Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11387

64 (2017) 251–254
February

The use of activated carbon modified with polypyrrole as a supporting electrode for lithium ions adsorption in capacitive deionization

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Received 4 April 2016; Accepted 11 June 2016

ABSTRACT

Nowadays, lithium is a raw and substantial material used in various industries. In this paper, we investigated a possibility of preparation of selective and effective lithium adsorbent, used in an electrode for capacitive deionization process. Polypyrrole (PPy) modified activated carbon is applied to supporting electrode manufacturing. Lithium adsorbent was obtained by solid-state reaction of lithium and manganese carbonate and titanium dioxide. The structure of obtained material was confirmed by X-ray diffraction. The supporting electrode was prepared in series of various content of PPy. The best adsorption system of lithium ions, from diluted aqueous solution, was revealed by lithium adsorbent and supporting electrode containing 2% PPy. The electrosorption capacity for LiCl was maintained at 36.9 mg g^{-1}. In the same system, electrosorption of NaCl was 18.09 mg g^{-1} and of KCl 9.07 mg g^{-1}. That confirmed selectivity of obtained material toward lithium.

Keywords: Lithium adsorbent; Polypyrrole; Capacitive deionization

1. Introduction

Lithium is a substantial raw material. Due to its exceptional properties, such as low molecular weight (6.431 g $mole^{-1}$) and low standard potential (–3.045 V), lithium possesses very high energy and power density. It finds application in many various industry branches, for example, in glass and ceramics, lubricating greases, air treatment or polymer production. However, the highest application of this element is observed in rechargeable lithium ion batteries production, where its consumption is increasing year by year and reached 175,000 metric tons of lithium carbonate equivalents in 2015 [1].

Lithium sources can be divided into two sections: primary and secondary ones. The former group includes natural sources, for example, minerals (spodumene), clays (hectorite), salt lakes, underground brine reservoir and so on. The latter group of secondary resources involves spent lithium ion batteries, which are the most considerable carriers of this element [2]. Lithium extraction from ores or minerals is followed by leaching, while its extraction from brines includes evaporation, precipitation, adsorption and ion exchange. Lithium recovery from lithium ion batteries is followed by precipitation, ion exchange or solvent extraction and electrolysis [2]. For the future, seawater can be regarded as the most promising resource of lithium, as the amount of lithium is there estimated at $2.5{\cdot}10^{14}$ tons in total, while the average concentration of Li^+ is 0.17 ppm. Due to such low concentration, its efficient separation has turned to be a critical target. Conventional methods, such as precipitation, solvent extraction or other, are not suitable for lithium recovery from such diluted solutions. Therefore, the adsorption method is considered to be an effective alternative for solution of this problem.

Adsorption of lithium ions from brines and seawater is very difficult, because of other ions presence in the solution, amount of which is usually bigger than the Li+ content. In this case, it is necessary to develop a special sorbent, which will be able to selectively remove lithium ions from dilute

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Presented at the conference on Membranes and Membrane Processes in Environmental Protection (MEMPEP 2016), Zakopane, Poland, 15–19 June 2016.

solutions. The frequently applied inorganic adsorbent is a composite of spinel-type manganese oxide. Current research, however, considers preparation of inorganic lithium selective adsorbent, which is based on Li-Ti-O and Li-Mn-O complexes. An adsorbent that combines both of these complexes is characterized by high Li selectivity and sufficient mechanical properties provided by Mn-O structures and high hydrophilicity offered by Ti-O units.

Capacitive deionization (CDI) process is a separation technology involving ions removal from dilute solution, by means of electrical potential difference between two electrodes. Conventional CDI process operation consists of two phases: adsorption and desorption. In the adsorption phase, an applied electrical potential results in ions transport, through the electrode pores and adsorption in electrical double layers (EDLs). After a while, all the available pore's volume becomes saturated, and the sorption capacity of the system is achieved. For system regeneration, the adsorbed ions are released from electrodes, by a reduction or reversing of polarity. Hence, it is possible to obtain a stream, enriched in the desorbed ions, while electrodes regain their sorption capacity.

The most important parts of the whole CDI system are carbon electrodes that should be characterized by the following features: high specific surface area (SSA) available for adsorbed ions, high stability at wide pH and voltage range, conduct electricity, low resistance between electrodes and current collector, wettability and low costs of production. The most common material used for CDI electrodes preparation is activated carbon [3]. However, activated carbon does not exhibit the selective nature dedicated to only one kind of ions, for example, only lithium or potassium ions. Modifications, which are able to change surface character of activated carbon or application of another selective adsorbent for electrodes preparation, are considered to be useful solution of the problem.

