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► To cite this version:

Soumaya Gmar, Alexandre Chagnes. Recent advances on electrodialysis for the recovery of lithium from primary and secondary resources. Hydrometallurgy, 2019, 189, pp.105124 -. <10.1016/j.hydromet.2019.105124>. <hal-03488248>

HAL Id: hal-03488248

<https://hal.science/hal-03488248v1>

Submitted on 20 Dec 2021

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Recent advances on electrodialysis for the recovery of lithium from primary and secondary resources

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Abstract

The small world of lithium is booming due to the emergence of electric vehicles. The development of sustainable and economic processes to recover lithium from primary and secondary resources is essential to face up the expected global demand of lithium. Electrodialysis seems to be an interesting alternative among the different technologies available to produce lithium from brines, ores and spent lithium-ion batteries via hydrometallurgical route. However, electrodialysis is presently mainly used at industrial scale in water treatment. This paper gives an overview of recent advances in the development of electrodialysis technology, which could be an asset for the next generations of processes involved in lithium production.

Keywords: Brine, electrodialysis, lithium, lithium-ion batteries, separation.

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1. Introduction

Lithium is widely used for many industrial applications, including more especially lithium-ion batteries (44% of the global production in 2013), ceramics and glasses (12% of the global production in 2013), greases (11% of the global production in 2013) and other applications such as metallurgy, pharmaceutical industry, primary aluminium production, etc., which represented 33% of the global production in 2013 (Chagnes and Swiatowska, 2015; Dewulf et al., 2010; Maxwell 2014; Speirs et al., 2014; Swain, 2017). Recently, the small world of lithium has been booming in terms of exploration, mining and processing due to the expected huge increase of electric vehicles production that relies mainly on lithium-ion battery technology. Thus, lithium production is expected to triple between 2015 and 2025 (Pillot, 2018). Such a boom in lithium production is accompanied by a drastic increase of its price, which has been tripled for a little more than three years (from 5000 US dollars per tonne in 2014 to more than 15,000 by the end of 2017) (Pillot, 2018).

During the last decades, lithium has been mainly extracted from brines located in Bolivia, Argentina, Chile, and at a less extent from China and USA (Gruber et al., 2011; Swain, 2017). Recently, the increase of lithium price has stimulated the development of new projects, like in Australia, for the recovery of lithium from ores. Therefore, lithium production from minerals such as spodumene ($\text{LiO}_2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$), lepidolite ($\text{KLi}_{1.5}\text{Al}_{1.5}[\text{Si}_3\text{O}_{10}][\text{F},\text{OH}]_2$), petalite ($\text{LiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$) and amblygonite ($\text{LiAlPO}_4[\text{OH},\text{F}]$) is significant, and can be even considered the main route for lithium production (Kesler et al., 2012; Meshram et al., 2014; Siame and Pascoe, 2011; Sverdrup 2016; Wang et al., 2018). In a very near future, lithium-ion batteries are expected to be an alternative source of lithium (and other metals such as cobalt, nickel, manganese, copper and aluminium) (Chagnes and Pospiech, 2013). Lithium production from spent lithium-ion batteries could be strategic for many countries since such wastes may contribute to lithium supply in many countries where no primary lithium is available.

Lithium brine recovery is a long process that involved drilling in order to access the underground salar brine deposits, brine pumping to the surface and brine distribution to ponds where solar evaporation are implemented for 10-20 months. During the solar evaporation stage, magnesium and potassium chloride salts precipitate before lithium precipitation. In some cases, reverse osmosis is used to concentrate the lithium brine in order to speed up the evaporation process. Lithium salt is recovered and washed with water in order to remove impurities. Refining process is afterward implemented in order to produce high-grade salts for

lithium-ion battery production (LiOH , Li_2CO_3) or for lithium metal production by electrowinning (LiCl) (Chagnes and Swiatowska, 2015). Recently, Eramet has developed an original process, which by-pass the solar evaporation stage thanks to the implementation of a direct solid-liquid lithium extraction by means of a new sorbent material (Boualleg et al., 2015). Likewise, Batman Tenova and Solvay have also developed a new process to extract lithium from brine. This process relies on a liquid-liquid extraction stage based on the use of a new extractant, which is very efficient for lithium extraction [Jonathan, 2014, 2017]. It is a very interesting process as it allows to produce the desired lithium salt (LiCl , LiOH , Li_2CO_3) without any significant flowsheet modifications.

Lithium extraction from ores involves pyrometallurgical or hydrometallurgical stages (Chagnes and Swiatowska, 2015). In the case of lithium salt production from spodumene, lithium concentrate is produced by gravity, heavy media, flotation, and magnetic separation. Afterwards, α -spodumene is converted into β -spodumene at 1070-1090 °C in order to get easier lithium extraction by sulphuric acid at 250 °C. The residue is then washed with water at 90 °C in order to dissolve lithium sulphate. Impurities such as iron, aluminum, magnesium, calcium, etc., are removed by precipitation. The purified leach liquor is afterward treated using ion exchange to concentrate lithium. Carbonation of the lithium-rich solution is thereafter applied to precipitate battery-grade lithium carbonate (purity>99.5%).

Presently, the implementation of membrane processes in lithium production flowsheets is very limited whereas this technology could reduce significantly the operating costs by decreasing advantageously the number of stages providing that membrane cost and membrane selectivity would be appropriate. Reverse osmosis is the most used membrane process in brine treatment, and it could be implemented in lithium extraction from lithium ores since it is an efficient way to concentrate lithium before lithium carbonate precipitation providing that membrane fouling issues would be fixed (Somrani et al., 2013). Nanofiltration was tested to recover lithium from brines or seawater but low lithium recovery rate was obtained (55%) and poor selectivity towards magnesium and boron was achieved (Wen et al., 2006). Recently, Eramet included reverse osmosis and nanofiltration technologies in their new process for lithium extraction from brine [Martin, 2019] whereas Batman Tenova included membrane technologies for calcium/magnesium removal before lithium extraction [Lipp, 2014; Lipp, 2017].

Although, electrodialysis is mainly used for water desalination, this technology could be easily implemented in hydrometallurgical processes for the recovery of lithium from brine or

geothermal fluids as well as in processes for the recovery of lithium from leach solution of spodumene concentrate (Amy et al., 2017; Galama et al., 2014; Gmar et al., 2015; Gmar 2016; Gmar et al., 2017a, 2017b; Liu et al., 2016; Tanaka et al., 2003). Only few studies are devoted to the use of electrodialysis for lithium recovery from primary and secondary resources. However, more and more papers have been published on this topic since 2013.

This paper addresses a thorough review of recent advances about the use of electrodialysis in processes for the recovery of lithium from primary resources (brines, seawater, geothermal fluids, lithium ores) and secondary resources (spent lithium-ion batteries). It highlights advantages and disadvantages of this technology as well as recent progresses required for stimulating the integration of this technology in hydrometallurgical processes for the production of high-grade lithium salts.

2. Principle of electrodialysis

Electrodialysis (ED) is a membrane process that allows ion separation under the influence of an electrical potential difference (Strathmann, 2004). Figure 1 shows a schematic diagram of a typical electrodialysis cell consisting of a series of anion- and cation-exchange membranes arranged in an alternating pattern between an anode and a cathode. Under an electrical potential applied between the anode and the cathode, the positively charged cations migrate towards the cathode and the negatively charged anions move towards the anode. The cations pass easily through the negatively charged cation-exchange membrane while they are retained by the positively charged anion-exchange membranes. Likewise, the negatively charged anions pass through the anion-exchange membranes and they are retained by the cation-exchange membranes. The overall result is an increase in ion concentration in alternate compartments (concentrate), while the other compartments simultaneously become depleted (diluate).

The ED efficiency is assayed by calculating the recovery efficiency of the targeted ion i ($R(i)$ in %), the current efficiency of the electrodialyser ($\eta(i)$ in %), the Specific Energy Consumption of the electrodializer (SEC), the Separation Coefficient between lithium and another species X ($SC_{X/Li}$), the Permselectivity index ($P_{Li/M}$), the Concentration Ratio ($CR(i)$ in %), the Separation efficiency ($S(i)$ in %) and the Survival Ratio (SR in %) defined as follows :

$$R(i) = \frac{(C_{i,c} - C_{i,c}^0)V_c}{N_i} \times 100 \quad (1)$$

where $C_{i,c}$, $C_{i,c}^0$ and V_c are the concentration of the targeted ion i in the concentrate (or cathodic) compartment (in mol L⁻¹), the initial concentration of targeted ion i (in mol L⁻¹) in the concentrate (or cathodic) compartment and the volume of the concentrate (or cathodic) compartment (in L), respectively. N_i denotes the initial amount of targeted ion in the feed compartment (in mol).

$$\eta(i) = \frac{(n_t - n_0)z.F}{N \int_0^t I(t)dt} \times 100 \quad (2)$$

where n_t is the amount of targeted ion (in mol) at time t (in s) in the concentrate (or cathodic) compartment, n_0 is the initial amount of targeted ion (in mol) in the concentrate (or cathodic) compartment, I is the current passing through the electrodialyzer, F is the Faraday constant, z is the charge of the targeted ion and N is the number of cell pairs in ED stack.

$$SEC = \frac{\int_0^t E I dt}{N_R} \quad (3)$$

where E is the applied potential (V), I is the current (A), t is the operating time (s) and N_R is the amount of the targeted ion transferred from the feed compartment into the concentrate (or cathodic) compartment (in mol or g). SEC represents the energy requested for recovering one mole of the targeted ion (in kWh mol⁻¹ or kWh g⁻¹).

$$CR(i) = \frac{C_t}{C_0} \times 100 \quad (4)$$

where C_0 and C_t are the initial and final concentrations of the targeted ion in the concentrate compartment before and after electrodialysis process.

$$SR = \frac{C_{i,a}}{C_{i,a}^0} \times 100 \quad (5)$$

where $C_{i,a}^0$ and $C_{i,a}$ are the concentrations of the targeted ion in the anodic compartment before and after electrodialysis, respectively.

$$SC(M-Li) = \frac{C_M/C_{Li}}{C_M^0/C_{Li}^0} \quad (6)$$

where C_M , C_{Li} , C_M^0 and C_{Li}^0 are the concentrations of M and lithium ions in the diluate (or anodic) compartment at the steady state, and initially in the feed solution of the electrodialyser, respectively.

$$P(\text{Li}/\text{M}) = \frac{C_{\text{Li},c}V_c / C_{\text{M},c}V_c}{C_{\text{Li}}^0 / C_{\text{M}}^0} \quad (7)$$

where $C_{\text{Li},c}$, $C_{\text{M},c}$ and V_c denote the concentrations of lithium and M ions in the concentrate (or cathodic) compartment and the volume of the concentrate (or cathodic) compartment, respectively.

$$S(i) = \frac{C_i^0 - C_i^f}{C_i^0} \times 100 \quad (8)$$

C_i^0 and C_i^f are the initial and final concentrations of the targeted ion in the diluate (or anodic) compartment, respectively.

