

Simultaneous Production of Lithium Hydroxide and Sulfuric Acid from Lithium Sulphate by Conventional Electrodialysis

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The production of lithium hydroxide from lithium sulphate has gained increasing attention due to the growing demand associated with lithium-ion batteries, with electrodialysis emerging as an attractive alternative to conventional processing routes. In this study, the simultaneous production of lithium hydroxide and sulphuric acid from lithium sulphate monohydrate was evaluated using conventional electrodialysis with a configuration consisting of cation- and anion-exchange membranes. Nine experimental trials were conducted by varying the applied voltage (6, 10.5, and 15 V) and the initial lithium sulphate concentration (6, 9, and 12 g/L), employing a three-compartment system. The experimental results indicate that the highest concentrations of lithium hydroxide and sulphuric acid were obtained when operating the electrodialysis cell at an applied voltage of 15 V and an initial lithium sulphate concentration of 12 g/L. Under these conditions, concentrations of 0.153 mol/L of LiOH and 0.067 mol/L of H₂SO₄ were achieved after 240 minutes of operation. Furthermore, the results showed that the average electrical efficiency reached 75%, while the specific energy consumption was approximately 15.7 kWh/kg of LiOH produced. These findings demonstrate the feasibility of conventional electrodialysis without a bipolar membrane for the simultaneous generation of LiOH and H₂SO₄, offering an energetically competitive alternative for the utilisation of lithium sulphate solutions.

1. Introduction

The growing demand for lithium-ion batteries for applications in energy storage, electric mobility, and electronic devices has increased the need for high-purity lithium compounds, among which lithium hydroxide stands out. This compound is essential for the manufacture of high-performance cathode materials, which has driven the search for more efficient and sustainable production processes with lower environmental impact compared to conventional chemical routes (Swain, 2017; Gmar et al., 2019). In this context, the valorisation of lithium sulphate solutions derived from hydrometallurgical processes and intermediate purification streams represents a relevant technological opportunity.

The industrial production of lithium hydroxide from lithium sulphate is commonly carried out through chemical precipitation processes, such as reaction with calcium hydroxide, followed by solid–liquid separation and purification stages. However, these routes present significant disadvantages, including the generation of solid by-products, high consumption of chemical reagents, multiple processing steps, and substantial effluent treatment requirements (Grageda et al., 2020; Velásquez, 2019). In addition, sulphuric acid recovery is not typically integrated into the process, which limits the full utilisation of the chemical system and reduces overall resource efficiency.

Electrodialysis has emerged as an electrochemical technology capable of separating and transforming ionic species using ion-exchange membranes under an electric field, offering advantages such as continuous operation, reduced reagent consumption, and potential integration with lithium recycling and purification processes (Strathmann, 2010). Several studies have demonstrated its application in lithium hydroxide production, particularly through configurations incorporating bipolar membranes, which enable the simultaneous

generation of acid and base (Jiang et al., 2014; Chen et al., 2021; Wei et al., 2024). However, such configurations increase system complexity, membrane costs, and operational requirements.

Despite advances in electrodialysis using bipolar membranes, there is comparatively limited information regarding the feasibility of conventional electrodialysis configurations employing only cation- and anion-exchange membranes for the conversion of lithium sulphate into lithium hydroxide and sulphuric acid. This approach could reduce system complexity, simplify operation, and lower costs; however, it requires a detailed evaluation of process performance, conversion efficiency, and energy consumption under different operating conditions (Harrison, 2017; Asadi et al., 2024; Henderson et al., 2024). Furthermore, it is necessary to understand how variables such as applied voltage and initial salt concentration influence the simultaneous production of acid and base in three-compartment systems.

In this context, the present study aims to experimentally evaluate the simultaneous production of lithium hydroxide and sulphuric acid from lithium sulphate monohydrate solutions by means of conventional electrodialysis using cation- and anion-exchange membranes. The influence of applied voltage and initial lithium sulphate concentration on product concentration, conversion yield, and process energy consumption was investigated to identify favourable operating conditions and assess the feasibility of this electrochemical alternative.

2. Materials and Methods

2.1 Chemicals

Lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) with a purity of 99.90% was used as the feed salt in all electrodialysis experiments and was supplied by CIMATEC S.A.C. The solutions were prepared at initial concentrations of 6, 9, and 12 g/L using deionised water. Deionised water was also used to initially fill the acid and base compartments of the electrodialysis system.

The concentrations of lithium hydroxide and sulphuric acid formed during the process were determined by acid–base titration. Hydrochloric acid (HCl) was used as the titrant for lithium hydroxide quantification, whereas sodium hydroxide (NaOH) was employed for sulphuric acid determination. Phenolphthalein was used as the acid–base indicator. All reagents were of analytical grade and were used without further purification.

