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journal or publication title	Fusion Engineering and Design
volume	136
number	A
page range	377-380
year	2018-11
URL	http://hdl.handle.net/10655/00012948

doi: 10.1016/j.fusengdes.2018.02.045

Lithium isotope separation using displacement chromatography by cation exchange resin with high degree of cross-linkage

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We studied the effect of the extremely high cross-linkage degree on the isotope separation in cation exchange. The cation exchange resin with 90% degree of cross-linkage was synthesized by suspension polymerization. The lithium isotope separation was obtained by the displacement chromatography using this synthesized cation exchange resin. From the results of our previous research, the isotope separation coefficient increases with the degree of cross-linkage. However, it was found from the present work that the isotope separation is saturated in the case of very high degree of cross-linkage.

Keywords: lithium isotope separation, cation exchange, resin cross-linkage effect, displacement chromatography

1. Introduction

Tritium is expected to be used as fuel in fusion future reactor. However, natural abundance of tritium among other hydrogen isotopes is very low [1]. Therefore, artificial tritium breeding method is necessary. For the tritium breeding, ⁶Li enrichment is required, since tritium could be generated from the ⁶Li (n, α) T reaction [1]. Even though ⁷Li could produce tritium by the ⁷Li (n, n'α) T reaction as well, the cross-section values were smaller, and this makes ⁷Li undesirable for tritium breeding [2]. Natural lithium has two stable isotopes; ⁶Li (7.5%) and ⁷Li (92.5%) [3]. Enrichment of ⁶Li becomes important because its natural abundance is low, while ⁷Li could be used as pH controller in PWR [4]. The only industrial-scale application for lithium isotope enrichment is mercury-amalgam method. Although this method has high value of isotope separation coefficient, the large amount of toxic mercury is used and wasted from the site [5]. Therefore, lithium isotope enrichment method with mercury-free is required. Recently, various lithium isotope separation methods; membrane separation [6], electro-migration [7], solvent extraction using crown ether [8], chromatography using crown-ether resin [9], have been reported. The cation exchange method is also one of the promising methods with probably promising isotope separation coefficient and mercury-free, since the existing chemical engineering techniques are applied [4,10–13].

The cation exchange method for lithium isotope separation was first performed and reported by Taylor and Urey [10]. The wide-range of isotope separation coefficients have been obtained and reported by performing cation exchange reaction for separating lithium isotope [4,11,12]. According to their reports, the inorganic cation exchangers have the higher isotope separation coefficients than organic cation exchanger in general. This reason is explained by the amounts of dehydration among lithium ion in cation exchanger [11]. In the report of Ref. [13], organic cation exchanger is used

since it is generally appropriate in engineering chromatography point of view. In our previous work, it was found that the isotope separation in the cation exchange depends on the cross-linkage degree of the resin and the isotope separation coefficient increases with the cross-linkage degree [4,13]. On the other hands, the ion-exchange capacity of resin decreases with the cross-linkage degree, since the functional group is attached with benzene rings without cross-linkage [12]. In the present work, the influence of extremely high cross-linkage degree, i.e., 90% on the lithium isotope separation was investigated to obtain the limitation of cross-linkage effect and to find the sufficient condition of cation exchange resin for lithium isotope enrichment.

2. Experimental

The porous-type cation exchange resin was synthesized by suspension polymerization. The resin was based on styrene and divinylbenzene (DVB) where the ratio between them is 1:9 respectively, so that the cross-linkage of resin is maintained around 90%. Fig. 1 shows the synthetic method of the cation exchange resin. The synthesis was initiated by mixing NaCl (Purity: 99.5%, Nacalai Tesque, Inc.) and T.C.P. (tricalcium-phosphate) (Purity: 10% suspension, Taihei Industrial Co., Ltd.) for 10 minutes to maintain the 100 RPM. Methyl benzoate (Purity: 98.0%), bis(2-ethylhexyl) phthalate (Purity: 97.0%), styrene (Purity: 99.0%), divinylbenzene (94.0 – 97.0%), 2,2' azobis(isobutyronitrile) (Purity: 98%), 1,1' azobis (cyclohexane-1-carbonitrile) (Purity: 95%) were obtained from Wako Pure Chemical Ind., Ltd. Those chemicals were introduced into the mixture for another 10 minutes. And then A-80 rapizoru (Purity: 80%, NOF CORPORATION) and methyl cellulose (Grade: 60SH-50, Shin-Etsu Chemical Co., Ltd.) were inserted to the mixture for 10 minutes to maintain 100 RPM. The mixture then was stirred according to the following sequences; 2 h at 333 K, 4 h at 343 K, 10 h at 363 K and 10 h at 363 K

Fig. 1. Synthesis method scheme for the cation exchange resin.

