

Mixed-Cation LiCa-LSX Zeolite with Minimum Lithium for Air Separation

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Abstract

The aim of this work was to reduce/minimize Li in Li-LSX by replacing the 70% Li^+ cations in Li-LSX that are bonded to the interior or inaccessible sites which are not used for adsorption. Thus, mixed-cation LiCa-LSX containing minimum lithium were prepared by exchanging small fractions of Li^+ into Ca-LSX, followed by dehydration under mild conditions to avoid migration/equilibration of Li^+ cations. Comparisons of adsorption isotherms of N_2/O_2 and heats of adsorption for the LiCa-LSX samples with that for pure-cation Li-LSX and Ca-LSX provided strong evidence that significant amounts of these Li^+ cations indeed remained on the exposed sites (SIII). The mixed-cation LiCa-LSX samples were compared against the pure-cation Ca-LSX and Li-LSX based on their performance for oxygen production by PSA, via model simulation. The results showed that the mixed-cation LiCa-LSX samples yielded significantly higher O_2 product productivities at the same product purity and recovery than their pure-cation precursor (Ca-LSX).

Introduction

The demand for oxygen and nitrogen spans over a wide range of industries including oil refining, medical, metal production, food processing, and chemicals to name a few. Cryogenic distillation of liquefied air and pressure swing adsorption (PSA) are the two major technologies for high and low-to-medium volume productions, respectively.¹

Air separation by adsorption is based on the unique adsorption property of zeolites which have high N_2/O_2 selectivities due to the interactions between the electric field gradient of the zeolitic cation and the quadrupole moment of N_2 .² Commercial PSA oxygen production began in 1972. A major breakthrough occurred in 1989 with the invention of Li-LSX (i.e., low silica type-X, Si/Al = 1) zeolite by Chao.³ In the preparation of Li-LSX, the as-synthesized Na-LSX is ion-exchanged by Li cations via conventional means. It was found that below approximately 70% Li exchange, the N_2 capacity was unchanged, while it increased nearly linearly upon further increase in Li exchange from 70% to 100%. This phenomenon has been explained by the occupancy of different cation sites; the N_2 (and O_2) molecules can interact only with cations occupying the exposed sites. The cation sites for faujasite are shown in Figure 1. For Li-X, only sites III (SIII) are accessible to N_2 (and O_2); Li^+ on SII is not “accessible” due to electron shielding effects by the surrounding framework oxygen and the small size of the Li ion.

The site occupancies have been characterized⁴⁻⁶ and are shown in Table 1. It is noted that, after ion exchange, zeolites need to be thermally dehydrated prior to isotherm measurements (and during manufacturing), typically at above 673 K for 4 or more hours. Under such

treatment, cations migrate or diffuse to their equilibrium positions or sites. For zeolites containing mixed cations, it has long been observed that the lighter cations tend to migrate to the lower numbered sites (SI, SI', SII'', SII). For example, in mixed CeNaCa-X zeolite, Na and Ca are at lower-numbered sites while Ce(III) cations are located at outer sites, and in mixed NaSr-X zeolite, Na⁺ is at SI while Sr²⁺ is at SII.⁷ This ordering is also seen in the mixed LiNa-LSX system discussed above.

As mentioned, since its invention Li-LSX has been the sorbent of choice for air separation by PSA or Vacuum Swing Adsorption (VSA). A wide variety of other zeolites have also been considered, particularly the LSX zeolites containing alkali-earth metal cations. These cations are divalent and hence they form strong electrostatic interactions with N₂ molecules (as well as O₂). Thus, intense interests were attracted to the mixed-cation LSX zeolites containing Li and an alkali-earth metal.⁸⁻¹³ Coe et al.⁸⁻¹¹ studied various binary exchanged X-zeolites containing varying lithium-calcium and lithium-strontium mixtures all of which provided enhanced nitrogen sorption capacities over those of the pure samples. Sircar et al.,¹² also showed a binary ion-exchanged Type-X zeolite of calcium and strontium. Their invention was especially useful in the adsorption of N₂ from an air stream at superambient pressure to produce an O₂-rich product stream. Furthermore, Chao et al.,¹³ presented mixed ion-exchanged zeolites of type-A and type-X with lithium (30% - 90%) and alkaline earth metals (10% - 70%) such as Ca²⁺ and Sr²⁺, with high N₂ adsorption capacity. It is important to note that these mixed cation zeolites required over 70 mol% Li⁺ (and < 30 mol% alkali-earth cation). Typically, 90% Li⁺ was required. Moreover, it was necessary to ion exchange Li⁺ first, followed by exchange for the alkali earth cations. Of particular interest was the Ca-LSX zeolite¹⁴ due to its high N₂ capacities over that of

