The evaluation of the effectiveness of lithium separation by hybrid capacitive deionization from geothermal water with the uncertainty measurement application

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ABSTRACT

We present an innovative method of lithium removal from geothermal water by hybrid capacitive deionization (HCDI) process working with tree-stage operation: electrosorption on electrodes and desorption with and without an electrical field. The conducted tests showed that the system was able to selectively capture lithium salt. It was noted the total adsorption capacity was on the level of 800 mg of salt per gram of electrode material. The process repeatability was evaluated within three runs conducted at the same conditions. The effectiveness of the HCDI process was calculated by means of the classic deterministic method and taking into account the uncertainty for the determination of the salt concentration.

Keywords: Lithium separation; Hybrid capacitive deionization; Measurement uncertainty; Geothermal water

1. Introduction

Lithium possesses an important position in energy storage systems. It results from its standard potential (–3.045 V) and the lowest molecular mass (6.941 g/mol), that causes high level of capacitance and significant miniaturization of batteries [1]. The EU has published two directives to promote electrical vehicles: the Directive 2009/33/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of clean and energy-efficient road transport vehicles and the Directive 2006/32/EC of the European Parliament and of the Council of 5 April 2006 on energy end-use efficiency and energy services [2]. Due to the growing market of electrical vehicles and portable devices, the demand for lithium dramatically increases and the worldwide consumption of lithium reached 37,800 tonnes in 2016 [3]. Such situation provides a growing shortage of lithium due to its limited resources. The total content of lithium in seawater and oceans is estimated at 2.5×10^{14} kg [4] with an average concentration of 0.17 mg/L [2]. Salt lakes contain 1,000–3,000 mg/L of lithium [2], while geothermal water up to 15 mg/L. Lithium from saline water can be recovered by ion-exchange, solvent extraction, coprecipitation, membrane processes, evaporation and adsorption [2]. Among the listed methods, the selective adsorption seems to be the most effective [5]. However, the application λ-MnO_2 in fixed bed system is characterized by energy consumption of 288 GJ/kg of lithium and it is still too high to be implemented to industry [5]. To merge selectivity with low energy requirements, a new process of lithium recovery from aqueous solutions should be developed. In our previous papers, we presented such innovative hybrid

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capacitive deionization (HCDI) method for lithium extraction from geothermal water [6].

Generally, capacitive deionization (CDI) is a method for adsorption/desorption operation that uses the external electrical field as a driving force [7]. The developed HCDI system is a modification of CDI. It comprises of a lithium selective adsorbent as a cathode and activated carbon electrode coated with an anion-exchange membrane as a composite anode [6,8]. Under action of the electrical field, ions are separated and migrate to electrode according to their sign. The investigated lithium–manganese–titanium oxide (LMTO) as a lithium selective electrode [10] allows to remove lithium ions from real geothermal water. By applying triple electrical modes of operation, electrosorption followed by first desorption with zero voltage and second one with reversed voltage, the initial monovalent ions ratio of Na:K:Li 656:6.5:1 was reduced to 51:0.6:1. The salt adsorption capacity (SAC) reached the level of 800 mg/g and energy consumption was as low as 0.183 W h/g of the salt [6]. Moreover, it was possible to re-extract lithium with 73% efficiency.

The idea of HCDI is based on the splitting of a feeding water into three streams: the postsorption stream (A), the first desorption stream obtained after washing the unbiased system (D) and the second desorption stream obtained after washing the reverse biased system (D2). The stream A was formed by the solution after electrosorption process, when the external voltage was applied. The stream D was obtained, when the system was fed with deionized (DI) water and ions accumulated on the surface of electrodes were washed out. This step was conducted without any voltage. The stream D2 was obtained, when the system was filled with DI water and washed up with the reversing external voltage. The mass balance resulting from the summary ion contents in these three streams should be equal to the initial value in the feeding water. In practice, these values relatively differed each to other because of the measurement uncertainty related to the used analytical techniques. The main aim of the work was to indicate that the measurement uncertainty was a significant factor that had to be taken into consideration, when the effectiveness of HCDI process was evaluated.

2. Materials and methods

2.1. Geothermal water quality

All tests were carried out using a real geothermal water obtained from Western Carpathian Region with minerals content of 24.2 mg/L, total hardness of 369 mg $CaCO_3$/L and lithium concentration of 15 mg/L. The used geothermal water could be classified as the hydrochemical type 2.3% Cl-Na. The physical parameters and the chemical composition of the raw water is presented in Table 1.