2.2 Electrodes

The electrolytic cell used in the experiments was equipped with a titanium anode coated with a mixture of ruthenium and iridium oxides ($\text{Ti-RuO}_2\text{-IrO}_2$) and a pure titanium cathode. The electrodes offer excellent corrosion resistance and stability, mainly due to the IrO_2 . Both electrodes had dimensions of 5 cm × 10 cm × 1.5 mm. This type of anode exhibits good electrochemical activity, particularly for oxygen evolution reactions in sulphate-containing solutions, making it suitable for electrodialysis systems where the occurrence of undesired side reactions is to be minimised.

2.3 Ion exchange membranes

A heterogeneous cation-exchange membrane (MK-40) and a heterogeneous anion-exchange membrane (MA-41), both manufactured by Schekinoazot (Russia), were used. The effective working area of each membrane was 96 cm². Prior to each experiment, the membranes were conditioned by immersion in a 5% NaCl solution for 48 h to ensure adequate hydration and swelling. The main physicochemical characteristics of the membranes used are presented in Table 1.

Table 1: Characteristics of the membranes used

Membrane	Electric resistance ($\Omega \cdot \text{cm}^2$)	Ion-exchange capacity (meq/g dry membrane)	Transport number	Thickness (μm)
MK-40 (cation)	2	2	>0.98	520
MA-41 (anion)	<11	1.6	0.98 ± 0.02	530 ± 20

2.4 Electrodialysis system configuration

The electrodialysis system consisted of a three-compartment cell arranged in a front–rear configuration. The assembly included, in sequence from the negative to the positive electrode: negative electrode (cathode), cation-exchange membrane (CEM), membrane spacer, anion-exchange membrane (AEM), and positive electrode (anode), all housed between two end plates of the cell.

The system was operated in recirculation mode for a total duration of 4 h per experiment. The voltage was supplied using an adjustable DC power supply (model UTP-3704S, 0–32 V, 0–3 A). During operation, each

compartment was connected to an external recirculation loop. The working volumes in the recirculation reservoirs were 0.5 L for each stream (salt, base, and acid).

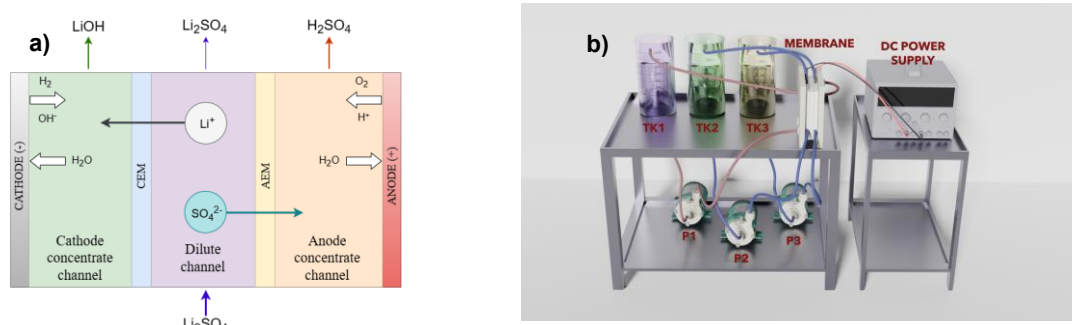


Figure 1: a) Configuration of the membrane b) Digitized schematic diagram of the experimental equipment.

2.5 Design of experiment

A full factorial design (3^2) was employed to evaluate the effects of applied voltage and initial $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ concentration, each at three levels, on lithium hydroxide and sulphuric acid production, current efficiency, and energy consumption. An increase in both factors raises the electric current and, consequently, the rate at which lithium hydroxide forms; however, this increase results in higher energy consumption. A total of nine experiments were conducted, as shown in Table 2.

Table 2: Experimental process parameters and levels

Factors	Units	Levels		
		Low	Medium	High
Voltage applied	V	6.0	10.5	15.0
Initial concentration of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$	g. L^{-1}	6	9	12

2.6 Methods of chemical analysis

Lithium hydroxide and sulphuric acid concentrations were determined by acid–base titration using 0.05 M HCl for the basic compartment and 0.05 M NaOH for the acidic compartment, with phenolphthalein as the indicator. Molar concentrations were calculated according to Eq. (1):

$$C = \frac{C_t \cdot V_t}{V_m} \quad (1)$$

where C is the concentration of the analyte (mol/L), C_t is the concentration of the titrant (mol/L), V_t is the volume of titrant consumed (L), and V_m is the sample volume (L).

2.7 Calculation of energy consumption and current efficiency

The total electrical charge transferred during each experiment was determined from the measured current as a function of time, according to Eq. (2):

$$Q = \int_0^t I dt \quad (2)$$

where Q is the transferred electrical charge (C), I is the current (A), and t is the operating time (h).