Li-LSX. Thus, for mixed-cation LiCa-LSX, it was specifically stated that fully exchanged Li-LSX was prepared first, followed by Ca^{2+} exchange,^{8, 10, 13}. In all cases, well over 70% Li^+ was needed to see the effect of Li^+ .

The demand for lithium has been rising steeply due to the application of lithium ion batteries for energy storage and due to its limited reserves worldwide. As a result, the price of lithium has been surging since 2016 while the reserve is dwindling. Therefore, the motivation for this work is to develop zeolites for air separation in which lithium is substantially reduced or replaced by a low-cost and abundant alkali-earth metal cation, such as Ca^{2+} . Using LiCa-LSX as an example, our strategy is to first exchange as-synthesized Na-LSX to fully-exchanged Ca-LSX, followed by exchange of a small fraction of Ca^{2+} by Li^+ . During the ion exchange process (in an aqueous solution such as LiCl_2) and prior to any heat treatment, it is reasonable to assume that these Li^+ cations are located on SIII because they are the most accessible ion exchange sites and are hence exchanged first. Equally important, in this work the dehydration step is performed at the lowest possible temperature in a relatively short time to avoid diffusion and equilibration of Li^+ ions to lower-number or interior sites.

In this work, we focused on four synthetic zeolites: two pure-cation zeolites (Ca-LSX and Li-LSX) and two mixed-cation zeolites (2.5%LiCa- and 4.2%LiCa-LSX, both in mol%) for the PSA/VSA system. The mixed cation samples will be represented as follows henceforth: 2.5% LiCa-LSX and 4.2% LiCa-LSX = $\text{Li}_{2.5}\text{Ca}_{46.75}$ -LSX and $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX respectively. These zeolites will be compared for their PSA/VSA separation performance using a proven PSA model.

Experimental Section

Materials

The analysis gases obtained from Cryogenic Gases included: helium (99.995%, prepurified), nitrogen (99.998%, prepurified), and oxygen (99.6%, extra dry).

Luoyang Jianlong micro-Nano New materials Co., Ltd., China, supplied the Na-LSX zeolite (powder form) with a Na exchange extent of 99.5% ($\text{Na}/(\text{Na} + \text{K})$) and a Si/Al ratio of 1.005. Calcium dihydrate 99% and lithium chloride 99% were both obtained from Sigma Aldrich.

Preparation of Ca-LSX zeolite

Na-LSX zeolite was used as the starting sorbent for the ion-exchange procedure which could be readily exchanged with most cations. To obtain pure Ca-LSX zeolite, Na-LSX was ion-exchanged with a 1.0 M solution of calcium chloride (with ~ 3 equivalent excess of Ca^{2+} to Na^+) at ambient conditions and stirred for a minimum of 6 hrs. The solution was decanted and a 3X CaCl_2 solution was added, and the ion-exchange procedure was repeated 6 times. The sample was vacuum filtered after the final ion-exchange, washed with copious amounts of deionized water, and air dried at 298 K for 24 hrs. One of the main differences between this study and other published literature^{8,14} is the fact that here-in, Li ions are introduced into Ca-LSX as opposed to Ca cations being incorporated into Li-LSX zeolite.