3. Lithium extraction by electrodialysis from various resources

Although membranes are at the center of several technologies including diffusion dialysis, electrodialysis and electrolysis, there is lack of information about their chemical structure, likely because of confidentiality. More information concerns the physical properties of these membranes. Table 1 gathers few properties about electrodialysis membranes used for potential applications in lithium extraction from brines, ores and spent lithium-ion batteries. Standard ion exchange membranes are not selective for mono/divalent ions with the same charge. In contrast, special-grade cation exchange membranes (e.g. monovalent-selective Neosepta CMS and Selemion CSO), and anion exchange membranes (e.g. Neosepta ACS and Selemion ASV), are selective to monovalent ions over divalent ions (Saracco, 1997; Sara, 1994). Monovalent-selective cation exchange membranes can be based on either charge-rejection, where a thin oppositely charged layer is used to hinder the permeation of divalent cations (in the case of Neosepta CSO a thin poly(ethylene imine) layer), or by using a crosslinked layer with lower hydration, where the divalent ions with their larger hydrated ion size are hindered (in the case of Neosepta CMS). These special-grade ion exchange membranes, however, are much more expensive than the standard-grade ion exchange membranes (Post et al., 2010).

Membrane processes are implemented in various industries including salt production, demineralization in food industries, industrial wastewater reclamation, desalination (tap wapter), acid recovery, substitutional reaction and extractive metallurgy at a lesser extent. The following parts of this paper are focused on the use of these membranes for the selective recovery of lithium from seawater, brine, geothermal fluids, ores and spent lithium-ion batteries.

3.1. Seawater, Brine and geothermal fluids

3.1.1. Cationic and anionic membranes

Several authors demonstrated that electrodialysis could be used to extract lithium from aqueous solution even at low lithium concentration levels. The main challenges in lithium extraction by electrodialysis consist in developing efficient process allowing to recover lithium very selectively towards monovalent cations and divalent cations present in seawater, brine and geothermal fluids. This challenge is especially important since lithium is usually at low concentration whereas the other ions are present in solution at high concentration (especially in the case of seawater in which lithium concentration is around few tens mg/L). Such a separation can be achieved providing that high selective membrane are implemented in the electrodialyser.

Commercial membranes like the anionic exchange membrane AR204SXR412 (homogenous polystyrene/Divinyl benzene copolymer) and the cationic exchange membrane CR67-MK111 (Homogenous polystyrene/Divinyl benzene) provided by Arak Petrochemical Complex Company (Iran) were used by Parsa et al. (Parsa et al., 2015) in an electrodialyser composed of four cells. The use of these membranes allowed producing a solution containing 7650 mg L⁻¹ lithium hydroxide and only 105 mg L⁻¹ Na⁺ while the initial lithium and sodium concentrations in the feed solution were 1.35 g L⁻¹ and 27.8 g L⁻¹, respectively. A good recovery efficiency of 27.52% was thus obtained while the separation coefficient and the permselectivity reached SC(Na-Li)=1.25 and P(Li/Na)=3.53, respectively.

More sophisticated membranes were also designed at the laboratory scale in order to enhance electrodialyser performances for lithium production. In a recent patent, (Fauvarque and Lepinasse, 2018) designed a new cationic exchange membrane exhibiting high selectivity towards lithium. Diazo[2,2,2]bicyclooctane (DABCO) was grafted onto polyepichlorohydrin by means of a chemical route described in the patent. In order to improve the chemical resistance, boron nitride was added in the membrane formulation and DABCO was partially replaced by sulfonated amine-poly-(ether sulfone). The lithium conductivity was improved by adding lithium-ion conductive glass ceramic, i.e. Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O₁₂ called LiCGC™ (Ohara company, Japan). This membrane exhibited the following properties: ionic conductivity=0.16 S cm⁻¹, permselectivity=0.95-1, ion exchange capacity=1.1 meq g⁻¹, swelling rate=35%. This new membrane was used at a current density of 0.1 A to treat a synthetic solution containing 0.35 g L⁻¹ lithium and 1.15 g L⁻¹ sodium. The results revealed

that lithium recovery in cathodic compartment depended on the weight percentage of LiCGC incorporated in the membrane. Lithium recovery rates of 91.26% and 25.89% were obtained after 3 hours in the presence of 47.8% and 48.2% LiGGC in the membrane, respectively. By decreasing the current to 0.05 A, the electrodialysis treatment of a synthetic solution containing 0.7 g L⁻¹ lithium and 2.3 g L⁻¹ sodium led to a dramatic decrease of the lithium recovery rate (15%) but the leak rate of sodium was only equal to 4.3%. The P(Li/Na) was about 3.48 and the transport number of lithium was estimated to be four times higher than that of sodium.

Likely, the use of other sophisticated membranes based on the use of commercial membranes impregnated with appropriate ionic liquids were also investigated to extract lithium from seawater and from an aqueous solution containing sodium and divalent cations such as calcium and magnesium (Hoshino 2013a, Hoshino, 2013b). These studies showed that the use of ionic liquid impregnated onto the membrane surface improves significantly the lithium selectivity towards divalent cations providing that the ionic liquid exhibits good transport properties towards lithium ions.

Figure 2a shows the configuration of the electrodialyzer cells for the selective recovery of lithium towards calcium and magnesium. Selemion™ AMV, which is a polystyrene matrix cross-linked with divinylbenzene on which ammonium groups are grafted in the presence of chloride counter-anions (the exact nature of ammonium groups has never been reported by the provider or in the literature), was used as anionic membranes. The cationic membranes were made of Gortex impregnated with N-methyl-N-propylpiperidium-bis-(trifluoromethanesulfonyl) imide (ionic liquid) in order to increase lithium transportation through the membrane. Before ionic liquid impregnation, Nafion 324 (perfluorated membrane reinforced with poly(tetrafluoroethylene) fibers) was deposited onto the Gortex membrane in order to increase the lifespan of the impregnated membrane by reducing ionic liquid loss into the aqueous solution during electrodialysis operation (Nafion 324 deposition onto Gortex surface led to an increase of the recovery rate of lithium from R(Li⁺)=5.9% to R(Li⁺)=22.2%). It was demonstrated in this work that the presence of this ionic liquid into the Gortex-Nafion 324 membrane significantly improved the selectivity for lithium towards sodium, potassium, calcium and magnesium (SC(Na-Li)=1.28; P(Li/Na)=59.40; SC(K-Li)=1.23; P(Li/K)=5.39; SC(Mg-Li)=1.28; P(Li/Mg)=26; SC(Ca-Li)=1.25; P(Li/Ca)=7.18). The same strategy was used for the extraction of lithium from seawater (Hoshino, 2013b). For this goal, Selemion™ CMV (Asahi Glass Company, Japan) impregnated with N,N,N,-trimethyl-N-

propylammonium-bis(trifluoromethanesulfonyl)-imide was used as cationic exchange membrane (Figure 2b) in order to treat a ‘concentrated seawater’ produced by a preliminary electrodialysis operation with Selemion™ CSO monovalent selective cation exchange membrane (Asahi Glass Company, Japan). Selemion™ CMV and N,N,N,-trimethyl-N-propylammonium-bis(trifluoromethanesulfonyl)-imide were chosen because of their bad transport properties towards lithium ions. With this system, lithium remained in the ‘concentrated seawater’ while the other cations migrated to the cathodic compartment through the membrane ($SR(Li^+)=63\%$ at 3V).