The change of activated carbon surface properties can be assisted by surface area alteration. Moreover, to improve the capacity and desalination performance of activated carbon electrode, another component can be added, for example, a conductive polymer. The polymer should enable the control of electrical stimulus; it should characterize with very good electrical and optical properties; it should possess a high conductivity/weight ratio; and also, it can favorably be biocompatible and biodegradable. Polypyrrole (PPy) is one of the highly researchable material, due to its exceptional electrical behavior, stimulus-responsive properties and good chemical stability [4].

The goal of this study was to evaluate the CDI system, consisting of PPy modified carbon electrode and lithium selective electrode, for enhanced extraction of lithium chloride from diluted solution. The performed research aimed to determine if a modification of a supporting electrode designated for chloride anions removal could improve the lithium chloride recovery ratio for aqueous solutions.

2. Materials and methods

2.1. Synthesis of inorganic lithium adsorbent

Lithium selective adsorbent was obtained by solid-state reaction at 500°C, with the use of Li_2CO_3, $MnCO_3$ and TiO_2. All reagents were delivered by Sigma-Aldrich Sp. z. o. o. Poznan, Poland company. The amount of each element was determined gravimetrically, and the Li/Mn ratio was maintained at the level 1:3, while the content of TiO_2, in prepared samples, was fixed to 5% wt. After solid-state reaction, the prepared precursor of lithium adsorbent was acidified for 24 h. Then, the material was washed by deionized water, dried and grinded.

2.2. Synthesis of polypyrrole modified activated carbon

Modification of surface properties of activated carbon was carried out by introduction of conductive polymer, such as PPy at volume of activated carbon (AC), type YP-50F, supplied by Kuraray Chemical Co. LTD. Osaka, Japan. PPy was supplied by Sigma-Aldrich, and it was added to activated carbon in the following ratios: 1%, 2%, 5%, 8% and 20% wt.

2.3. Synthesis of electrode for capacitive deionization

All electrodes were prepared by mixing 90% wt. of lithium adsorbent or modified activated carbon with 10% wt. of poly(vinyl chloride), dissolved in cyclohexanone (3.5% wt. solution of polymer). The obtained mixture was vigorously stirred using mechanical stirrer for 3 h, at room temperature. Finally, the slurry was cast on the graphite current collector, and the electrode of 100 μm thickness was formed by a casting knife. The evaporation of solvent was carried out for 2 h in a vacuum dryer.

2.4. CDI system

To study the effectiveness of lithium adsorption, a Fumatech laboratory electrodialyzer FT-ED-100-4 was used. The device consisted of two different electrodes, which were divided by spacer of thickness 200 μm. The lithium selective electrode was formed from lithium adsorbent, and the supporting electrode was prepared from PPy modified activated carbon. The scheme of the CDI system is presented in Fig.1.

To investigate selectivity of lithium adsorbent, solutions of LiCl, NaCl and KCl, of 10 mM concentration, were used. The adsorption process was carried out for 30 min at 25°C. In the experiment, the electrosorption capacity was defined according to the Eq. (1):

$$\text{Electrosorption capacity}, \frac{\text{mg}}{g} = \frac{(C_\text{o} - C_f)\cdot V}{m} \tag{1}$$

where C_0 and C_f mg dm^{-3} are the initial and final salt concentration, respectively; V dm^3 is the solution volume; and m and g, are the mass of both electrodes.

2.5. Analytical section

2.5.1. X-ray diffraction analysis

The structure of crystalline phases was investigated by means of X-ray diffraction. The measurements were performed at 2θ angle ranging from 5° to 120°, at room temperature, with 0.02° step and rate of 3°C min^{-1}, using Philips X'Pert PW 3040/60 diffractometer ($K\alpha$ = 1.5418 Å) with Cu lamp (30 mA and 40 kV).