Current efficiency was calculated by considering the theoretical amount of substance produced by the applied charge, according to Faraday's law, as shown in Eq. (3):

$$\eta_c = \frac{C_{\text{LiOH}} \cdot V_{\text{LiOH}} \cdot z \cdot F}{Q} \times 100 \quad (3)$$

where η_c is the current efficiency, C_{LiOH} denotes the final concentration of LiOH, V_{LiOH} is the final volume of the LiOH solution, z corresponds to the ionic valence ($z = 1$), and F is Faraday's constant (96485 C/mol).

The specific energy consumption of the process was estimated using Eq. (4):

$$E = \frac{U \int_0^t I dt}{m} \quad (4)$$

where E is the specific energy consumption (kWh/kg), U is the applied voltage (V), and m is the mass of LiOH produced (kg).

3. Results and Discussion

The evolution of lithium hydroxide and sulphuric acid concentrations during electro dialysis is presented in Figures 2. The effect of the applied voltage (6, 10.5, and 15 V) and the initial lithium sulphate monohydrate concentration (6, 9, and 12 g/L) on the generation of both products was evaluated over 240 min of operation.

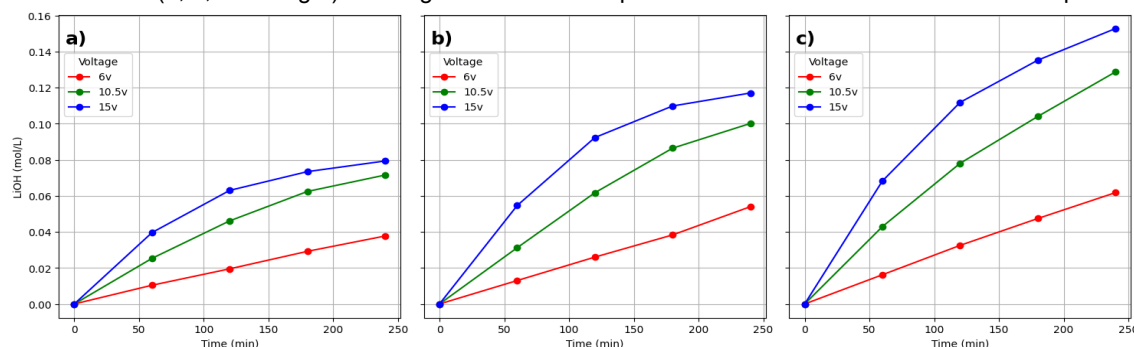


Figure 2: Evolution of LiOH concentration during electro dialysis at different voltages and initial salt concentrations a) 6 g/L; b) 9 g/L and c) 12 g/L.

Table 3 shows that increasing the applied voltage and the initial $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ concentration promotes the formation of both products, in agreement with reports for bipolar membrane electro dialysis systems in which these parameters influence process performance (Jiang et al., 2014; González et al., 2023). The LiOH/ H_2SO_4 molar ratio was higher than the stoichiometric value (≈ 2), indicating non-equimolar ionic transport.

Table 3: Final concentrations of LiOH and H_2SO_4 after 240 min of electro dialysis

Voltage (V)	$C_0 \text{ Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (g/L)	Final LiOH (mol/L)	Final H_2SO_4 (mol/L)	LiOH/ H_2SO_4 ratio
6.0	6	0.038	0.020	1.9
6.0	9	0.054	0.029	1.9
6.0	12	0.062	0.034	1.8
10.5	6	0.072	0.036	2.0
10.5	9	0.100	0.049	2.1
10.5	12	0.129	0.059	2.2
15.0	6	0.079	0.038	2.1
15.0	9	0.117	0.052	2.2
15.0	12	0.153	0.067	2.3

Figure 3 shows the evolution of the current during electro dialysis, where higher initial values were observed at higher voltages and concentrations, followed by a gradual decrease over time. This behaviour has been described in electro dialysis systems, in which the current depends on the electrical driving force as well as on transport and polarisation phenomena within the system (Jiang et al., 2014; Asadi et al., 2024).