Electrodialysis were also used for the recovery of lithium from brines of various compositions (Guo et al., 2018; Nie et al., 2017a; Ji et al., 2017; Ji et al., 2018; Zhao et al., 2018; Jiang et al., 2014). Most of these studies focused on lithium-magnesium separation and/or the effect of other ions on electrodialysis efficiently (Na^+ , K^+ , Ca^{2+} , SO_4^{2-} , HCO_3^-). Lithium and magnesium separation is a tricky challenge in electro-membrane and membrane processes since these ions exhibit similar radii in aqueous solutions. Table 1 reports a comparison of electrodialysis and nanofiltration technologies for the recovery of lithium from brine (Wen et al., 2006). This table shows clearly that electrodialysis is an interesting alternative to nanofiltration since electrodialysis leads to better recovery rate, lower energy consumption and higher lithium-magnesium separation factor than nanofiltration. CIMS cationic exchange membranes combined with ACS anionic exchange membranes (ASTOM company, Japan) or Selemion CSO combined with Selemion ASA (Asahi Glass Company, Japan) were used to extract lithium from Chinese brines (Guo et al., 2018; Nie et al., 2017a). Good lithium-magnesium selectivities were achieved by using CIMS and ACS membranes as $[Mg^{2+}]/[Li^+]$ ratio was reduced by 2.35 and the recovery rate reached 76.45% with an energy consumption equal to $0.094 \text{ kWh g}^{-1} \text{ Li}$ when a Voltage of 10 V was applied. Selemion CSO and Selemion ASA also led to interesting results since these membranes permitted to reduce $[Mg^{2+}]/[Li^+]$ ratio by 19 and to reach a permselectivity index $P(Li/Mg)=33$ while achieving a lithium recovery rate of 94.5% with a very low energy consumption ($0.0019 \text{ kWh g}^{-1} \text{ Li}^+$) under optimized conditions (Nie et al., 2017a). It was demonstrated that the presence of K^+ and Ca^{2+} was not detrimental to selectivity and efficiency of the electrodialysis process. However, other similar studies regarding the treatment of other brines by the same membranes lead to the conclusion that the electrodialyser efficiency in terms of selectivity, recovery rate and energy consumption depends strongly on brine composition (Niel et al., 2017b; Ji et al., 2017). In particular, it was demonstrated that the negative effect of Na^+ on

electrodialysis performance must not be neglected since the recovery rate, current efficiency and separation coefficient decreased dramatically from 71.2% to 39.7%, from 11% to 2% and from 8.7 to 1.8 when $[\text{Na}^+]/[\text{Li}^+]$ ratio increased from 1 to 20, respectively (Ji et al., 2018). The same negative effect of K^+ on lithium extraction and Li-Mg separation was also reported. Conversely, the presence of sulphate in brine improved the electrodialysis performance as the presence of sulphate was responsible for an increase of lithium recovery rate ($R(\text{Li})=70\%$ at $[\text{SO}_4^{2-}]/[\text{Cl}^-]=0.3$) and an increase of $\text{SC}(\text{Li-Mg})$ from 8 to 14.7 when $[\text{SO}_4^{2-}]/[\text{Cl}^-]$ increased from 0 to 0.3. The authors explained this observation by the use of selective membranes towards monovalent ions and due to electrostatic attraction between sulphate and magnesium ions. On the other hand, the presence of sulphate in brines involved a slight decrease of the energy consumption (0.018 KWh g^{-1} of Li and 0.012 KWh g^{-1} of Li when $[\text{SO}_4^{2-}]/[\text{Cl}^-]$ increased from 0 to 0.3). Likewise, the presence of hydrogenocarbonate ions in brines improved the electrodialysis performance in terms of lithium-magnesium separation likely due to the formation of MgHCO_3^+ , which exhibits low mobility through cationic exchange membranes because of its large steric hindrance.

3.1.2. Bipolar membrane

Bipolar membrane is another technology which could find advantageous application in the recovery of lithium, and more particularly in boron-lithium separation. This technology is a special type of layered ion exchange membrane that consists of two polymer layers carrying fixed charges. One of this polymer layers is only permeable to anions while the other one allows only cation transport. No ion transport can occur from one side to the other side. A typical characteristic of bipolar membranes is the disproportionation reaction of water molecules in the hydrophilic junction, which are split into hydroxide ions and protons when an electric potential is applied to the bipolar membranes (Badruzzaman et al., 2009; Li et al., 2016). Proton and/or hydroxide ions can thus react with salts present in the effluent.

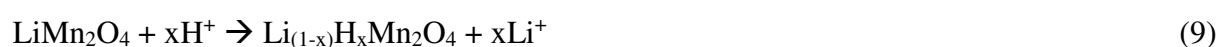
Bunani et al. used bipolar membranes in electrodialysis system to investigate lithium-boron separation in order to produce high-grade lithium hydroxide salt (Bunani et al., 2017). For this goal, they used synthetic solutions containing various concentrations of lithium and boron ranging from 34 and 340 mg L^{-1} and from 100 to 1000 mg L^{-1} , respectively. Figure 3 shows the setup used in this study. The electrodialyser was composed of ten CMB cationic exchange membranes (C), ten AHA anionic exchange membranes (A), and ten bipolar membranes (Neosepta BP-1E) provided by ASTOM company (Japan). In the electrodialyser, borate ions are transported through the anionic exchange membranes and react with the

proton produced by water dissociation at the hydrophilic junction of the bipolar membranes to form a neutral species (H_3BO_3), which cannot be transported through the ion exchange membranes. Lithium moves across the cationic exchange membrane and reacts with hydroxide ions produced by water dissociation onto the bipolar membrane surface to form lithium hydroxide, which cannot be transported through the ion exchange membranes. Thus, the use of both anionic exchange membranes and bipolar membranes permits to separate lithium and boron, and to produce lithium hydroxide and boric acid. Furthermore, a good selectivity for lithium ions towards sodium ions ($\text{SC}(\text{Na-Li})=3.4$) was obtained thanks to the good permselectivity of the cationic exchange membranes. An increase of the applied voltage from 25V to 35V led to an important increase of lithium recovery rate from 44% to 72% while the energy consumption increased from 14.4 to 24 Wh L^{-1} . However, such an increase of voltage was responsible for a decrease of current efficiency from 21.5 to 18.2%. Other membranes such as PCCell bipolar membranes (PCCell GmbH, Germany) combined with PC SK (cationic exchange membranes composed of $-\text{SO}_3^-$ functional groups) and PC Acid 60 (anionic exchange membranes composed of $-\text{NH}_4^+$ functional groups), or Neosepta CMB and AHA membranes combined with bipolar membrane BP-1E were also used to separate lithium from boron (Bunani et al., 2017b; Ipekçi et al., 2018).

Jiang et al. developed a global flowsheet involving electrodialysis operations with bipolar membranes as well as cationic and anionic exchange membranes (JCM-II-05 and JAM-II-05 membranes, Beijing Tingrum Membrane Technology Development Company Ltd., China) in order to treat brines after removing magnesium and calcium by precipitation with Na_2CO_3 [Figure 4] (Jiang et al., 2014). A voltage of 15V and a flowrate of 22 L h^{-1} were applied during the electrodialysis of the above-mentioned solution containing 879 mg L^{-1} lithium. At the end of the electrodialysis operation, lithium concentration in the concentrate compartment was 3485 mg L^{-1} and the purity was estimated to 95% (concentration ratio $\text{CR}=396\%$). Afterward, LiOH was produced from Li_2CO_3 by using electro-electrodialysis with bipolar membrane (EEDBM). In this system two cation exchange membranes CMX and two bipolar membranes BP-1 provided by Tokuyama Company (Japan) were used in the electrodialysis system. The stack was divided into five compartments as illustrated in Figure 5. Lithium was recovered in Base 1 and Base 2 compartments. High current efficiency (99%) and low energy consumption (0.0023 kWh g^{-1} of Li) were obtained when initial lithium carbonate concentration in the concentrate compartment was equal to 0.18 mol L^{-1} and a current density of 30 mA cm^{-2} was applied. Under these operating conditions, lithium hydroxide solution

with a purity of 95% was produced and the production cost was estimated to 2.59 U.S. \$/kg LiOH, which is very low given that lithium hydroxide price is around 14.67 U.S. \$ /kg.

Another interesting electrodialysis system involving bipolar membranes was developed by Hwang et al. in order to produce lithium hydroxide from brine (Hwang et al., 2016). These authors investigated the efficiency of bipolar membrane electrodialysis for electric desorption of lithium in order to recover lithium as lithium hydroxide from LiMn_2O_4 . The electrodialyser was composed of three Neosepta cationic exchange membranes CMX and four Neosepta bipolar membranes BP-1 (Astom Company, Japan). Protons produced by water dissociation onto the bipolar membranes surface allowed stripping lithium from LiMn_2O_4 :



The resulting lithium ions moved across the cationic exchange membrane and reacted with OH^- ions formed by water dissociation onto the bipolar membrane surface (Figure 6). High lithium stripping rate (70%) and high current efficiency (70%) were obtained after 120 min. at 26 V with a flowrate of $0.44 \text{ cm}^2 \text{ min}^{-1}$.

Table 3 summarizes the different systems reported in the litterature to recover lithium from seawater, brines and geothermal fluids.

3.2. *Lithium ores*

Less papers were published about the use of electrodialysis technologies for lithium extraction from ores than from brine. Paper reported the use of FKS-PET-130/FAS-PET-130 (FuMA-Tech GmbH, Germany), CJMC/CJMA (Hefei ChemJoy Polymer Materials Company, Japan) and Neosepta AMX/CMX for the treatment of synthetic solutions containing 6 wt% Li_2SO_4 , which is a typical concentration in leaching solution produced by sulphuric attack of lithium ores (Zhou et al., 2018). It appeared that Neosepta AMX/CMX membranes led to the best electrodialysis performances thanks to their high exchange capacity, relatively low water uptake and dense structure while exhibiting the lowest transport numbers. However, this study does not take into account the presence of other ions that can drastically changes electrodialysis performances as discussed previously. An interesting study was published by Martin et al. on the development of an electrodialysis process to produce Li_2CO_3 from Zinwaldite (Martin et al., 2017a). The corresponding flowsheet is reported in Figure 7. In this process, silicon tetrafluoride was eliminated at 950 °C for 3 hours. After milling, direct pressurized carbonation in the presence of water was implemented in order to produce lithium solution. The highest lithium dissolution yield reached 75% at 230 °C under

100 bar at a liquid/solid ratio of 100. After filtration, the obtained solution of lithium hydrogen carbonate ($[\text{LiHCO}_3]=2.60 \text{ g L}^{-1}$; $[\text{Li}^+]=266 \text{ mg L}^{-1}$) was concentrated by electrodialysis. For this goal, a membrane stack composed of ten cell pairs of CMS and AMX Neosepta membranes (Astom Company, Japan) was used. After applying 10 V, lithium hydrogen carbonate concentration in the concentrate compartment was equal to 83.2 g L^{-1} (8.48 g L^{-1} lithium) and energy consumption used for this operation reached $0.0035 \text{ KWh g}^{-1}$ of lithium. The concentration ratio was around 3200 % after 3 hours and lithium yield was 96%. Finally, high purity lithium carbonate (purity=99.2%) was produced by precipitating LiHCO_3 at 90°C according to the following reaction:



The same authors developed another flowsheet to produce lithium carbonate from zinnwaldite concentrate containing 3 wt% Li_2O (Figure 8) (Martin et al., 2017b). After mineral processing steps (crushing, dry magnetic separation), the obtained concentrate was digested by hydrochloric acid at 110°C under atmospheric pressure (extraction yield of lithium= 90%). The resulting leach solution contained 3.9 g L^{-1} . Afterwards, iron was precipitated as $\text{FeO}(\text{OH})$ by adding $\text{Na}_4[\text{Fe}(\text{CN})_6]$. Aluminium, fluoride and potassium were removed as $(\text{Na}_{2.6}\text{K}_{0.4})\text{AlF}_6$ by using NaF and NaOH . Finally, solid-liquid separation was performed in order to recover a solution containing 2 g L^{-1} lithium. This solution fed an electrodialyser equipped with ten cell pairs of CMS and AMX monoselective membranes provided by Astom company (Japan). After applying 10 V for 5 hours, lithium concentration in the concentrate compartment reached 7 g L^{-1} (energy consumption= $0.0107 \text{ kWh g}^{-1}$ of lithium; concentration ratio=350%). Lithium was then concentrated to 10 g L^{-1} by evaporation at 50°C and 80 mbar. Finally, Li_2CO_3 with a purity greater than 98% was produced after precipitation by Na_2CO_3 at 90°C .

Table 4 summarizes the different systems reported in the literature to recover lithium from ores.

3.3. Spent lithium-ion batteries

Only few papers concern the use of electrodialysis in lithium-ion batteries recycling. Song and Zhao described a method combining precipitation and electrodialysis in order produce lithium carbonate (Song and Zhao, 2018). A synthetic solution representative of leach solution of cathodes from spent lithium-ion batteries were prepared by dissolving appropriate

metal salts in deionized water (3.27 g L⁻¹ Li, 0.25 g L⁻¹ Co, 0.28 g L⁻¹ Mn, 0.25 g L⁻¹ Ni, pH=4.1, etc.) [Figure 9].

Firstly, the solution was purified by adding NaOH in order to quantitatively precipitate metal at pH 12, except lithium that remained in solution. Secondly, sodium phosphate, seed crystal and polyacrylamide flocculant were added in the purified solution in order to precipitate lithium phosphate (precipitation yield=93%). Afterwards, lithium phosphate was dissolved in sulfuric acid and used as feed solution in electrodialysis in order to concentrate lithium. For this goal, an electrodialysis cell containing only one cation exchange membrane (Nafion 117 composed of a perfluorocarbon polymer grafted with SO₃⁻ groups provided by Dupont) was used. The initial concentration of lithium and phosphorus in the anolyte compartment were 43 and 64 g L⁻¹, respectively. High separation coefficient between phosphorus and lithium was achieved (SC(P-Li)=3). This method led to the production of a catholyte containing 30.8 g L⁻¹ lithium. Furthermore, the energy consumption was low (SEC=0.027 KWh g⁻¹ of lithium) compared to other membrane technologies such as nanofiltration, i.e. SEC=5.45 KWh g⁻¹ of lithium (Wen et al., 2006). Lithium carbonate was produced by adding carbonate in the catholyte after removing the permeated phosphorus in the form of Li₃PO₄ by increasing the pH. Finally, the purified catholyte contained 22.5 g L⁻¹ lithium and the obtained lithium carbonate salt matched with national standard.

Lizuka et al. (Lizuka et al., 2013) reported the use of bipolar membrane electrodialysis for the separation of lithium and cobalt contained in aqueous solution produced by leaching of LiCoO₂ electrodes (lithium and cobalt concentrations in solution were equal to 0.02 mol L⁻¹). The electrodialysis cell was composed of an anionic exchange membrane (Selemion AMV provided by Asahi Glass Company, Japan), a cationic exchange membrane (Selemion CMV provided by Asahi Glass Company, Japan) and two bipolar membranes (Neosepta BP-1E provided by Astom company, Japan) as displayed in Figure 10. The applied potential and flow rate were fixed at 20V and 0.375 L min⁻¹, respectively. Values of pH and EDTA concentration were chosen in order to form Co(EDTA)²⁻ since this species was able to migrate across the anionic exchange membrane while lithium cation moved across the cationic exchange membrane as illustrated in Figure 10.

The best operating conditions to separate lithium and cobalt at a recovery rate of 99% for each metal were: applied voltage=20 V, flowrate=0.375 L.min⁻¹, EDTA concentration=0.02 mol L⁻¹ and pH=4. However, this chelating method causes usually membrane fouling, which are responsible for a dramatic decrease of membrane performances (Chaudhary et al., 2000)

Afifah et al. (Afifah et al., 2018) studied lithium-cobalt separation by using five electrodialysis cells containing monovalent selective ion exchange membranes, i.e. PC-MVK as cation exchange membrane and PC-MVA as anion exchange membrane purchased from Polymer chimie Altmeier GmbH (Heusweiler, Germany). The value of the applied potential did not influence significantly the separation efficiency since an increase from 5V to 15V was responsible for a small increase of the separation efficiency from 98.63% to 99.4%. Conversely, an increase of applied voltage from 15V to 20V led to an increase of cobalt concentration in the concentrate compartment from 0.297 mmol L⁻¹ to 0.526 mmol L⁻¹, and consequently, a significant decrease of the purity of the lithium product from 93.69% to 88.38%. Furthermore, an increase of the applied voltage from 15V to 20V led to a significant increase in energy consumption and a decrease of current efficiency from 25% to 8% due to the concentration polarization phenomenon. The flowrate also influenced the separation efficiency since an increase from 66.63% to 70.91% was observed when the flowrate varied from 10 to 15 L h⁻¹.

Table 4 summarizes the different systems reported in the literature to recover lithium from spent lithium-ion batteries.

4. Conclusions

Electrodialysis is a simple process, and efficient method to separate and recover lithium from various resources while allowing to reduce chemical reagent consumption and reducing the global environmental impact of lithium salt production. This technology was used to concentrate Li₂SO₄ and to produce LiCl, LiOH and Li₂CO₃ from primary and secondary resources. Electrodialysis can be used to produce lithium salts with purity greater than 95% while keeping a high extraction efficiency rate (around 80%) and low energy consumption. However, efforts must be done to increase further the purity of the final product in order to produce high-grade lithium salts. For this goal, electrodialysis can be also implemented in refinement processes. More efforts must be paid to develop new membranes with a high selectivity for lithium towards divalent cations present in brines or divalent metals present in spent lithium-ion batteries such as cobalt, nickel and manganese.

Acknowledgements

This work was supported by the French National Research Agency through the national program "Investissements d'avenir" with the reference ANR-10-LABX-21 - RESSOURCES21.

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TABLES

Table 1: Membrane characteristics.

Membranes	Thickness (μm)	Ion exchange capacity (meq.g ⁻¹)	Swelling degree (%)	Resistance (Ω.cm ²)	Transport number
FAS-PET-130	125	1.07	19.7	2.9	0.95
FKS-PET-130	127	0.74	19	3.7	0.99
CJAM	200	1.05	20	2.8	>0.98
CJCM	145	1.2	22	3.5	>0.98
Neosepta AMX	134	1.25	16	2.35	0.91
Neosepta CMX	164	1.62	18	2.91	0.98

Table 2: Comparison of electrodialysis and nanofiltration performance during lithium recovery.

Technology	R (%)	[Mg ²⁺]/[Li ⁺]	SEC (kWh.g ⁻¹ Li ⁺)
Electrodialysis (5.9 A. m ⁻²)	94.5	150	0.0019
Nanofiltration	55	5.76	5.47

Table 3: Membranes used in ED processes for the recovery of lithium from seawater, brines and geothermal fluids.

Experimental conditions	Efficiency
Gortex membrane impregnated with an ionic liquid (ionic liquid: N-methyl-N-propylpiperidinium bis (trifluoromethane-sulfonyl)imide) sandwiched between two Nafion 324 membranes, E=3 V (Hoshino, 2013a)	R (Li ⁺) = 22.2%, SC(Na-Li)=1.28, P (Li/Na) = 59.40, SC(K-Li)=1.23, P(Li/K)=5.39, SC(Mg-Li)=1.28, P(Li/Mg)=26, SC(Ca-Li)=1.25, P(Li/Ca)=7.18
Cation exchange membrane Selemion™ CSO, E=3 V, (Hoshino, 2013b)	Concentrating seawater CR (Li) = 200%