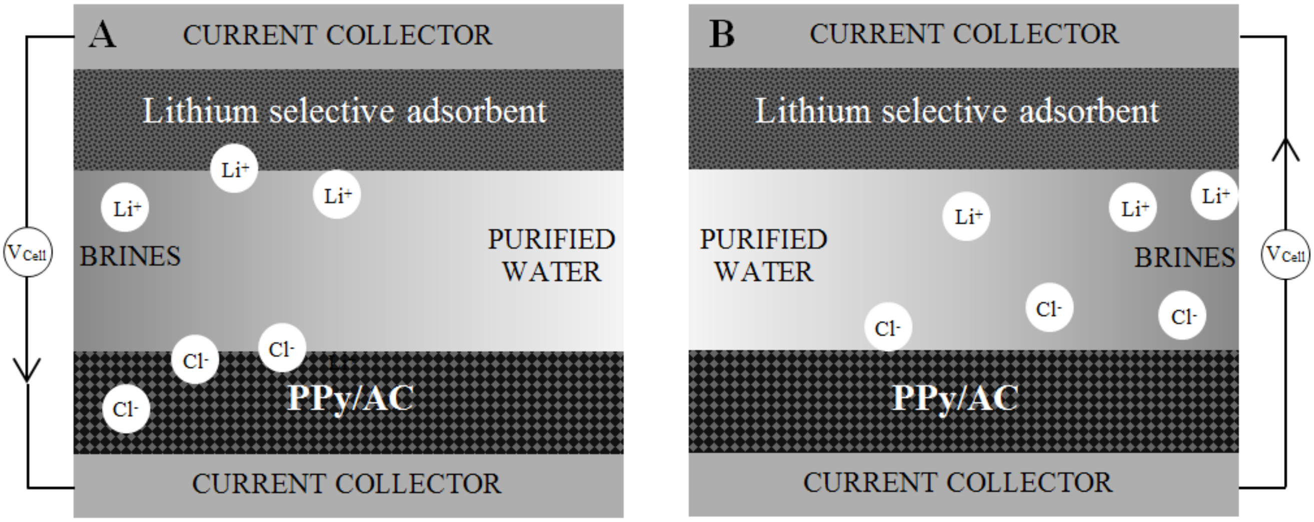

Fig. 1. Schematic diagram of (A) adsorption and (B) desorption process. The system consists of lithium selective adsorbent and modified activated carbon.

2.5.2. Analysis of material porosity

The porous texture of materials was analyzed by N_2 sorption at 77 K, using Autosorb IQ gas sorption analyzer. The Brunauer–Emmett–Teller (BET) method, based on an adsorption data of nitrogen in the relative pressure (p/p0) ranging within 0.02–0.2, was used to determine an SSA.

3. Results and discussion

3.1. X-ray diffractometer (XRD) analysis

The structure and crystalline phases of the adsorbent were investigated by XRD. In Fig. 2, the XRD patterns for lithium adsorbent are shown. The diffraction peaks at 2θ = 25.5° and at 2θ = 82° correspond to Ti element, while peaks at 2θ = 19°, 36° and 44° are assigned to manganese oxide forms. Moreover, the prepared lithium adsorbent characterized with a cubic structure. It could be expected that homogenous structure was possible to be obtained by sintering lithium and manganese carbonates with titanium dioxide.

3.2. Surface area of materials

The morphology and pore sizes of obtained materials were determined by means of N_2 BET isotherms.

The pore structure, pore size and SSA of material used for electrode preparation were vital considering the CDI system performance. Hence, their analyses were necessary. The BET equation was used to calculate the SSA, using adsorption data. The SSAs, pore sizes and pore volumes are presented at Table 1. The values of SSA decreased with an increasing content of PPy in samples. Moreover, the same effect was observed for pores volume and pore sizes. It could suggest that the addition of PPy deteriorated the surface properties.

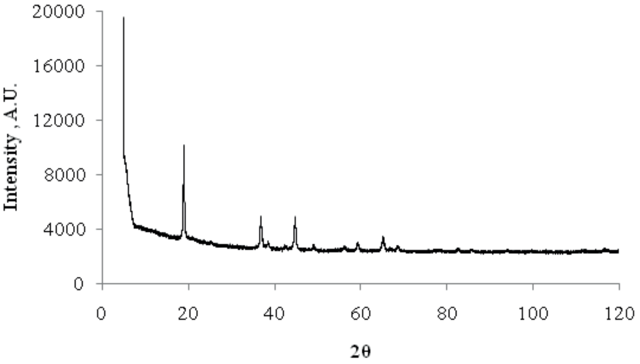

Fig. 2. X-ray diffractometer (XRD) patterns for lithium adsorbent.

Table 1
BET surface areas, pore volumes and pore sizes for the obtained samples

Samples	Specific surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore diameter (nm)
Lithium adsorbent	54.9	0.113	1.03
PPy1%/AC	1,273	0.714	1.74
PPy2%/AC	946	0.576	1.89
PPy5%/AC	617	0.325	2.28
PPy8%/AC	549	0.286	2.42
PPy20%/AC	476	0.254	2.59
AC	1,672	0.757	1.65

3.3. Capacitive deionization

The results of electrosorption capacity in the CDI process performed with the use of supporting electrode of various PPy content are presented in Fig. 3. It can be seen that the voltage directly influenced the electrosorption capacity and the maximum value of salt adsorption was reached at 0.7 V. The value of electrosorption capacity changed non-linearly with increasing amount of PPy. Moreover, the highest salt adsorption was achieved for electrode that contained

2% of PPy. The comparison of the obtained data leads to the conclusion that the addition of PPy to supporting electrode improved lithium adsorption. According to results shown in Fig. 3, the electrode with 2% wt. content of PPy, operated at 0.7 V voltage, was regarded as the most efficient system.