Preparation of LiCa-LSX

A pre-determined equivalent amount of Li^+ enough to exchange the desired target Ca^{2+} in the Ca-LSX zeolite (assuming hypothetically that all Li^+ would undergo exchange) was used to prepare the mixed cation samples. This was achieved by using a 0.1 M LiCl solution exchanged with 1.5 g of Ca-LSX with Li^+ equivalent = 0.15 and 0.3. The mixture was stirred for 1 hr at 298 K

followed by vacuum filtration without washing and dried in an oven for 24 hrs at 298 K. It should be noted that, due to the preference of LSX for Ca^{2+} over Li^+ , the actual Li^+ exchange was substantially less than the amount of Li^+ in the liquid phase, as determined by ICP results.

Sample pretreatment and isotherm measurements

All pure gas adsorption equilibrium analysis on the studied pure and mixed ion-exchanged samples were carried out with a Micromeritics ASAP 2020 Sorptometer which uses the volumetric measurement technique. Prior to analysis, all samples were degassed/dehydrated in-situ the Micromeritics to remove all adsorbed moisture and/or adsorbed gasses.

The pretreatment conditions varied per sample and were as follows: 8 hrs at 648 K and 623 K for Li-LSX and Ca-LSX respectively. 1 hr at 623 K for $\text{Li}_{2.5}\text{Ca}_{46.75}$ -LSX and $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX while the ramp rate for all dehydration conditions was 283 K/min. The 1 hr at 623 K pretreatment condition allows most of the theoretically determined Li^+ to remain on site III while not allowing adequate time for all Li^+ cations to diffuse to the lower-numbered sites (SI and SII). The temperature of 623 K was determined to be the lowest temperature that was adequate for full dehydration of Li-LSX.¹⁵ In the work of Hutson et al., residual water amounts and N_2 isotherms were measured on Li-LSX after dehydration at various temperatures up to 723 K, and full dehydration was seen after dehydration at 623 K.¹⁵ All studied samples were pretreated under vacuum: 30 μmHg for the pure samples and 60 μmHg (due to the short pretreatment time) for the mixed samples.

Sample Characterization

The samples were compositionally characterized using an ICP-OES (Inductively Coupled Plasma – Optical Emission Spectrometer) system at Galbraith Laboratories Inc. in Knoxville, Tennessee. ICP is an analytical technique that quantifies the elemental composition of samples in various states (e.g. powders, liquids, suspensions, etc.). Powders are usually digested by an acid (highly concentrated HNO_3 , HCl , or H_2SO_4) or a combination of acids with the resulting solution then nebulized into the core of the instrument's inductively coupled argon plasma at elevated temperatures. The high temperature vaporizes, ionizes and thermally excites the analyte species in the solution which are then detected and quantified by the OES by measuring (in % or ppm concentration) the element's characteristic wavelength from the intensity of the emitted radiation.

Results and Discussion

Analytical sample characterization

As mentioned above, the mixed ion-exchanged samples were compositionally analyzed and quantified for Li and Ca content using an Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) system. The extent of the Li^+ exchange obtained from the mixed ion-exchanged samples by ICP were 2.5%Li and 4.2%Li (mole percent and on a dry basis) represented as $\text{Li}_{2.5}\text{Ca}_{46.75}\text{-LSX}$ and $\text{Li}_{4.2}\text{Ca}_{45.9}\text{-LSX}$ respectively. The results of the analyzed LSX sample are presented in Table 2.

Nitrogen adsorption isotherms

As stated earlier, the volumetric technique was used to measure the equilibrium N_2 adsorbed amounts to pressures of 1 atm. N_2 experimental adsorption isotherms on the studied

sorbents at temperatures 298 K, 323 K and 343 K after *in vacuo* dehydration are shown in Figures 2-4 respectively. Upon inspection, Ca-LSX shows the highest N₂ adsorption capacity followed by Li_{2.5}Ca_{46.75}-LSX and Li_{4.2}Ca_{45.9}-LSX at ambient conditions respectively. The pure Ca-LSX sample shows a high capacity for N₂ at 298 K in comparison with other published data.^{2,8} Figure 2 (N₂ isotherms at 298 K and 101 kPa) also reveals that the introduction of such low Li amounts changes the adsorptive properties (low pressure knee of the pure zeolite) of the mixed cation zeolite. The sorbents' high N₂ capacities are attractive properties for air separation by PSA.