Four anionic exchange membranes AR204SXR412 (homogenous polystyrene/Divinyl benzene copolymer) and four cationic exchange membranes CR67-MK111 (Homogenous polystyrene/Divinyl benzene), sodium contaminated lithium bromide solution ($[Li^+]=27.8 \text{ g L}^{-1}$, $[Na^+]=1.35 \text{ g L}^{-1}$, $E=7 \text{ V}$, (Parsa et al., 2015)	$R(Li^+) = 27.52\%$, $SC(Na-Li)=1.25$ and $P(Li/Na)= 3.53$,
Cationic exchange membrane: (Diazo[2,2,2]bicyclooctane (DABCO) grafted onto polyepichlorohydrin modified by boron nitride and lithium-ion conductive glass ceramic (LiCGC TM), current density= 0.1 A , $[Li^+]= 0.35 \text{ g L}^{-1}$, $[Na^+]=1.15 \text{ g L}^{-1}$ (Fauvarque and Lepinasse, 2018)	$R(Li^+)=91.26\%$
Cationic exchange membrane (Diazo[2,2,2]bicyclooctane (DABCO) grafted onto polyepichlorohydrin modified by boron nitride and lithium-ion conductive glass ceramic (LiCGC TM), current density= 0.05 A , $[Li^+]=0.7 \text{ g L}^{-1}$, $[Na^+]=2.3 \text{ g L}^{-1}$ (Fauvarque and Lepinasse, 2018)	$R(Li^+)=15\%$, $P(Li/Na)=3.48$
11 CIMS cation exchange membranes and 10 ACS anion exchange membranes, $E=10 \text{ V}$, brine in china ($Li^+= 1.03 \text{ g L}^{-1}$), $\frac{Mg^{2+}}{Li^+}=35.18$, linear flow velocity= 6.2 cm s^{-1} , (Guo et al., 2018)	$R(Li^+)=76.45\%$ with 0.094 Kwh g^{-1} Li^+ , $\frac{Mg^{2+}}{Li^+}$ reduced by 9, production of $5.95 \text{ g L}^{-1} LiCl$, i.e. $0.98 \text{ g L}^{-1} Li$
20 cation exchange membranes Selemion CSO and 20 anion exchange membranes Selemion ASA, brine in china ($[Li^+]=0.15 \text{ g L}^{-1}$, $\frac{Mg^{2+}}{Li^+}=150$), temperature= $15 \text{ }^\circ\text{C}$, linear velocity= 8.5 cm s^{-1} , current density = 5.9 A m^{-2} (Ni et al., 2017a)	$R(Li^+)=94.5\%$ with $0.0019 \text{ kWh g}^{-1}$ Li^+ , $\frac{Mg^{2+}}{Li^+}$ was reduced by 18.75, $P(Li/Mg)= 33$
40 of monovalent cation exchange membranes CSO and a 40 anion exchange membranes ASA, brine in china ($\frac{Mg^{2+}}{Li^+}= 20.7$, $[Li^+]=4.42 \text{ g L}^{-1}$, $[SO_4^{2-}]=30.1 \text{ g L}^{-1}$), $E=20 \text{ V}$, linear velocity= 7.1 cm s^{-1} , (Ni et al., 2017b)	$R(Li^+)=90.5\%$ with $0.0045 \text{ kWh g}^{-1}$ Li^+ , $\frac{Mg^{2+}}{Li^+}$ reduced by 10, $P(Li/Mg)=9.89$.

10 pairs of CIMS-ACS monovalent selective ions exchange membranes, brine in china ($\text{Li}^+ = 148 \text{ mg L}^{-1}$, $\frac{\text{Mg}^{2+}}{\text{Li}^+} = 60$), $E=5 \text{ V}$, linear velocity= 6.2 cm s^{-1} , $\text{pH} = 4-5$ (Ji et al., 2017)	$R(\text{Li}^+) = 72.46\%$, $\frac{\text{Mg}^{2+}}{\text{Li}^+}$ reduced by 8.6, $\text{SC}(\text{Mg-Li}) = 12.48$, $\text{P}(\text{Li/Mg}) = 8.21$
10 pairs of CIMS-ACS monovalent selective ions exchange membranes, Chinese brine ($[\text{Li}^+] = 0.05 \text{ mol L}^{-1}$, $\frac{\text{Mg}^{2+}}{\text{Li}^+} = 20$, $\frac{\text{SO}_4^{2-}}{\text{Cl}^-} = 0.3$), $E=6 \text{ V}$, linear velocity= 5.7 cm s^{-1} (Ji et al., 2018)	$R(\text{Li}^+) = 70\%$ with 0.012 KWh g^{-1} ^1Li , $\text{SC}(\text{Li-Mg}) = 14.7$
11 monovalent selective cation exchange membranes CIMS and 10 monovalent selective anion exchange membrane (ACS), chinese brine ($\text{Li}^+ = 0.05 \text{ mol L}^{-1}$, $\frac{\text{Ca}^{2+}}{\text{Li}^+} = 5$), $E=5 \text{ V}$, linear velocity= 6.2 cm s^{-1} , $T=30 \text{ }^\circ\text{C}$ (Zhao et al., 2018)	$R(\text{Li}^+) = 73.3\%$, $\text{SC}(\text{Ca-Li}) = 3$
5 cation exchange membranes (JCM-II-05) and 4 anion exchange membranes (JAM-II-05), Chinese brine ($[\text{Li}^+] = 879 \text{ mg L}^{-1}$, $E=15\text{V}$, flowrate= 22 L h^{-1} , (Jiang et al., 2014)	$\text{CR}(\text{Li}^+) = 396\%$, production of Li_2CO_3 (purity =95%)
2 cation exchange membranes CMX and 2 bipolar membranes BP-1, current density= 30 mA cm^{-2} , $\text{Li}_2\text{CO}_3 = 0.18 \text{ mol L}^{-1}$, flowrate= 22 L h^{-1} (Jiang et al., 2014)	Production of LiOH (purity=95%) with $0.0023 \text{ kWh g}^{-1} \text{ Li}$, current efficiency =99%.
10 CMB cation exchange membranes (C), ten AHA anions exchange membranes (A), and 10 bipolar membranes (Neosepta BP-1E), synthetic aqueous solutions ($[\text{Li}^+] = 340 \text{ mg L}^{-1}$, $[\text{B}] = 1000 \text{ mg L}^{-1}$, $E=35 \text{ V}$ (Bunani et al., 2017a)	$R(\text{Li}^+) = 97.7\%$ Production of LiOH
10 PC SK cationic exchange membranes, 10 PC Acid 60 anionic exchange membranes and 10 PCCell bipolar membrane, $E=15 \text{ V}$, $\text{pH}=9.25$, synthetic aqueous solution ($[\text{Li}^+] = 250 \text{ mg L}^{-1}$, $[\text{B}] = 850 \text{ mg L}^{-1}$, volume sample solution= 0.5 L) (Bunani et al., 2017b)	$R(\text{Li}^+) = 88.4\%$ Production of LiOH

Neosepta membranes (ten CMB cationic exchange membranes, ten AHA anionic exchange membranes and ten BP-1E bipolar membranes, synthetic aqueous solution (Li^+)=(340 mg L ⁻¹ ,[B]=1000 mg L ⁻¹), E=30 V, $[\text{NaOH}]_I$ in base compartment=0.05 mol L ⁻¹ , (Ipekçi et al., 2018)	R(Li)=62% Production of LiOH, Separation of lithium and boron (S=94.7%)
Neosepta membranes (three cation exchange membranes CMX and four bipolar membranes BP-1), E=26V, flowrate of 0.44 m cm ⁻² min ⁻¹ , 6 g of LiMn ₂ O ₄ dissolved in 500 mg L ⁻¹ of LiCl (Hwang et al., 2016)	Desorption rate=70%, current efficiency=70% Production of LiOH

Table 4: Membranes used in ED processes for the recovery of lithium from ores.

Experimental conditions	Efficiency
4 cation exchange membranes and 5 anion exchange membranes (Neosepta CMX/AMX), 6 wt% Li ₂ SO ₄ , E=6V, $\frac{V_c}{V_d}=0.1$, High Volume Ratio Concentrating mode, (Zhou et al., 2018)	Concentrating Li ₂ SO ₄ , CR=263.83%
10 cell pairs of CMS and AMX Neosepta membranes, E=10 V, ([LiHCO ₃]=2.60 g L ⁻¹ ; [Li ⁺]=266 mg L ⁻¹ , (Martin et al., 2017a)	Concentrating LiHCO ₃ , CR= 3200%
10 cell pairs of CMS and AMX monoselective membrane, E=10 V, [Li ⁺]=2 g L ⁻¹ (Martin et al., 2017b)	Concentrating Li ⁺ , CR=350%

Table 5: Membranes used in ED processes for the recovery of lithium from spent lithium-ion batteries.

Experimental conditions	Efficiency
1 cation exchange membrane (Nafion 117), typical spent lithium-ion batteries solution (3.27 g L ⁻¹ Li, 0.25 g L ⁻¹ Co, 0.28 g L ⁻¹ Mn, 0.25 g L ⁻¹ Ni, pH=4.1, etc.) (Song and Zhao, 2018)	Separation of lithium and phosphorus (SC(P-Li)=3), production of Li ₂ CO ₃ (purity=99.3%)
1 anionic exchange membrane (Selemion AMV) and 1 cationic exchange membrane (Selemion CMV), two bipolar membranes (Neosepta BP-1E), E=20 V, flowrate=0.375 L min ⁻¹ , leached solution produced from spent lithium-ion batteries oxide containing LiCoO ₂ electrode ([Li ⁺]=[Co ²⁺]=0.02 mol L ⁻¹ , pH=4, [EDTA]=	Separation and recovery of lithium and cobalt (R (Li ⁺) = R (Co ²⁺)=99%

0.02 mol L ⁻¹ (Lizuka et al., 2013)	
5 cation exchange membrane (PC-MVK) and 5 anion exchange membrane (PC-MVA), E=15 V, flowrate=15 L h ⁻¹ , [Li ⁺]=100 mg L ⁻¹ , [Co ²⁺]=300mg L ⁻¹ (Afifah et al., 2018)	Separation of lithium and cobalt, S (%)=99.4%