2.2. HCDI system

The batch-mode HCDI cell consisted of two parallel electrodes divided by a polypropylene spacer of 200 μm thickness to allow the solution to flow through. As a selective cathode material, the spinel of LMTO characterized in our previous studies [1,9,10] was used. To create the composite anode electrode, the activated carbon YP-50F Kuraray Chemical Co. Ltd., Osaka, Japan [11] and poly(vinyl chloride)

Table 1
The physical parameters and the chemical composition of the geothermal water

Li^+ (mg/L)	15.7
TDS (mg/L)	23,400
pH	7.8
Eh (mV)	–6
Cond. (mS/cm)	38.2
Hardness (mg $CaCO_3$/L)	369
H_2SiO_3 (mg/L)	17.8
Na^+ (mg/L)	10,298
K^+ (mg/L)	102.1
Ca^{2+} (mg/L)	63.7
Mg^{2+} (mg/L)	50.3
Sr^{2+} (mg/L)	33.5
Cl^- (mg/L)	11,421
HCO_3^- (mg/L)	1,462

modified with ethylene diamine as an anion exchange membrane [10,12] were selected. The whole system consisted of HCDI cell, recycling tank, peristaltic pump, digital electrical conductometer, pH meter and DC power supplier (KD3005 Digital-Control DC Power Supply). All tests were conducted at a constant voltage mode, CV, equalled to 2 V at 25°C.

The HCDI process for lithium extraction was carried out under three electrical modes. At the first one, the constant voltage of 2 V was used. It was applied for 3 min. After that time, the solution was collected and encoded as A. In the second mode, the circulating solution was changed to DI water and the system was washed for 1 min without an external voltage. The solution enriched with ions was collected and signed as D. Finally, in the third mode, the circulating solution was replaced with DI water and the voltage was reversed for 3 min. The collected solution was named D2.

2.3. Analytical methods

During the HCDI process, the quality of the feed solution and the concentrate was monitored by measuring the following parameters – temperature, electrical conductivity and alkalinity – immediately after sampling the solution from the recycling tank. Inorganic components were determined at the accredited laboratory (PCA AB 1050) using the inductively coupled plasma mass spectrometry, ICP-MS (ELAN 6100, Perkin Elmer, USA) and inductively coupled plasma optical emission spectrometry ICP-OES (Optima 7300DV, Perkin Elmer, USA). The second method was used for lithium determination. For chloride and alkalinity determination, titration methods were applied. All analyses were performed immediately after sampling three solutions A, D and D2. Details about preparation of samples and their analyses are presented elsewhere [13–15]. The basic parameters of the method for determination of lithium concentration are shown in Table 2.

2.4. Process metrics

The SAC is a measure of the extracted salt normalized to the amount of adsorbing material. When SAC is normalized

Table 2
Parameters of lithium determination method

Analytical technique	ICP-OES ISO 11885:2007
Limit of determination LOD (µg/L)	5
Precision as RSD (%)	1
Recovery (%)	108
Measurement uncertainty (%)	12

Fig. 1. Charge-discharge curves in the function of the conductivity (a), current and external voltage (b) over time.

by the process time, we obtain the average salt adsorption rate (ASAR). In all performed experiments, these both metrics were calculated as:

$$SAC = [(C_0 - C_f)V]/m \qquad (1)$$

$$ASAR = SAC/t_{charge} \qquad (2)$$

where C_0 (mg/L) and C_f (mg/L) are initial and final salt concentration, V (L) is the solution volume, m (g) is the mass of both electrodes, t_{charge} (s) is charging time.

The energy consumption in unit of Watt per gram of adsorbed salt was expressed as follows:

$$W = UI/m_{salt} \qquad (3)$$

2.5. Measurement uncertainty

Measurement uncertainty is a parameter associated with all analytical methods and used for each step of the analytical procedure. Any analytical result cannot be interpreted correctly without a basic information about its uncertainty, that is defined as 'a parameter associated with the final result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement' [22]. It takes into account all possible sources of errors that can occur during the whole analytical procedure including sampling, samples preparation, transportation, storage and final analysis. There are some methods of uncertainty estimation [17–22]. In this paper, the measurement of uncertainty for determination of lithium concentration was declared by the certified laboratory of AGH University of Science and Technology and it was used during estimation of HCDI effectiveness.