Oxygen adsorption isotherms

Figures 5-7 show O₂ experimental adsorption isotherms on the studied sorbents at 298 K, 323 K, and 343 K respectively. A comparison of the different sorbents shows that Ca-LSX adsorbed significantly more oxygen than Li-LSX (slightly above 60%), and the mixed cation LSX fell in between. This result is expected because Ca²⁺ has higher polarizability than Li⁺ and the van der Waals interactions were the main interactions for adsorption of O₂ which has a very low quadrupole moment. The lower O₂ capacities for the mixed cation LSX are favorable for PSA separation. This result also indicates the presence of some Li⁺ cations on SIII in the mixed-cation samples.

It should be noted that the differences in adsorption capacities of both gases on the studied sorbents are due to the magnitude of interactions between the Ca²⁺, Li⁺ and the sorbates which in turn are due to the location of the cations within the zeolite's framework. Figure 1 shows the 5 different cation sites in the faujasite-type (X and Y) zeolites. It should be noted that only sites

II and III (SII and SIII) are accessible to the sorbate while SI (inside the double ring) and SII' (within the beta cage) are inaccessible to the sorbate molecule. As mentioned, the electric field around the cations in the exposed sites are however, partially shielded (cation size dependent) by the surrounding oxygen atoms thereby significantly lowering the interactions between the sorbate molecule and the SII cations. For example, the small Li cation can sit crystallographically very low within the face of the single 6-ring (SII), allowing the electric field to be nearly completely shielded by the six surrounding framework oxygen atoms thereby allowing the sorbate-sorbent energy to be entirely contributed by the Li cation sitting on SIII². For a larger cation like Ca, its shielding can be substantially weaker due to its size.

Pure component isotherms

The equilibrium adsorption isotherms of N₂ and O₂ on the various sorbents in this study were fitted with the Langmuir-Freundlich (L-F) isotherm model. Figures 2-7 show just a few of the experimentally obtained isotherms. All others could be found in the supplementary material. The temperature dependence of the isotherms allowed calculation for the isosteric heats of adsorption, as to be discussed further below.

$$Q = \frac{Q_{\text{sat}}^* KC^n}{1 + KC^n} \quad (1)$$

where Q is the adsorbed amount with the rest being fitting constants from experimental data. A fitting model is usually required to interpolate the measured values. Also, the interpolation of the said data is quite sensitive to the choice of the fitting model and minute deviations from the true value can cause significant errors in thermodynamic calculations.^{16,19}

Heats of adsorption

At near ambient temperature, there is a negligible ($3RT/2$) difference between the sorbate-sorbent interaction energy and the experimental heats of adsorption.² For a basic understanding of the experimental results, the sorbate-sorbent interaction energies for the gas-sorbent pairs could be estimated by calculating the potential energies between the gas molecule and a free or isolated cation such as Ca^{2+} , Li^+ , etc. A breakdown of the theoretical total sorbate-sorbent potential (ϕ_T) for physical adsorption is shown in our previous work.²⁰ It is worth noting that for the adsorption of gas molecules on zeolites, the main interaction energies are between the gas molecules and the metal cations on its surface. Though interaction energies between the gas molecules and the oxide atoms on the surface also exists, they are significantly weaker than those formed with the cations.

Here-in, the isosteric heats of adsorption of the gas-sorbent pairings were estimated by the application of the Clausius-Clapeyron relation^{17,18,21} as shown below:

$$\ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

where ΔH_{vap} is the heat of adsorption, R is the gas constant (8.3145 J/mol K), while P_1 and P_2 are the corresponding pressures at temperatures T_1 and T_2 . Such calculations are very sensitive to errors in the equilibrium pressure. This means that interpolations can sometimes introduce significant uncertainties into the calculated isosteric heat determined by using fitted experimental data.

