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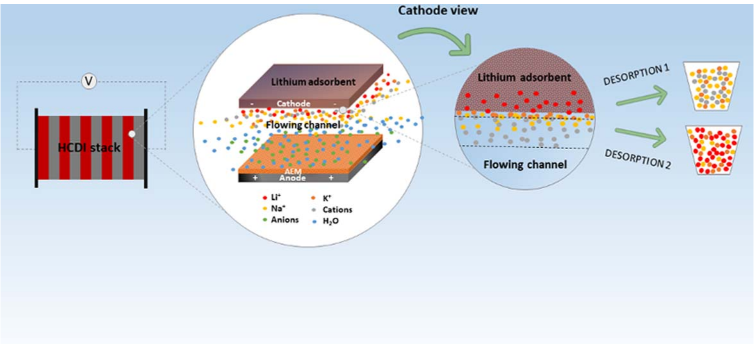
Lithium capturing from geothermal water by hybrid capacitive deionization

Anna Siekierka[a,*], Barbara Tomaszewska[b], Marek Bryjak[a]

[a] *Wroclaw University of Science and Technology, Department of Polymer and Carbon Materials, Wyb. St. Wyspianskiego 27, 50-370 Wrocław, Poland*
[b] *AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Mickiewicza 30 Av., 30-059 Kraków, Poland*

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate a novel mode for hybrid capacitive deionization, HCDI, that allows selective extraction of lithium ions from geothermal water. The HCDI cell was comprised with cathode made of lithium selective material and anode consisting of activated carbon coated with anion-exchange membrane. To confirm ion-exchange character of the process, based on ions diffusion/migration into electrodes, impedance spectroscopy and cyclic voltammetry were applied. By optimizing the process mode it was possible to obtain lithium enriched stream and remove up to 73% of lithium captured by the electrode. The process was characterized by an extremely high salt adsorption capacity of 800 mg/g and total energy consumption on the level of 0.183 Wh per 1 g of adsorbed salt.

1. Introduction

Lithium has been of significant interest in many fields of science and technologies. The global market of lithium salt is growing fast and it is expected to reach 30 $ billion value by 2020. Increasing rapidly demand of this element is caused by its application for electronics and batteries mostly [1]. The available lithium resources can be divided into two main categories: natural like minerals, salt lakes, underground brines or seawater, and artificial like recycle from electronic waste and lithium ions batteries [2]. It should be mentioned here that seawater, the richest resources of lithium, is still out of technological interest due to low lithium concentration of 0.1–0.2 mg/dm^3. From the technological point of view, the most promising lithium resource is groundwater where concentration of Li^+ is between 10 and 15 mg/dm^3 [3]. That situation makes geothermal water, and its reverse osmosis (RO) brines, to be perspective source for lithium extraction.

Geothermal water desalination require an electric or thermal technology to concentrate or to precipitate particular elements. A variety technologies have been developed over years. RO and multistage flash distillation require a large amount of energy that generates almost 50%

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[*] Corresponding author.
E-mail address: anna.siekierka@pwr.edu.pl (A. Siekierka).

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Table 1
Comparison of energy consumption for water treatment technologies.

Technology	Energy consumption		Ref.
	Wh/g	kWh/m^3	
Electrodeionization (EDI)	–	7.7	[6]
Reverse osmosis (RO)	–	1.1	[7]
Electrodialysis (ED)	0.99	–	[8]
Conventional CDI	–	0.4	[9]

of total production cost [4,5]. A search for less energy consuming technique was finalized with launching capacitive deionization, CDI, based on the use of supercapacitors. The comparison presented in Table 1 puts CDI as the most economical method.

The development of CDI has initiated a search for other methods with architecture similar to capacitive deionization but applying different electrode materials. One of such approaches is to use desalination batteries that consist of cation insertion electrode and chloride-capturing electrode, most frequently made of silver [5].

The goal of this paper was to demonstrate an efficiency of new hybrid capacitive deionization system, HCDI, for selective recovery of lithium ions from real geothermal water. The evaluated system was comprised of lithium-capturing electrode, built with lithium-titanium-manganese oxide material, LMTO, and activated carbon electrode coated with anion-exchange membrane made by poly(vinyl chloride) modified with ethylene diamine (PVC-EDA). At the first, it was shown innovative modes for running HCDI process that allowed to selectively remove lithium ions from multicomponent aqueous solution. To express the selective properties of HCDI we selected the geothermal water from Carpathian region in Poland. Secondly, the performances of HCDI were expressed by the energetic factors and related to selective lithium desorption in spots of electrochemical measurements.