(after 12 h keeping time), the stirring sequence was chosen to ensure regular temperature increase during synthesis reaction [13]. The resulted mixture was then filtered and dried to define the yield, which is around 100%. By this, we obtained the base polymer. Following the procedure, the base polymer was sulfonated by tetrachloroethylene (Purity: 99.0%) and chlorosulfonic acid (Purity: 97.0%) that were obtained from Wako Pure Chemicals Ind., Ltd. The base polymer was initially conditioned using tetrachloroethylene for 8 h in 313 K. And then chlorosulfonic acid were mixed into the mixture for 12 h at 313 K. following the procedure, the synthesized resin is filtered by flowing sodium chloride as well to change the H-form resin into Na-form resin. The synthesized resin was then dried and sieved to obtain defined particle size distribution of the resin. The synthesized cation exchange resin was evaluated by SEM (VE-8800, KEYENCE) and IR-spectroscopy (IRAffinity-1S, Shimadzu) using KBr-techniques. Samples are prepared by grinding the resin and KBr, where the ratio of KBr and the resin in KBr tablet is 1:1000.

The synthesized resins were packed in a water jacketed chromatographic column with 8 mm inner-diameter and 1 m length. It was preliminarily conditioned to H⁺-form by using 1 mol/L HCl solution, then rinsed with deionized water to remove free H⁺ ions until the pH of effluent became neutral. About one-meter lithium adsorption band was formed in the column by introducing 50 mL of ca. 0.5 mol/L CH₃COOLi and was eluted by 150 mL of ca. 0.5 mol/L CH₃COOK solutions which fed at the flow rate of 0.35-1.00 mL/min and pressure below 3.5 MPa. The column temperature was kept at 308 ± 1.0 K by circulating thermostat controlled water. 200 fractions of eluents were then collected with approximately 1 mL of

sample in each tube by a fraction collector (CHF100AA, Advantech). 1 wt% of nitric acid solution was prepared as the diluent solution for the measurement of concentration and isotopic ratio. The measurement of concentration and isotopic ratio were performed by using Inductively-Coupled Plasma Mass Spectroscopy (7700x, Agilent). After the measurement of lithium concentration, the concentration of lithium in the sample solutions were adjusted at ca. 10 ppb for the isotope ratio measurement.

Fig. 2. Chromatography experiment scheme

3. Results and Discussion

The SEM photograph of the synthesized resin was shown in Fig. 2. This photograph shows a round-shape resin and it indicates a successful procedure of synthesis. IR-spectrum of synthesized resin is shown in Fig. 3. This figure shows that sulfo-groups and aromatic C-H structures are traced presence in the resin and it showed that the synthesis was performed well.

Fig. 3. The SEM photograph of the synthesized resin. (particle size = 100-300 μm , cross-linkage = 90%, $M = 100\times$)

Fig. 4. IR spectrum of the synthesized cation exchange resin.

The chromatographic concentration curve and isotopic ratio profile are given in Fig. 5. This figure shows the enrichment of heavier isotope in front-end boundary and lighter isotope in rear-end boundary which correspond to aqueous phase and resin phase respectively. It could be seen from this figure that front and rear band profiles were quite sharp at the boundaries. According to Suzuki *et al.*, lithium-7 is enriched in the aqueous side with more number of hydrated water molecules which exists in aqueous solution and lithium-6 is enriched in the less hydrated water molecules which exists in the resin phase [4]. It clearly means that heavier isotope is enriched in the side of the chemical form with the stronger binding force [14]. Furthermore, the isotopic ratio and concentration in the middle band were equal to the

original feed solution in the present work. This means no mixing occurred in the middle band during the experiment [15]. This confirms that isotope separation was successfully performed by using cation exchange resin with 90% degree of cross-linkage. However, it would be required to understand that if the claimed concentration and isotopic ratio curve in Fig. 5 would be more relevant when the experimental uncertainties are taken into account.