Figures 8 and 9 shows the isosteric heats of adsorption for N_2 and O_2 on various representative sorbents at different coverages. The N_2 experimental heats of adsorption followed the order: $\text{Ca-LSX} > \text{Li}_{2.5}\text{Ca}_{46.75}\text{-LSX} > \text{Li}_{4.2}\text{Ca}_{45.9}\text{-LSX} > \text{Li-LSX} > \text{Na-LSX}$.

The interaction energies for N_2 are mainly from the electrostatic energies. The interactions of N_2 with Ca^{2+} are significantly stronger than that with Li^+ . This is caused mainly by the higher electric charge of Ca^{2+} that doubles the charge of Li^+ , while the ionic radii are similar (0.69 Å for Li^+ and 1.0 Å for Ca^{2+}).

An almost similar trend is observed for the O_2 experimental heats of adsorption $Ca\text{-LSX} > Li_{4.2}Ca_{45.9}\text{-LSX} > Li_{2.5}Ca_{46.75}\text{-LSX} > Li\text{-LSX} > Na\text{-LSX}$. As discussed in the foregoing, this trend was caused by the fact that Ca^{2+} has a higher polarizability than Li^+ and the van der Waals interactions were the main interactions for adsorption of O_2 .

Cation Site Location

Table 1. shows the occupancy of cations in dehydrated X-type zeolites with pure cations. Several other studies have been employed to determine Li^+ in the extra framework of types X, Y, and A zeolites^{6,22,23} using solid state NMR and neutron diffraction methods. The Li cations were found to be evenly distributed with 32 cations each in SI' (energetically preferred over SI for monovalent cations), SII, and SIII for the Li-LSX (Si/Al = 1) zeolite as opposed to 22 cations in SIII for the X-zeolite. Single Crystal XRD, Powder XRD, and Powder XRD & Neutron Diffraction have all been used to determine the location of Ca ions mostly in Ca-X zeolites. It was found that for a fully dehydrated Ca^{2+} -exchanged FAU-type zeolite, the calcium cations were distributed among sites SI, SI' and SII.²⁴⁻³⁶

No Li^+ and Ca^{2+} location and site distribution studies were carried out in this study for the mixed-cation samples. Knowing that the SI and SI' sites are sterically inaccessible to the sorbate

gases (N_2 and O_2), it is therefore expected that only the Ca cations in SII and Li^+ in SIII are accessible to the sorbates.

For N_2 adsorption, as expected, the heats of adsorption followed the order: Ca^{2+} (42 kJ/mol) > Li^+ (22 kJ/mol) > Na^+ (20 kJ/mol). It is most interesting that the ΔH values for the mixed LiCa-LSX samples fell between that of pure Ca-LSX and Li-LSX. This result was a strong indication that the N_2 molecules were interacting with both exposed Ca and exposed Li cations. Furthermore, the intermediacy of the ΔH value (between Ca^{2+} and Li^+) indicates that some N_2 molecules were interacting with (or shared by) both Ca^{2+} and Li^+ in possibly a bridged configuration.

Further work has been done in our laboratory on the relationship between SIII occupancy of Li^+ in mixed-cation LiNa-LSX zeolite and the heats of adsorption of N_2 . It is shown that the N_2 heats of adsorption can indeed be used as an indicator of the presence of the lithium ions in SIII for mixed-cation zeolites (to be published).