3. Results and discussion

3.1. HCDI performance

The changes of current, voltage and conductivity during the process are presented in Fig. 1. It can be seen that the adsorption stage reached the equilibrium after 1–1.5 min. Similarly fast phenomena were observed for first and second stages of the desorption when ions were released from the volume of the electrode. The desorption was characterized by a rapid change for all observed cycles. One of the difference between these processes was the initial value of the current that could be referred to the initial resistance between HCDI electrodes. From the Ohm's Law, we know that
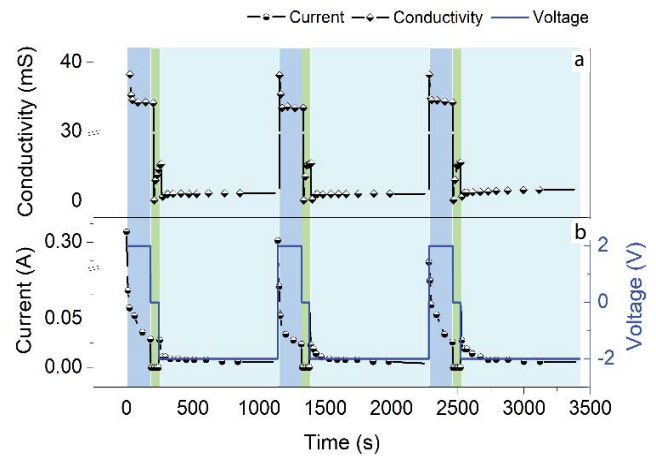
current decreases, when resistance of HCDI cell rises. That effect can be explained by a formation of a larger amount of air bubbles in circulating solutions and by charges collected on the electrical double layers. It should be remembered that the electromotive force in the HCDI process appears into the electrolytic nexus, which means that its value has the negative sign. It influences on the electrical efficiency of HCDI process, but not on the SAC and the value of process rates.

Fig. 2(a) shows the modified Ragone plot for determination of the ratio between the value of the adsorption capacity and time of the adsorption. The adsorption was the fastest step of the triple-stage HCDI procedure, when the ratio of ASAR achieved slightly 10 mg/g/s. This phenomenon can be explained by the large difference of the potential between the not-loaded electrodes and the high value of the initial TDS in the solution, viz. 23 g/dm³. That concentration gradient was one of the component of the driving force ensuring the potential difference between two electrodes. In our previous paper, we demonstrated that high value of SAC occurred according to Faradic processes and the formation of electric double
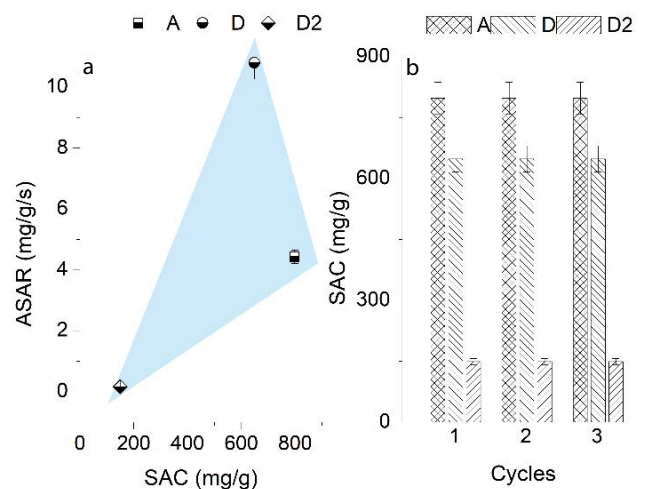

Fig. 2. The modified Ragone plot (a) and values of SAC for each steps of operation for three independent measurements (b).

layers [6]. Many factors contribute to this phenomenon: a redox reaction of ions in LMTO adsorbent, a spontaneous adsorption related to the specific surface area of electrodes as well as the formation of multilayers on solid-electrolyte interphases [6]. All of these processes could vitally affect SAC value.

To show that the process of HCDI can be repeatable, three independent measurements were performed. The values of SAC for each steps of HCDI are presented in Fig. 2(b). It can be concluded that the process, repeated after 5 d intervals, was characterized by the high cross sensitivity. The phenomena were observed for SAC and ASAR values.

