that occurs in the membrane [16].

3.2. Separation efficacy of sodium-ions

The rejection of sodium solutions with higher concentrations differs quite significantly from the rejection of lithium solutions with lower concentrations, except for the NF 2 membrane, without the assistance of an electric field. On lithium and sodium solutions, NF 2 membrane yielded identical results with a 40% rejection rate, but NF 1 membrane produced a lower rejection rate (10%). Prior research has also indicated high rejection due to low-concentration solutions [12].

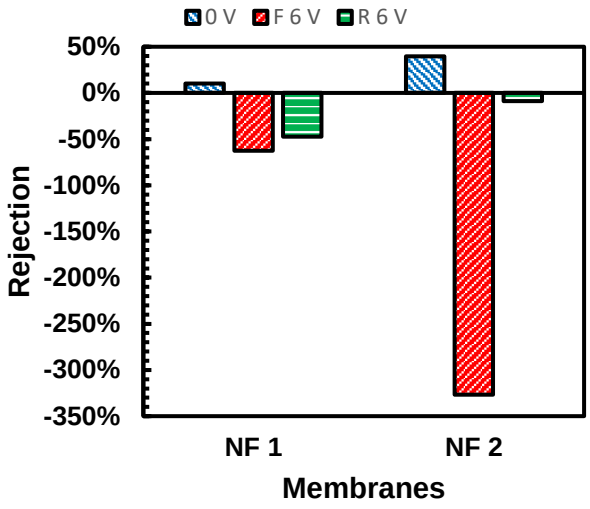


Figure 4. Sodium-ion rejection with a variation of EF on NF 1 and NF 2.

Using the forward EFs configuration, sodium ions are successfully concentrated (-327%) in the permeate due to the high concentration of sodium ions, system pressure, and electrostatic attraction [12]. Reverse EF causes sodium ions to concentrate in the permeate, which is in contrast to the lithium ions solution due to its high concentration.

4. Conclusions

The separation efficacy of lithium and sodium ions is significantly influenced by the concentration of the ions, pressure, and electric field. Separation with NF without the presence of EF was unable to reject lithium and sodium ions significantly. Forward EF configuration significantly reduces lithium and sodium ion rejection, effectively concentrating ions in the permeate. In comparison, reversed EF configuration results in lower rejection than filtration without an EF. Taking into account the one-salt solution scheme, it points to the possibility of rejecting lithium by using an assisted electric field membrane that concentrates sodium in the permeate.

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