PSA (or VPSA) cycle description

A standard, commercially used, five-step PSA (or vacuum pressure swing adsorption, VPSA) cycle similar to that described by Hutson et al.³⁷ was used in this study. The cycle configuration is shown in Figure 10 and the five steps are as follows: (step I) Pressurization with feed (air); (step II) High-pressure feed; (step III) Co-current depressurization; (step IV) Countercurrent blowdown; (step V) Low-pressure purge with the product. This standard PSA cycle and even more complicated cycles can be accomplished in a two-bed or four-bed systems with interconnections.³⁸

Each of the above steps ran for a duration of 30 seconds, thus the time required for the complete cycle was 2.5 mins. The model assumed only two components (i.e. O₂ and N₂). Since Ar (Argon) and O₂ both have similar adsorption capacities on LSX zeolites, the oxygen component was assumed to be 22% (21% O₂ and 1% Ar) for the simulation. The product of each cycle was comprised of a volumetric mixture of the output stream from the feed step and the co-current depressurization step. A portion of this product stream was used to purge another bed countercurrently in step V.

The performance of PSA for oxygen production is judged by three inter-related results: O₂ product purity, O₂ product recovery, and O₂ product throughput. When two of these are fixed, the other is also set provided the PSA operating conditions are optimized. To compare the performance of the sorbents developed in this work, the product throughputs of the sorbent were studied under several different cycle conditions.

Similarly, to facilitate a fair comparison of each sorbent's performance, the cycle conditions were optimized such that the product purity and product recovery obtained were the same for all sorbents in each simulation run. The product purity, product recovery, and product throughput in this study are defined as follows:

$$\text{Product Purity} = \frac{\text{Amount of O}_2 \text{ from Steps II and III}}{\text{Amount of N}_2 \text{ and O}_2 \text{ from Steps II and III}} \quad (3)$$

$$\text{Product Recovery} = \frac{(\text{O}_2 \text{ from Steps II and III}) - (\text{O}_2 \text{ from Step VI})}{(\text{O}_2 \text{ fed in Steps I and II})} \quad (4)$$

$$\text{Product Throughput} = \frac{\text{Amount of O}_2 \text{ produced per hour (t/h)}}{\text{Amount of sorbent used in the bed (t)}} \quad (5)$$

The mathematical model and the numerical method used for the PSA simulations have been explained in detail in an earlier work by Rege et al.³⁹ Hence, only the basic assumptions are listed here. The model used assumes the flow of a gaseous mixture of two components in a fixed bed packed with spherical adsorbent particles. The bed was considered to be adiabatic and the diffusional resistance is assumed to be negligible since the diffusion of O₂ and N₂ in the sorbents is relatively fast considering the long cycle time. Thus, local equilibrium existed between the gas and the solid phase for each gas component. Axial dispersion for mass and heat transfer was accounted for but dispersion in the radial direction is taken to be negligible. Axial pressure drop was neglected and ideal gas law was assumed to hold since pressures involved were near atmospheric. Also, the gas was assumed to have constant viscosity and heat capacity.

The pure component equilibrium amounts adsorbed on the respective adsorbents were fit using the well-known Langmuir-Freundlich isotherm with temperature-dependent constants. The equilibrium loading under mixture conditions were then predicted by the extended Langmuir-Freundlich equation in the simulation model:

$$q_k^* = \frac{q_{m_k} b_k p_k^{n_k}}{1 + \sum_{j=1}^m b_j p_j^{n_j}} \quad k = 1, 2 \quad (6)$$

The Langmuir-Freundlich parameters were assumed to be as follows:

$$q_m = k_1 e^{(k_2/T)} \quad \text{and} \quad b = k_3 e^{(k_4/T)}$$

The Extended Langmuir model is one of the simplest and most practical models for the prediction of binary gas adsorption behavior from pure component isotherms.⁴⁰ Using the

extended Langmuir-Freundlich model for binary mixtures, similar to the use of the extended Langmuir model, is also a simple yet reasonably good way of fitting binary experimental data, as shown by Mulgundmath et al.⁴¹

The values of the Langmuir-Freundlich equation fitting constants and the heats of adsorption are shown in Table 3 while Table 4 shows the PSA bed characteristics and the operating conditions used.

VPSA simulation results

The pressure ratio (ratio of the feed pressure P_H to the desorption pressure P_L) is an important operating parameter for PSA systems. In this study, the feed pressure of 120 kPa and 150 kPa with different pressure ratios were investigated and the same pressure ratios were employed for comparison of the studied sorbents.