The next parameter to be compared is the energy consumption during each step of the HCDI process. Table 3 presents the energy consumption for three conducted runs. From Fig. 1(b) one reads that initial current for adsorption was 0.342, 0.306 and 0.219 in the case of repeated cycles.

For the initial current demand, the ratio between first and third cycle was 1.8 that suggested an increase in the energy consumption by 60%. It should be underlined, however, that the values of SAC and ASAR did not change for all investigated cycles. In second desorption stage, D2, the ratio between first and third cycle of the initial current was 0.48 that corresponded to 43% decrease of the energy consumption. Hence, the calculated total energy consumption for the HCDI process showed the energy fluctuation on the level of 20%.

3.2. Lithium capturing and effectiveness assessment

One of the property of solutions with high TDS is the ion mass balance and the level of uncertainty for determination of ions concentration. The described HCDI process allows to realize a rapid adsorption with an extremely high capacity. The process is stable and repeatable in a time interval of several days. However, the principle of this research was to check if that HCDI could remove lithium ions selectively from a geothermal water, where lithium ions were in the minority. In the case of all ions appearing in the geothermal water, the adsorption capacity was the same in all investigated cycles. However, by applying a two-stage procedure for desorption, it was possible to enrich only one stream with lithium ions. The results are shown in Fig. 3.

According to data shown in Fig. 3, lithium ions were released from the volume of electrodes in the second stage of desorption, D2. This fact can be explained by the migration of lithium ions to the source of polarization. Chen et al. [16] described that lithium was accumulated on the electrode material creating a lithium layer. It was referred as one of

Table 3
The energy consumption of HCDI for each HDCI stage for three measurements

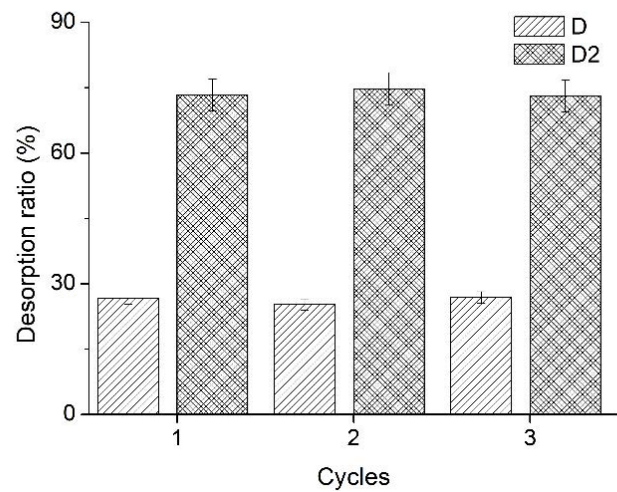| Energy consumption (W/g)				
	A	D	D2	A + D + D2
1	2.12	0	1.01	3.13
2	1.91	0	2.06	3.97
3	1.31	0	2.35	3.66

Fig. 3. The desorption ratio for lithium ions concentration divided into two desorption steps.

the major disadvantage of application lithium for batteries. In our case, the migration and accumulation phenomena of lithium in volume of electrode allowed to extract 73% of adsorbed ions in the second stage of the desorption. This fact was enhanced by the removal of other salts deposited onto the electrode surface in the first stage of desorption, D. Hence, it could be expected that lithium ions moved through surface layers and were entrapped into the volume of electrode materials. This is clearly seen in Fig. 3. When zero volt charge was used, the ions layer placed on the surface was washed out by DI water. When voltage was reversed, viz. D2 stage, lithium ions were released and enriched the second desorption stream.

The concentrations of lithium in analysed samples of the raw water and three solutions obtained during HCDI process (A, D and D2) are shown in Fig. 4. The raw geothermal water was characterized by lithium content of 15.7 mg/L. After HCDI process lithium concentration in water (solution A) decreased to 11.2–12.1 mg/L (depending on the cycle). In the first stage of the desorption (D), 1.2 mg/L of lithium was transferred to the solution and about 3.5 mg/L of Li$^+$ was released during the second stage (D2). The sum of lithium in A, D and D2 streams was higher than in the raw water. Despite the fact that the differences were not greater than 7%, an error in samples analysis could bias the final calculation of the process. Hence, the uncertainty analysis should be performed [15,17–23]. When uncertainty is taken into account, we should consider the obtained result as an interval not a single value. This approach causes that sum of concentrations for the three processed streams should also be presented as the interval (Fig. 4(b)). Hence, the sum of results obtained for A, D and D2 streams is in the range of measured uncertainty for the feeding water.