FIGURES

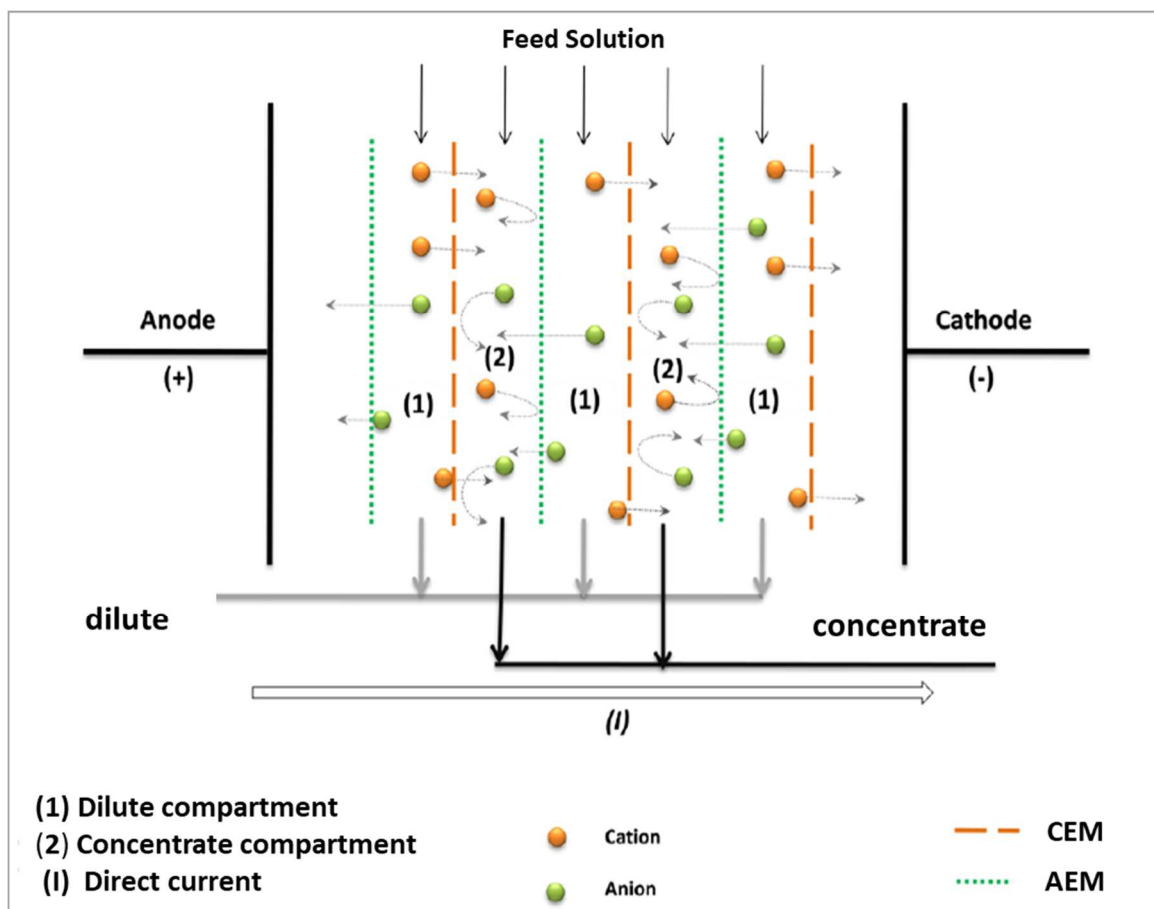
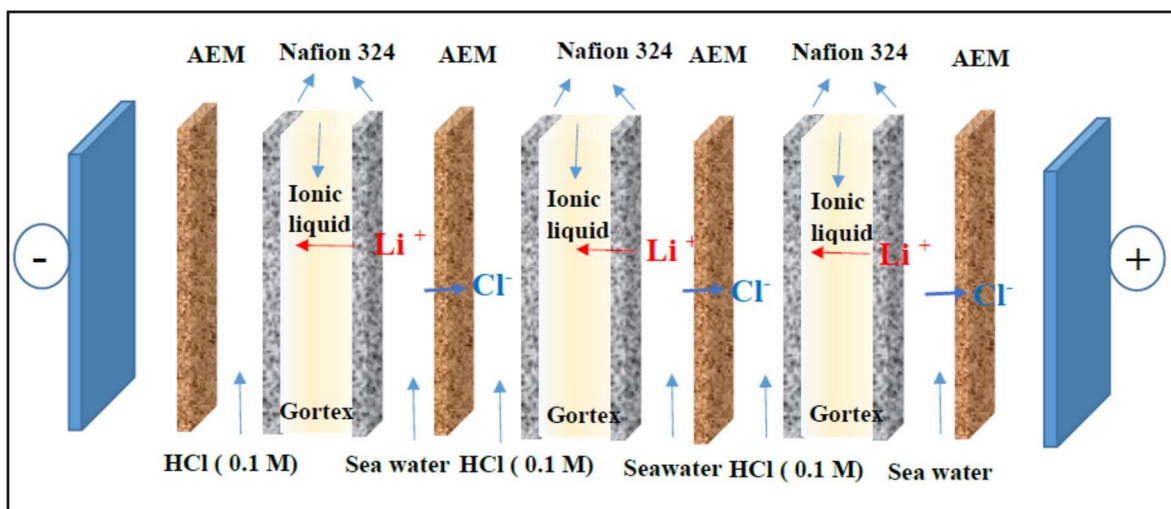


Figure 1. Principle of electrodialysis.

(a)



(b)

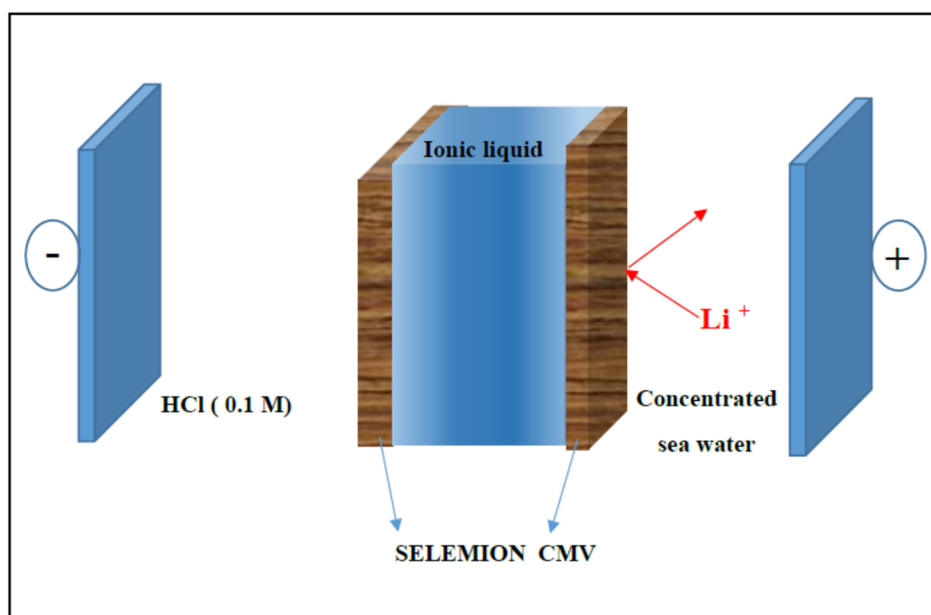


Figure 2. Electrodialysis principle for lithium recovery with (a) three cells of a SelemionTM AMV anion exchange membranes (Asahi Glass Company, Japan) and a cation exchange membranes combining a Gortex membrane impregnated with an ionic liquid (N-methyl-N-propylpiperidium-bis-(trifluoromethane-sulfonyl) imide) sandwiched between two Nafion 324 membranes and (b) one cell composed of a SelemionTM CMV cationic membrane impregnated with N,N,N,-trimethyl-N-propylammonium-bis(trifluoromethanesulfonyl)-imide (ionic liquid).

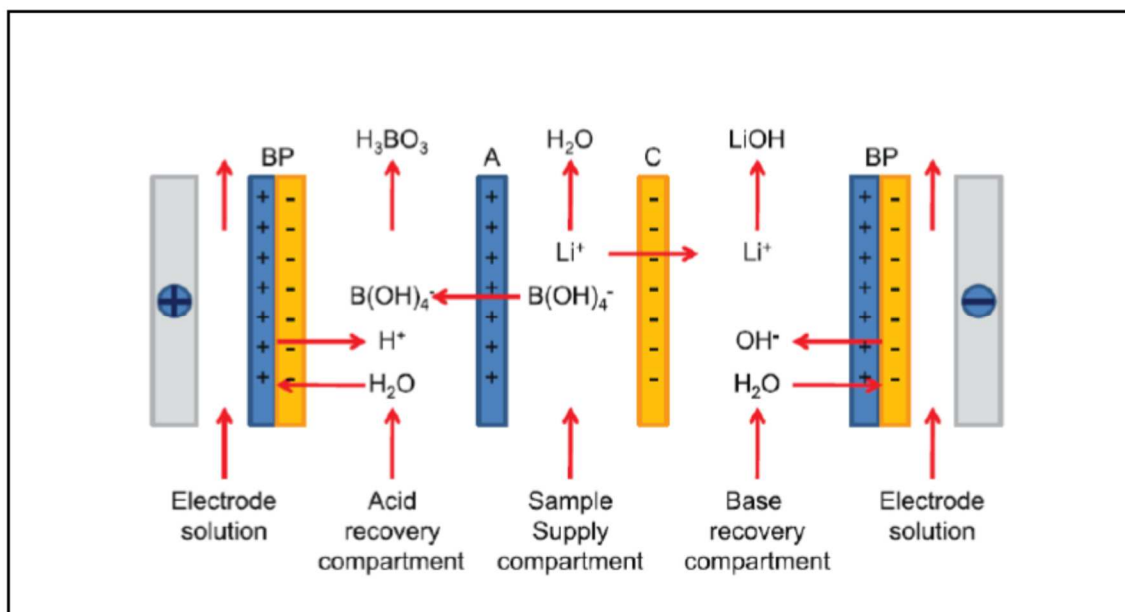


Figure 3. Setup used for Li/B separation by means of hybrid electrodialysis composed of anion and cation exchange membranes, and bipolar membranes.