2. Materials and methods

2.1. HCDI system design

The batch-mode HCDI test cell consisted of two parallel electrodes separated by a polypropylene spacer of 200 μm thickness to allow liquid solution flow through a channel. As an cathode material the spinel lithium-manganese-titanium oxide, LMTO, characterized in our previously study [10–13], was used. The LMTO adsorbent is characterized by a similar crystallinity to a $H_{0.6}Li_{0.08}Mn_{1.72}O_4$ (reference code: 01-089-0755) [9]. Activated carbon, AC, YP-50F Kuraray Chemical Co. LTD. Osaka, Japan [14] was applied to form anode. LMTO electrode was used for selective capturing of Li^+ ions and a AC electrode to capture anions. To prevent the effect of co-ions adsorption in the desorption step [4] an anion-exchange membrane was put on the surface of the AC electrode. As an anion-exchange membrane, AEM, we selected poly(vinyl chloride) modified by ethylene diamine, PVC-EDA. Details of membrane modification and preparation can found elsewhere [12,15]. The whole system consisted of HCDI cell, recycling tank, peristaltic pump (Elan, type 372.C), a digital electrical conductivity meter, pH meter and DC power supplier (KD3005D Digital-Control DC Power Supply). All experiments were conducted at constant voltage mode, CV with value of 2 V, at 25 °C.

2.2. Geothermal water quality

Tests were carried out using geothermal water with high mineralisation (TDS 2.3–2.5 g/dm^3), > 270 mg $CaCO_3$/dm^3 and lithium concentration > 15 mg Li^+/dm^3. The physical and chemical composition of crude water is presented in Table 2. The used geothermal water could be classified to the hydrogeochemical type 2.6% Cl-Na + I group. During running the HCDI process, the quality of feed water and concentrate were monitored by the following parameters – temperature, conductivity, and alkalinity – immediately after sampling solution from the recycling tank. Inorganic components were measured at the accredited laboratory (PCA-AB 1050 and PCA-AB 176) using the inductively coupled plasma mass spectroscopy method ICP-MS (ELAN 6100) and Inductively Coupled Plasma Optical Emission Spectrometer, ICP-OES (Optima 7300DV). Details about preparation of samples and their measurements are presented elsewhere [16–18].

2.3. Principles of operation

For the evaluation of HCDI system in lithium recovery from geothermal water two sets of process parameters were chosen. The first one was composed of CV-RCV-ZVC sequence, what meant adsorption at constant voltage (CV), desorption under reversing voltage (RCV) and final desorption under zero charge voltage (ZVC). The second set comprised CV-ZVC-RCV operations, where the desorption steps were conducted at opposite sequence as for CV-RCV-ZVC mode. The external voltage applied in the CV and RCV modes was 2 V. The time run of the HCDI process is presented in Fig. 1. The sequences of used process operations are juxtaposed in Table 3.

During the first step, the CV mode was applied and ions were removed from feed solution. It took place during first 3 min. The desalinated geothermal water was then collected and marked as solution A. The system was filled with deionized water (DI) and two stages of desorption process were carried out. Under RCV or under ZVC conditions, both lasting 1 min, adsorbed salts were removed. It was the first step of desorption. The obtained solutions were collected and marked as D1 and the system was filled with fresh DI water. In the next step, the second desorption process, lasting 5 min, was carried out. Charged electrodes released ions incorporated into volume of electrodes and produce enriched solution marked D2. Finally, the HCDI system was refilled with new portion of geothermal water and desalination procedure was repeated. Hence, the innovative system of removal lithium salt from geothermal water worked with following steps: adsorption A (performed always in CV mode), first desorption D1 (performed in RCV or ZVC mode) and second desorption D2 (also performed in relation ZVC or RCV mode). The indices A, D1 and D2 described the used electrical mode and were related to different salt concentration; thus A assigned solution after total salt adsorption while D1 and D2 showed solution obtained after first and second desorption.

2.4. Process metrics

Salt adsorption capacity (SAC) is a measure of extracted salt normalized to amount of used adsorptive material. When the amount of adsorbed salts was normalized to the process time and to the area of electrode (11.25 cm^2) we were able to get the average salt adsorption rate (ASAR), an useful metrics for process description. To characterize stack working in CV mode, the charge efficiency Λ (arb.uni.) was applied:

$$\Lambda = [(C_0 - C_f)\cdot V\cdot F]/\Sigma M\cdot Q \qquad (1)$$

where F is the Faraday constant, $F = 96{,}485$ ($C\cdot mol^{-1}$), ΣM is an average molar mass of salts in geothermal water, Q is a charge calculated by integration of current and time of the system charging.

Total energy consumption (E_{total}) was the sum of energy for adsorption (E_{ads}) and for desorption (E_{des}) processes. These metrics are computed from numerical integration of current versus time relationship [19,20]. Next useful metrics for characterization of HCDI process was energy normalized adsorption of salt (ENAS), expressed in grams per Joules of the total energy. That value quantifies the energetic efficiency of the desalination process. Last metrics describing hybrid capacitive deionization process was the electrical work expressed in Wh per gram of salt. It showed amount of energy needed by the system to adsorb or desorb 1 g of salt. To present the selective behaviour of HCDI