The degree of isotope separation is evaluated by the isotope separation coefficient, ε . The isotope separation coefficient is defined as the subtraction 1 from the separation factor on single stage [4]. The isotope separation coefficient was calculated by the following equation using chromatographic isotope ratio and concentration curve data,

$$\varepsilon = \frac{\sum C_i V_i (R_o - R_i)}{Q R_o (1 - R_o)} \quad (1)$$

where Q , C_i , V_i , R_o , and R_i are the ion-exchange capacity (mmol/g), lithium concentration (mol/L), the volume (ml), original isotope abundance, and the isotope abundance respectively [4]. The lithium isotope separation by means of cation exchange resin is based on the isotopic ratio between lithium ion in aqueous solution and lithium ion in the resin.

To evaluate the performance of the separation experiment by displacement chromatography, Fujii *et al.* proposed equations to analyze chromatographic data on isotope ratio [16]. Height equivalent to a theoretical plate (HETP) is one of them and was used in this work to assess the results of separation experiment. HETP is determined by the following equation,

$$H = \frac{\varepsilon}{k} + \frac{1}{k^2 L} \quad (2)$$

where H , ε , k , and L are HETP, isotope separation coefficient, slope coefficient, original isotope ratio and migration length, respectively [15].

The clear plateau of concentration curve indicates a successful separation experiment and it is important for

measurement of isotopic ratio, because the isotopic ratio curve is important for determining the isotope separation coefficient later. From Eq. 1, a separation coefficient, ϵ , of 0.0069 was obtained for the resin with 90% degree of cross linkage. The calculated ion-exchange capacity of the system was 0.47 mmol/g. **And H-form cation exchange resin was used in the experiment.** From Eq. 2, HETP was obtained 0.9 mm for the lithium isotope separation with 95 cm migration length. These three values are important chemical parameters obtained in the isotope separation experiment. The obtained HETP was comparable with the previous work [17]. HETP depends on size of resin, temperature, flow rate, etc. We have the plan to optimize the operation condition for minimizing the HETP. Because the smaller HETP indicates the better resolution and more theoretical plates in the column. The more theoretical plates in the column means more efficient.

Fig. 5. Chromatographic isotope ratio and concentration curve of lithium from isotope separation experiment using 90% degree of cross-linkage cation exchange resin.

The relationship between cross-linkage on the isotope separation coefficient is shown in Fig. 6. In this figure, the separation coefficient is increased significantly up until degree of 50%. However, more than 50%, in this case 90%, it shows that the separation coefficient is saturated. The latest value is still increased but not significantly. The increase of cross-linkage degree of resin rises its hydrophobicity. As a result, many hydration water molecules together with lithium ions are removed from the resin. This phenomenon has been confirmed by previous studies using NMR [4]. This fact of the isotope separation coefficient saturation shows that the dehydration effect by cross-linkage has limitation and the power of dehydration of organic resin cannot be increased to the comparable one of inorganic cation exchanger by cross-linkage effect [11]. In case of organic resin, which generally has higher dehydration degree, the maximum isotope separation coefficient was reported at 0.004 ± 0.001 value [11].

Fig. 6. Effect of cross-linkage degree on separation coefficient. ● : previous work [17], × : in this work.

The ion-exchange capacity of the styrene-divinylbenzene copolymer based cation exchange resin depends on the cross-linkage degree in theory, because the function group can be attached with the benzene ring of styrene **since the resin was in H-form**. The obtained capacity of synthesized resin corroborates this fact. The decrease of ion-exchange capacity would lower the separation performance [14]. Thus, if the isotope separation coefficient by using the cation exchange resin with higher cross-linkage degree is not so high in comparison with the lower cross-linkage resin, where the resin with 50% and 90% degree of cross-linkage resulted the separation coefficient of 0.0066 and 0.0069 respectively. This higher cross-linkage resin is unsuitable for industrial level isotope separation, since the amount of product is declined. Considering both the isotope separation coefficient and the ion-exchange capacity, the resin with about 50% degree of cross-linkage would be suitable for engineering use.

4. Conclusions

Porous-type cation exchange resin with 90% degree of cross-linkage was synthesized by the suspension polymerization. Lithium isotope separation using this synthesized cation exchange resin was performed by the displacement chromatography technique. We confirmed the isotope separation phenomenon by confirming a sharp boundary on the chromatographic curve at each band-end where light isotope is enriched in the resin phase and heavier isotope is enriched in the aqueous phase. It was confirmed that the isotope separation coefficient increases with the cross-linkage degree of the cation exchange resin, but it is saturated in the case of the extremely high degree of cross-linkage such as 90%.

Acknowledgments

This work is performed with the support and under the auspices of the NIFS Collaboration Research program (NIFS14KESA018).

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