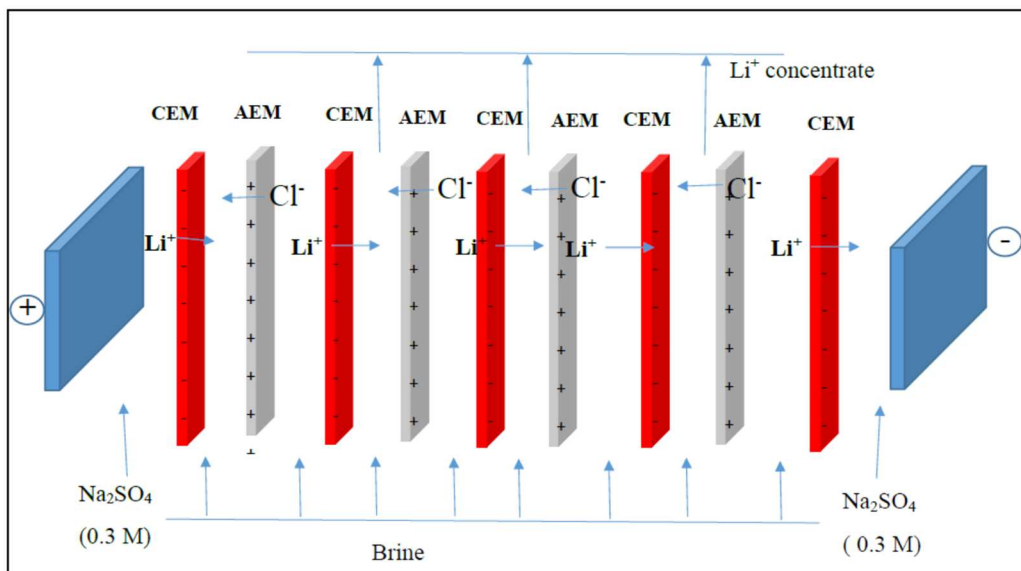


Fig. 4. Conventional electrodialysis.

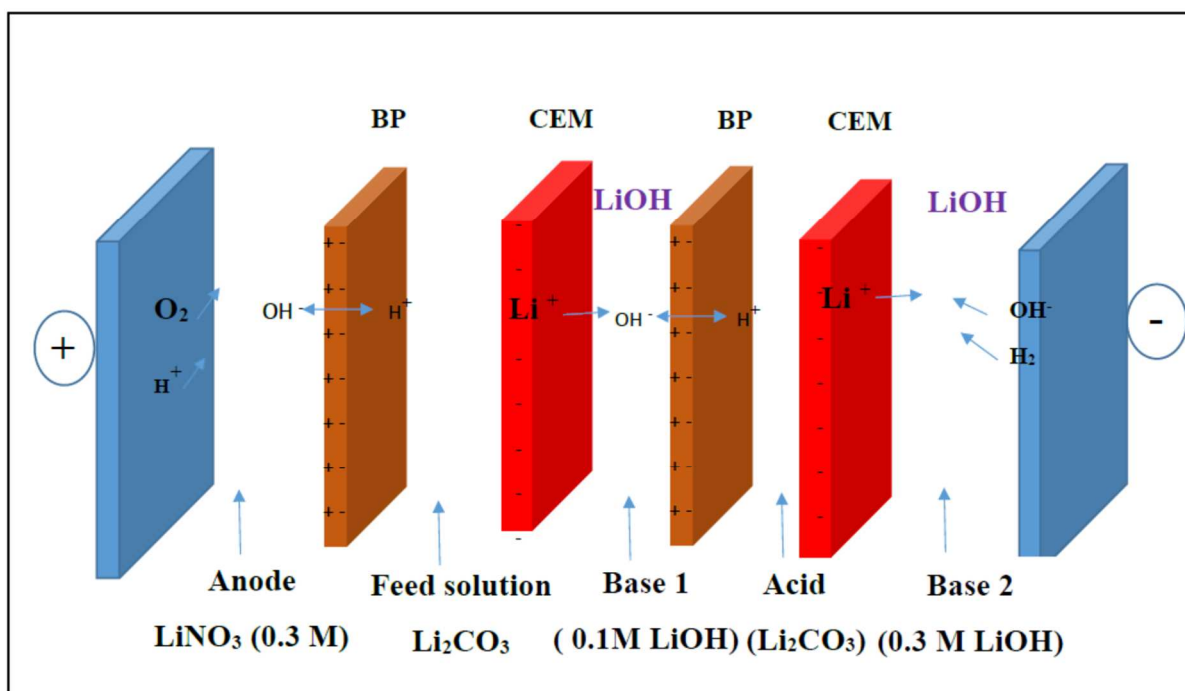


Figure 5. Electro-electrodialysis with bipolar membrane.

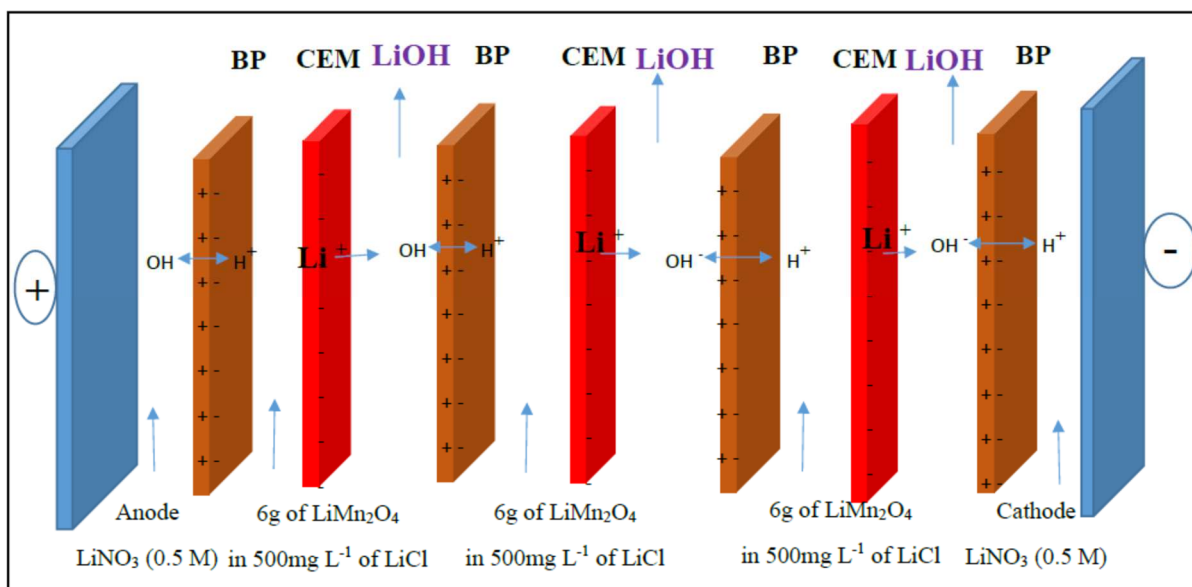


Figure 6. Lithium stripping from LiMn_2O_4 and LiOH production by means of bipolar membrane electrodialysis system.

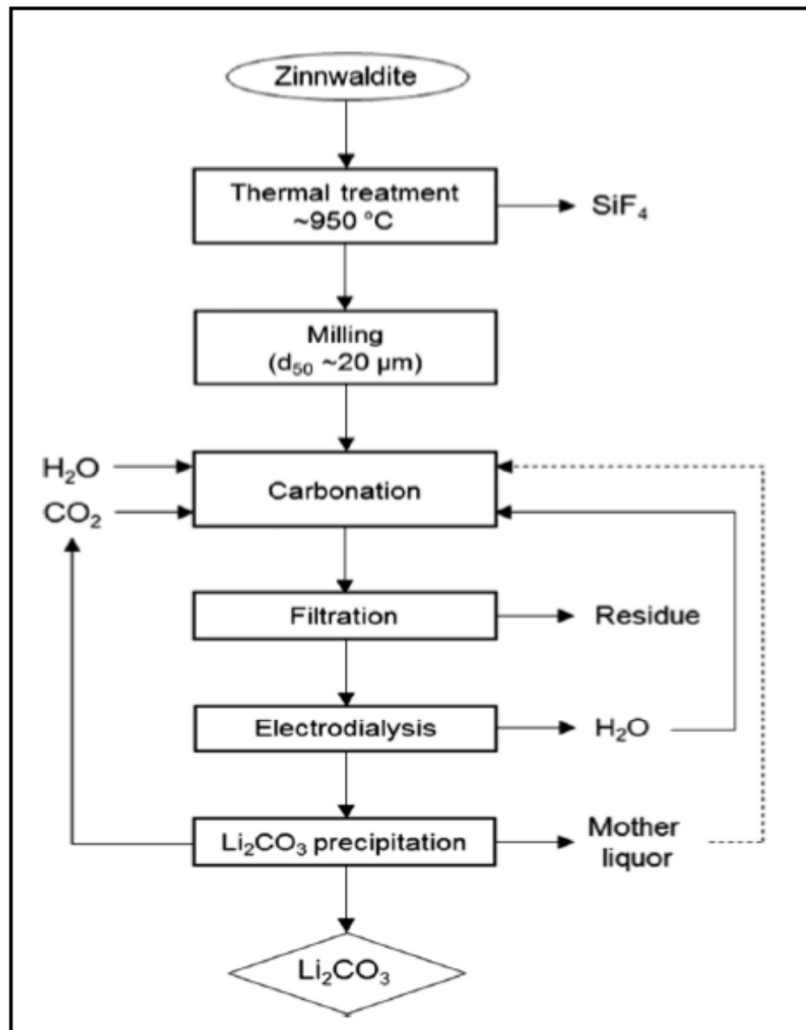


Figure 7. Flowsheet for Li_2CO_3 production of from Zinnwaldite concentrate.

