



Lithium dedicated adsorbent for the preparation of electrodes useful in the ion pumping method



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A B S T R A C T

In this paper, our studies on the extraction of lithium using a new desalination technology are presented. The combination of capacitive deionization with ion pumping batteries resulted in the hybrid CDI process. Hybrid CDI was composed by an electrode prepared from inorganic adsorbents (blended manganese and titanium oxides) and a counter electrode made of activated carbon. The structure and porosity of the adsorbents were investigated by SEM, XRD and BET analyses, while the pore size distribution was calculated according to the QSDFT model. The adsorbent with the best electrochemical performance was manganese oxide with a 5% content of titanium dioxide. It was characterized by enhanced electron conductivity and a structure that offers the highest hybrid CDI adsorption capacity for lithium. This material was used to build a negatively polarized electrode of the hybrid system that allowed ~ 36 mg/g sorption capacity for LiCl to be reached. The uptake of KCl and NaCl was 16 mg/g and 11 mg/g, respectively. Additionally, the best adsorbent was characterized by a 2 times smaller consumption of energy needed to extract lithium chloride in comparison to other monovalent salts.

1. Introduction

Lithium is a critical material used in many fields of industry. Due to its extraordinary properties, low molecular weight (6.431 g/mole) and low standard potential (-3.045 V), lithium is recommended for the long life batteries used in small and lightweight packages. According to a United States Geological Survey for Mineral Resources, document published in 2015, lithium is used in glass and ceramics (35%), lubricating greases (8%), continuous mould flux powders (6%), air treatment (5%), polymer production (5%), and also in other fields (9%) [1]. However, the most declared area of its application is in the production of lithium ion batteries (LIBs). Lithium consumption has increased from year-to-year and reached approximately 175,000 metric tons of lithium carbonate equivalents in 2015 [1].

Lithium resources can be divided into two groups: primary and secondary. The former one accounts for minerals like spodumene and hectorite, salt lakes and also underground brine reservoirs. The second group comprises of spent LIBs, which could also be a prominent resource for lithium [2]. Lithium extraction from minerals is based on leaching followed by precipitation, evaporation, ion-exchange, adsorption and/or solvent extraction. The last operations are also used for the recovery of lithium from salt lakes or brines. To recover lithium from LIBs, the following series of unit operations are used: leaching,

precipitation, ion-exchange and electrolysis [2]. The content of lithium in saltwater is estimated at $2.5 \cdot 10^{14}$ kg Li with an average concentration of 0.17 ppm for marine waters, 0.1–0.2 mg/dm³ for groundwater and ~ 15 mg/dm³ for geothermal waters enriched with Li⁺ ions [3,4]. However, this amount is not sufficient to cover the market demand. In such circumstances, some new resources with a low lithium concentration have to be exploited. To obtain lithium from them, traditional methods are not efficient enough and the search for new technologies has to be carried out. It seems that the adsorption method can be considered effective for dealing with such a problem. The process of lithium adsorption from diluted aqueous solutions can be carried out on various adsorbents. Some inorganic adsorbents with a spinel-type structure, mostly based on manganese oxide, have large selectivity to lithium salt and were used for the treatment of seawater and geothermal water [4,5]. The adsorption efficiency of spinel type-manganese oxides depends on the methods of adsorbent preparation, the sorbent components, the temperature of calcination and the conditions of the sorption process. Adsorbent that combines Li-Ti-O and Li-Mn-O complexes is characterized by high Li selectivity and strong mechanical properties that are given by Mn-O structures and the high hydrophilicity of Ti-O units [8–11]. The literature data are summarized in Table 1. To improve lithium uptake, the manganese bearing reactant was mixed with, or replaced by, other compounds. For example, the

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Table 1
Types of lithium adsorbents and conditions for the process.

No	Resources of lithium ions	Type of used adsorbent	Process Conditions	Max. uptake Li ⁺ [mg/g]	Ref.
1	LiCl solution C _{Li+} = 60.0 mg/l	Spinel-type lithium manganese oxide (LMO)	T = 25 °C t = 70 h	28.5	[6]
2	LiOH solution C _{Li+} = 0.1 mol/l Buffer solution C _{Li+} = 0.1 mol/l Brine C _{Li+} = 237 mg/l	Spinel manganese oxide (Lithium ion-sieve)	T = 25 °C t = 24 h	8.73 3.83 1.49	[7]
3	LiOH solution C _{Li+} = 2.0 g/l	H ₂ TiO ₃	T = 25 °C t = 24 h	21.00	[8]
4	Li ⁺ solution C _{Li+} = 0,1 mol/l	HMnO (HMO)	T = 25 °C	24.1	[9]
5	LiCl solution C _{Li+} = 6.08 mg/l	MnO ₂ 0, 5H ₂ O	T = 25 °C t = 48 h	10.05	[10]
6	LiCl + LiOH solution C _{Li+} = 0.05 mol/l	Li-Sb-Mn composite	–	33.23	[11]
7	C _{Li+} = 0.7 ppm	Magnetite-lithium manganese oxide	T = 25 °C t = 120 h	7.37	[12]

H_{1.6}Mn_{1.6}O - lithium adsorbent obtained by acidic treatment of LiMnO₂ - showed a maximum uptake of 10.8 mg Li⁺/g [9]. At the same time, the H₂TiO₃ - lithium sorbent synthesized from CH₃COOLi and Ti (OC₄H₉)₄ had an adsorptive capacity of 21.0 mg Li⁺/g [8–10]. Moreover, the composite of Li-Sb-Mn oxide obtained by heating mixtures of Li₂CO₃, MnO₂ and Sb₂O₃ with a different Li/Mn/Sb mole ratio showed lithium adsorption capacity as high as 33.2 mg Li⁺/g [11]. Therefore, it can be seen that sorbent capacity depends on the kind of used spinel, its specific structure and the conditions of the sorbent preparation.