In Fig. 4, the electrosorption capacity in relation to LiCl initial concentration is shown. In this case, the CDI system consisted of lithium selective adsorbent and supporting electrode with 2% wt. of PPy. It can be seen that electrosorption capacity was related to LiCl initial concentration.

In Fig. 5, the dependence of electrosorption capacity of LiCl, NaCl and KCl adsorption duration is presented. In this case, the properties of lithium selective electrode that formed the pair with supporting electrode with 2% content of PPy were evaluated. It can be seen that the slope of LiCl adsorption was the largest, and it could suggest that this process was the fastest in comparison with NaCl and KCl electrosorptions. The results of salt adsorption were: 33.4 mg g^{-1} for LiCl, 18.48 mg g^{-1} for NaCl and 9.08 mg g^{-1} for KCl, after 30 min of the process duration. In order to prove the exceptional properties of the developed system, we compared the obtained results with other inorganic adsorbents and systems. As it is was described in [5], for lithium manganese oxide ($LiMn_2O_4$), prepared by solid state reaction of Li_2CO_3 and $MnCO_3$ sintering, the maximum uptake was maintained at 25 mg g^{-1} of Li^+ after more than 4,000 min process duration, at cell potential of 1.0 V. Moreover, another system, which consisted of H_2TiO_3–lithium adsorbent synthesized with CH_3COOLi and $Ti(OC_4H_9)_4$, characterized with adsorptive capacity of 21.0 mg Li g^{-1} after 24 h of the process run [6]. Comparing the obtained results with literature data, it can be concluded that the developed system characterizes with higher electrosorption capacity obtained in shorter duration. Hence, the electrosorption capacity data confirmed the selective character of obtained lithium adsorbent.

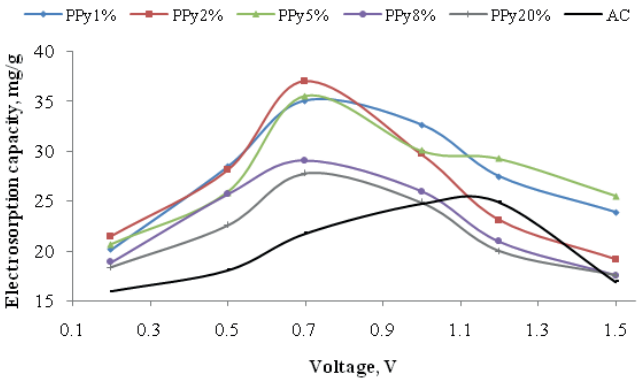

Fig. 3. The dependence of lithium chloride electrosorption capacity on voltage correlated with various content of PPy in supporting electrode.

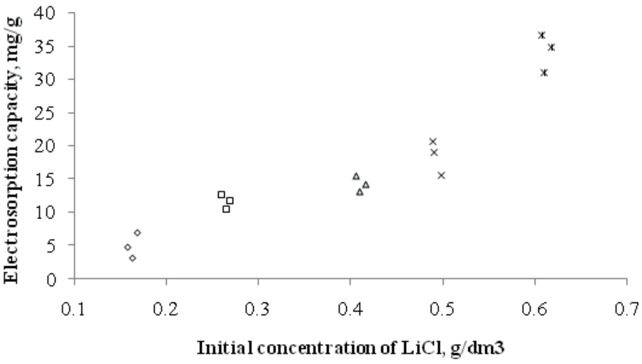

Fig. 4. The correlation of electrosorption capacity with initial concentration of LiCl. For each concentration, three independent measurements were carried out.

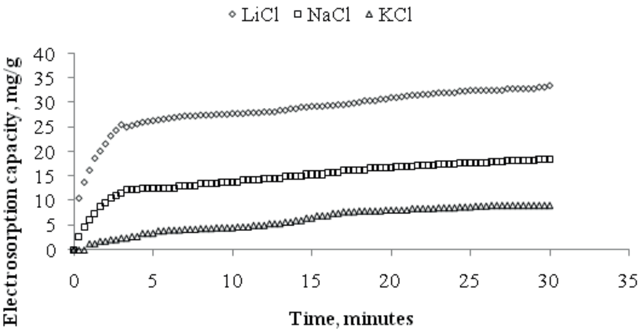

Fig. 5. The correlation of electrosorption capacity of various salts with adsorption process duration.

4. Conclusion

In the paper, the new system for lithium adsorption is discussed. The system consists of lithium selective electrode, characterized by high lithium ions selectivity and PPy modified activated carbon electrode for chloride anions capture. Electrode containing 2% wt. of PPy was found to be the best supporting electrode. According to the obtained data, it can be concluded that the developed system enables effective extraction of lithium ions from diluted aqueous solution. Moreover, running of the CDI process at 0.7 V voltage for 30 min allows to reach low-cost conditions for lithium chloride recovery.

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