4. Conclusions

- According to the obtained results it is possible to separate and re-extract lithium ions with 73% efficiency from a geothermal water. Additionally, during this process energy consumption achieves 3.59 W per 1 g of the adsorbed salt.
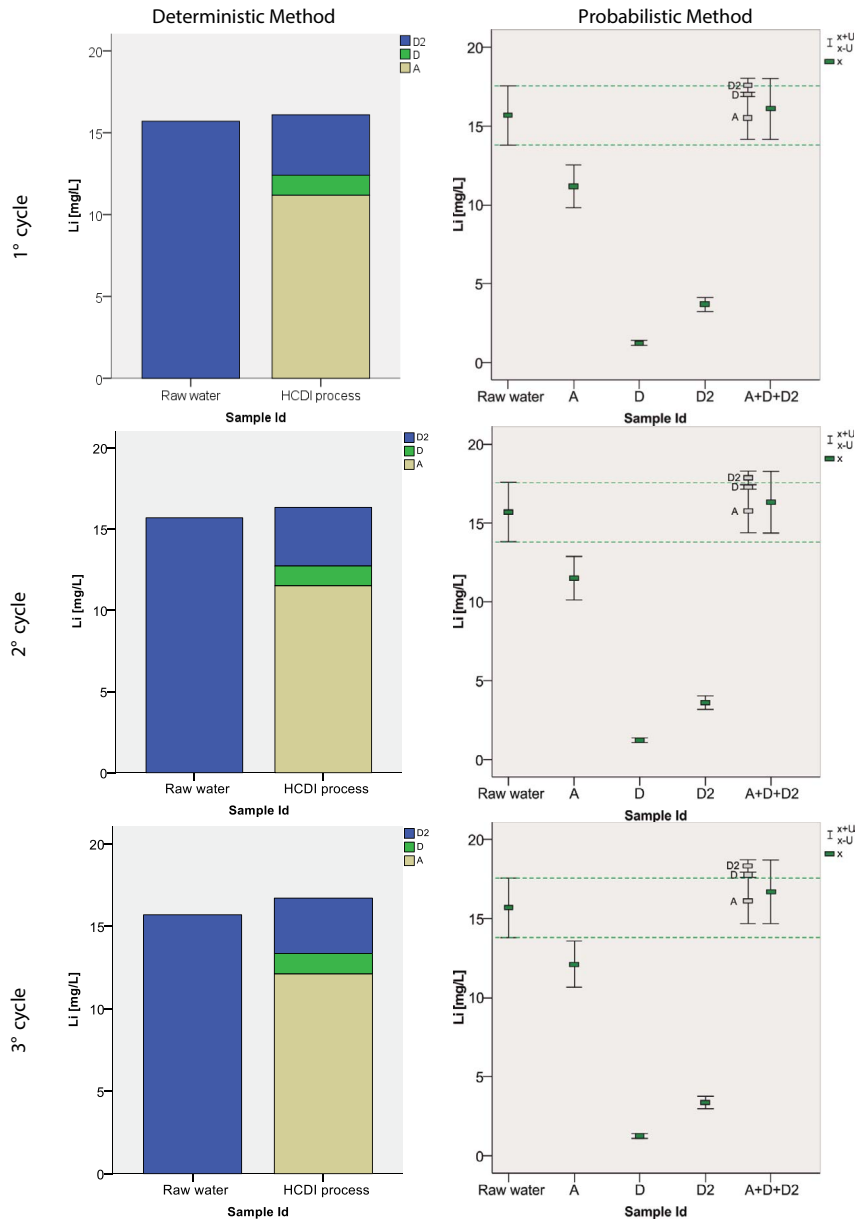
Fig. 4. Results of deterministic (left column) and probabilistic (right column) approaches for 1°, 2° and 3° cycles, respectively. Explanations: A – adsorption, D – first stage of desorption, D2 – second step of desorption, x – measurement; U – measurement uncertainty ($k = 2$, 95%).

- The deterministic approach is a functional tool to explain differences in concentration of ions in each of the HCDI process stage.
- Studies on uncertainty measurement should be expanded by the duplication of control samples, blanks and usage of spiked samples. The phenomena occurred during HCDI process could be biased by analytical errors and values of their uncertainty should be taken into account.

Acknowledgements

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