One of the most interesting processes of lithium recovery is capacitive deionization, which was discussed previously [13,14]. In the CDI process, activated carbons are generally usually used for preparing anodic and cathodic electrodes. There are a few papers dealing with the use of lithium selective sorbents to obtain electrodes for lithium extraction [3,6]. However, taking into account the different origin of sorption, the formation of an electric double layer in the case of CDI and also intercalation in spinel-like sorbents, the process of lithium electrosorption on inorganic material was named 'ion pumping' [15–17] and this term will be used in the paper.

The goal of the paper was to develop a search method for lithium dedicated materials suitable for the construction of electrodes for extracting lithium ions. In order to achieve this, materials prepared by mixing titanium oxide with manganese oxide were characterized. The inorganic adsorbent was obtained via solid-state reaction with Li₂CO₃, MnCO₃ and TiO₂. The second goal was to check if the presence of titanium oxide in an electrode improved lithium recovery by the system.

2. Materials and methods

2.1. Synthesis of Li-TiO₂-MnO₂

Adsorbents of Li-TiO₂-MnO₂ were prepared via a solid-state reaction using Li₂CO₃ (Fluka, 98%), MnCO₃ (Sigma-Aldrich, 99%) and titanium oxide synthesized from titanium (IV) isopropoxide. More details about the preparation of the titanium oxide particles can be found in SI-1A. The Li/Mn molar ratio was kept as 1:3 for all the samples, while the amount of titanium dioxide was 0%, 5%, 10% or 20 wt% for the particular samples, which will be numbered as P0, P5, P10 and P20, respectively. The content of titanium dioxide was determined gravimetrically. Prior to the reaction, each mixture was well mixed and then

kept in a furnace at 500 °C for 1 h under an air atmosphere. The lithium adsorbent was prepared after being treated with sintered sorbent with hydrochloric acid (1 M, 25 °C). The obtained material was then filtered, washed, dried and grinded.

2.2. The electrodes preparation

All electrodes were prepared by mixing 90 wt% of Li-TiO₂-MnO₂ adsorbent or activated carbon with 10 wt% of poly(vinyl chloride) (3.5% solution of PVC in cyclohexanone). Prior to mixing, the powdered material was dried at 80 °C overnight. The cooled powder was added to a PVC solution and stirred for 30 min at 40 °C in an ultrasonic reactor. The slurry was cast on a graphite current collector and electrode with a thickness of 80 μm was formed by a casting knife. Solvent was first removed by evaporation at 60 °C for 24 h, and later in a vacuum dryer. The formed electrodes were kept in DI water and rinsed before their use.

2.3. The system

2.3.1. Layout of the system

To study the desalination efficiency towards chloride salts, a Fumatech laboratory electro dialyzer FT-ED-100-4 was used. The stack was composed of two electrodes divided by 200 μm thick spacer. Details about preparation of electrodes can be found in the SI-1B section. Graphite foil was employed as a current collector for all the prepared electrodes. The cathode was prepared from Li-TiO₂-MnO₂ adsorbent, while the anode was prepared from the activated carbon of YP-50F (Kuraray Chem Co.). Aqueous solutions of LiCl, NaCl and KCl, a total volume of 100 ml at a 10 mM concentration, was circulated in the system at an average speed of 4 dm³/h. The cyclic time was 1 h where sorption and desorption processes were carried out for 30 min.

Desalination performance was evaluated under constant voltage mode (CV). The general parameters of conducting the CDI operation are presented in Table. S2-1. The electro dialyzer was biased by DC power from a Konrad KD3005D Digital-Control DC Power Supply with the following voltages: 0.25, 0.50, 0.75, 1.00, 1.25 and 1.5 V. The fluid properties were monitored with a U3401A Digit Dual Display Multimeter and a CPC-501 meter.

In all the experiments, the process metrics, as salt adsorption capacity (SAC) and average salt adsorption rate (ASAR), were calculated [18,19,34]:

$$\text{SAC} \left[\frac{\text{mg}}{\text{g}} \right] = \frac{(C_o - C_f) \times v}{m} \quad (1)$$

$$\text{ASAR} \left[\frac{\text{mg}}{\text{g} \cdot \text{s}} \right] = \frac{\text{SAC}}{t_{\text{charge}}} \quad (2)$$

where C_o [mg/dm³] and C_f [mg/dm³] are the initial and final salt concentration, v is the solution volume, m is the mass of both electrodes and t_{charge} is the charging time.

The important parameter for evaluating the separation stack working in the CV mode is charge efficiency Λ. This parameter was defined as the ratio of adsorbed salt over the charge and showed how a large electric charge was accumulated in the electrode pair during the charge (discharge) process in relation to the salt adsorbed per cycle [20].

$$\Lambda = \frac{(C_o - C_f) \cdot v \cdot F}{Q \cdot M} \quad (3)$$

where F is the Faraday's number (F = 96,485 C/mole), Q is the charge stored for charging steps and was calculated by integration of the current and time of charging, and M is the molecular weight of chloride salts (LiCl = 42.39 g/mole, NaCl = 58.44 g/mole, KCl = 74.55 g/mole).

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