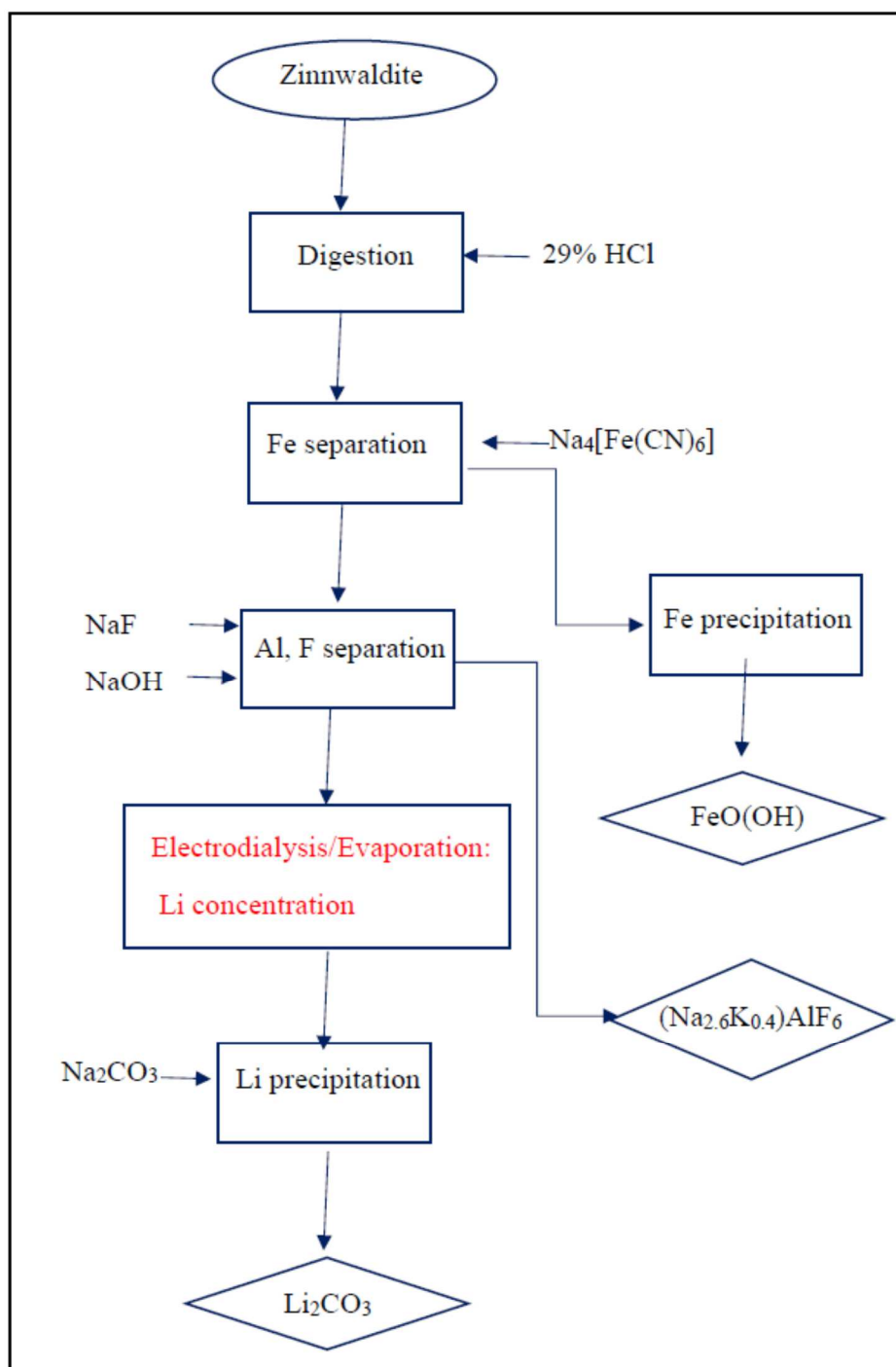


Figure 8. Flowsheet for Li_2CO_3 production from Zinnwaldite.

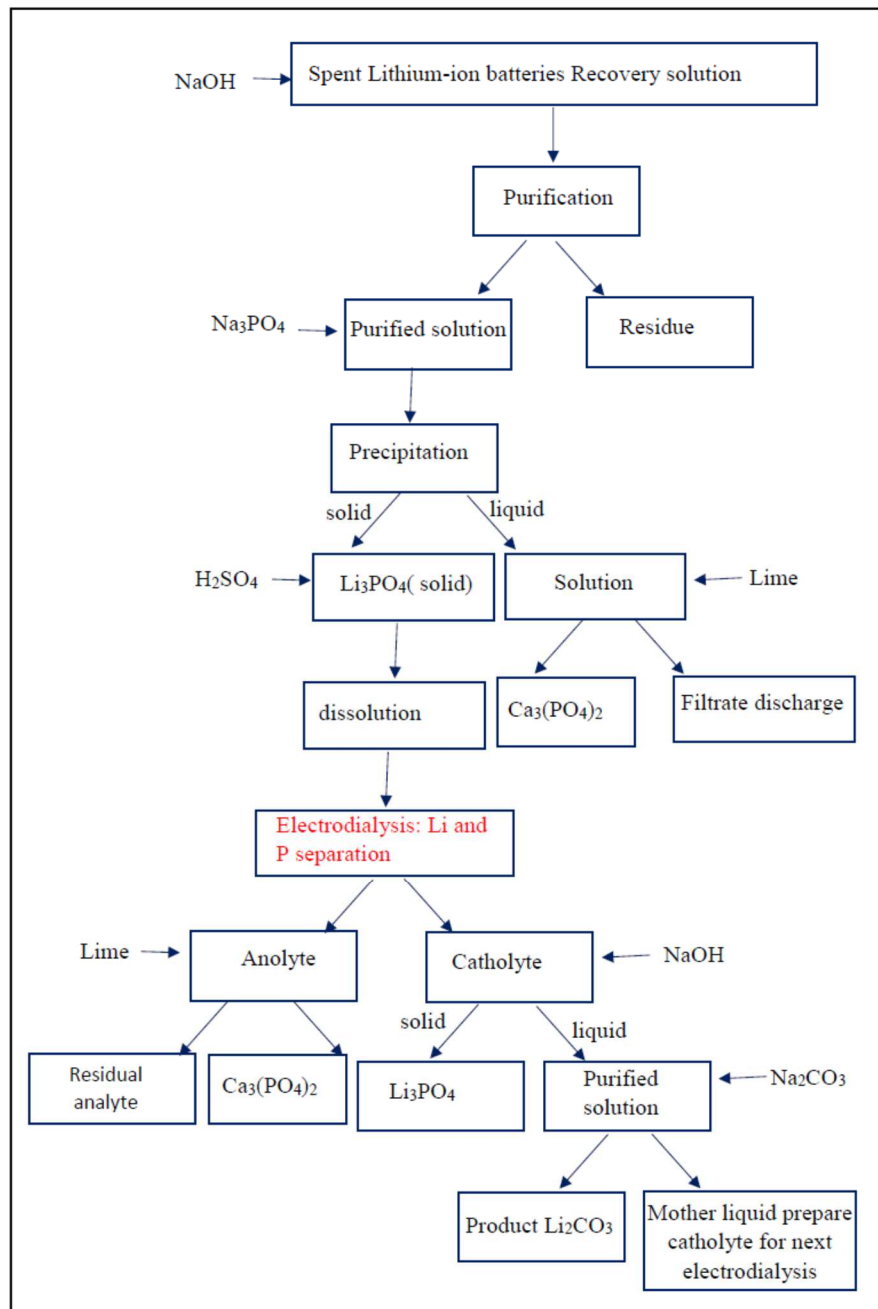


Figure 9. Lithium-ion battery recycling flowsheet including electrodesorption operation.

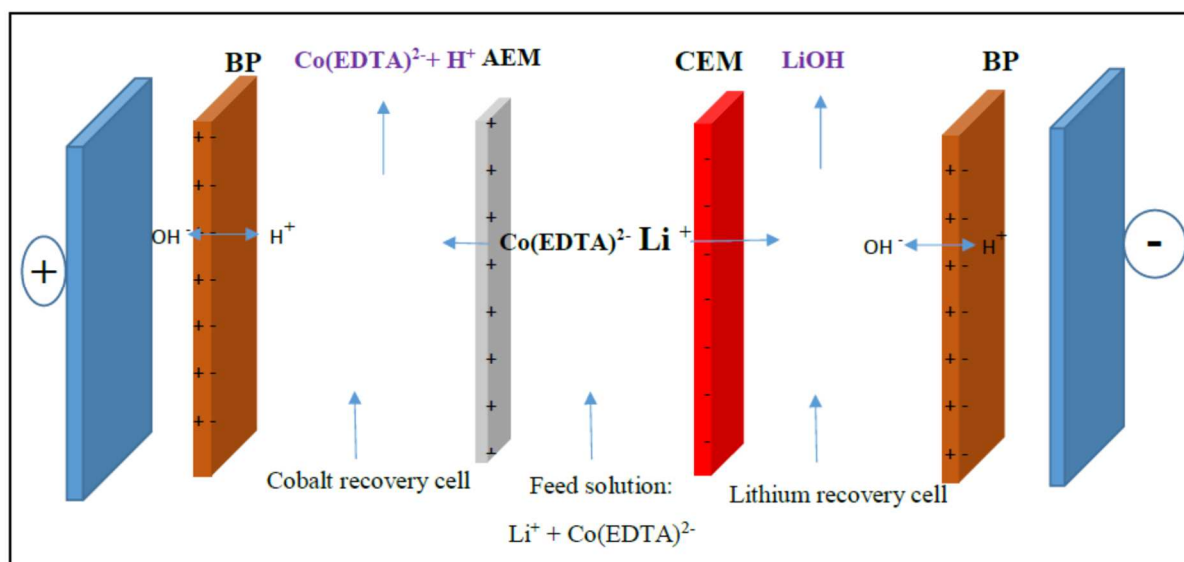


Figure 10. Lithium–Cobalt separation by means of bipolar membrane electrodialysis.