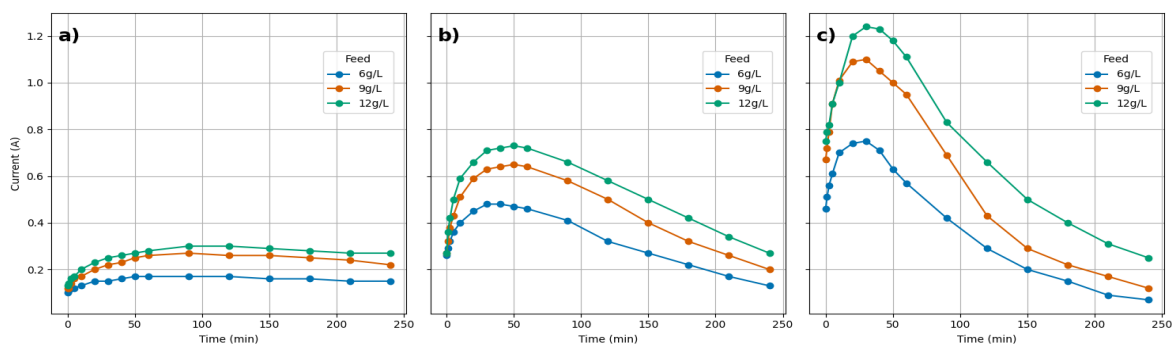


Figure 3: Evolution of the current during electro dialysis under different feed concentrations and applied voltages: a) 6 V, b) 10.5 V and c) 15 V.

Current efficiency and the total electrical charge associated with LiOH production are presented in Table 4, showing good electrochemical performance with variations depending on the applied voltage and the initial concentration, in agreement with reports for electrodialysis systems where electrical parameters influence process efficiency (Jiang et al., 2014; Grageda et al., 2020).

Table 4: Current efficiency and specific energy consumption during LiOH production

Voltage (V)	C_0 Li ₂ SO ₄ ·H ₂ O (g/L)	Total electric charge (C)	Current Efficiency η_c	Specific energy consumption (kWh/kg LiOH)
6.0	6	2292.3	0.794	8.46
6.0	9	3503.7	0.743	9.04
6.0	12	3943.3	0.756	8.89
10.5	6	4623.8	0.746	15.75
10.5	9	6577.9	0.734	16.01
10.5	12	7773.5	0.799	14.71
15.0	6	5072.2	0.754	22.26
15.0	9	7856.1	0.719	23.36
15.0	12	10191.5	0.723	23.21

The specific energy consumption of the process was evaluated based on the measured electrical charge and the applied voltage under each experimental condition, to assess the operational feasibility of the system, as shown in the final column of Table 4.

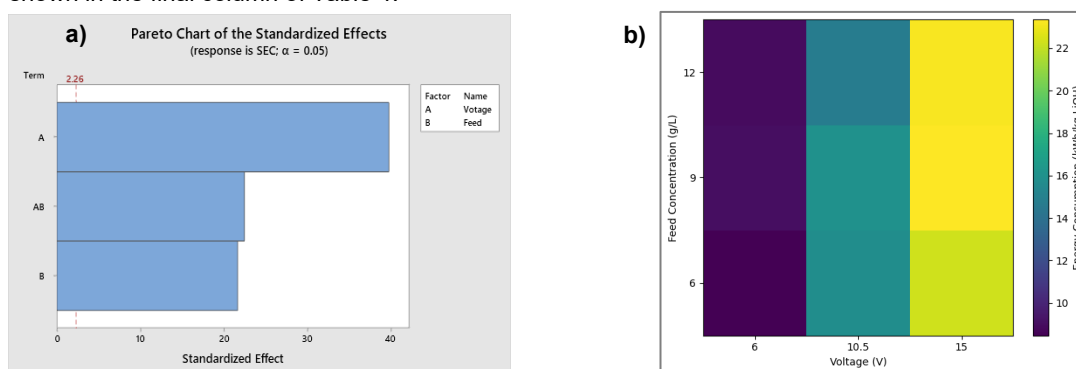


Figure 4: Effect of operating variables on specific energy consumption (SEC): a) Pareto chart of standardized effects; b) heat map of SEC versus voltage and feed concentration.

Figure 4 illustrates the influence of the operational variables on the specific energy consumption (SEC). The Pareto diagram (a) identifies voltage as the most influential factor, followed by feed concentration, while the heat map (b) confirms that SEC increases at higher voltages and concentrations. This trend is consistent with previous studies reporting increased energy consumption with higher applied potential in electrodialysis systems (Jiang et al., 2014; Grageda et al., 2020).

The results indicate that system performance is primarily governed by the applied voltage, which controls both the current and the energy consumption per unit of product. Although higher initial concentrations increase LiOH production, their impact on energy efficiency is lower compared to the effect of voltage. The progressive decrease in current suggests limitations due to concentration polarisation and increased resistance, which are typical of electrodialysis processes. Nevertheless, current efficiency remained high, indicating effective utilisation of the electrical charge. Overall, process energy optimisation should focus primarily on the operating voltage rather than on feed concentration.

4. Conclusions

In the present study, the operability of a three-compartment cell equipped with two independent ion-exchange membranes, designed to produce lithium hydroxide and sulphuric acid, was evaluated. Although higher voltages increased LiOH production, they also raised the energy demand, revealing a trade-off between productivity and efficiency. Feed concentration had a secondary effect, mainly influencing lithium recovery.

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