A summary of the simulation conditions and separation results for the studied materials is given in Table S1 (in the supplementary material). The feed and purge velocities were optimized so as to obtain the same product purity (near 95%) and recovery (near 52%) for all sorbents. Thus, the VPSA performance was judged by the O_2 productivities. Figures 11 and 12, which are both extracted from Table S1, shows the effect of pressure ratio on productivity for all four sorbents.

As can be seen from Figures 11 and 12, the higher the pressure ratio, the higher the productivity. It also shows that the O_2 productivity follows the following trend: (Li-LSX > $Li_{4.2}Ca_{45.9}$ -LSX > $Li_{2.5}Ca_{46.75}$ -LSX > Ca-LSX). The above result also justifies that Li-LSX is better than Ca-LSX for O_2 production and this is because the Ca-LSX zeolite has a higher heat of adsorption,

higher O₂ capacity, and a lower N₂ working capacity. Upon comparison, the trend (Ca-LSX > Li_{2.5}Ca_{46.75}-LSX > Li_{4.2}Ca_{45.9}-LSX > Li-LSX) for the N₂ heats of adsorption for the four sorbents appears to be the reverse of the O₂ productivity above. Since adsorption is an exothermic process, the temperature in the bed will increase in the high-pressure feed step thereby affecting the O₂ separation results. It can be seen from the isotherms that the adsorption amount of N₂ on Ca-LSX is higher than that of the Li-LSX at 298 K. However, when the temperature is higher than 323 K, the adsorption amount of N₂ on Ca-LSX is lower compared to Li-LSX. Hence, the working capacity decreases sharply with increasing temperature for N₂ adsorption on Ca-LSX. A higher N₂ adsorption capacity could be achieved by employing a higher feed velocity at the same product purity and recovery. It is seen in Table S1 that Li-LSX has the highest feed velocity at the same simulation pressure.

The adsorption capacity of O₂ also has an important effect on PSA performance. When the Li⁺ is exchanged into the Ca-LSX zeolite, the oxygen adsorption capacity decreased in comparison with Ca-LSX. The decrease is beneficial because the lower the oxygen adsorption capacity, the better the PSA separation performance. In order to quantitatively study the effects of N₂ heats of adsorption and O₂ adsorption capacity on the separation results, the Ca-LSX zeolite was employed to simulate air separation by using, hypothetically, the N₂ heats of adsorption and O₂ isotherm of Li_{4.2}Ca_{45.9}-LSX, respectively. For simplicity purposes, Ca-LSX@1 and Ca-LSX@2 will be used to denote the sorbent pairings of Ca-LSX with Li_{4.2}Ca_{45.9}-LSX N₂ heats of adsorption and Ca-LSX with Li_{4.2}Ca_{45.9}-LSX O₂ isotherm, respectively.

All other simulation conditions were maintained except the high-pressure feed which was set at 120 kPa. The feed and purge velocities were also optimized so as to obtain the same

product purity and recovery for both sorbents. Table 5 shows the simulation results while Figure 13 shows the separation results in comparison with the Ca-LSX and $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX sorbents. As can be seen from the result, the sorbent $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX has a higher O_2 productivity. Also, CaLSX@1 has a higher productivity than CaLSX@2. When the pressure ratio is 3, the O_2 productivity for sorbents CaLSX@1 and CaLSX@2 are 0.0584 $\text{tO}_2/\text{h/t}$ and 0.0519 $\text{tO}_2/\text{h/t}$ respectively which are 27% and 13% higher than that of pure Ca-LSX. The result also shows that the decrease in the N_2 heat of adsorption on Li^+ -exchanged Ca-LSX has more contribution than the decrease in O_2 adsorption capacity to enhance O_2 productivity. As can be seen from Table 2, the N_2 heats of adsorption on Ca-LSX is 43.39 kJ/mol, which is much higher than that of $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX (28.72 kJ/mol). The detrimental effect of the heat of adsorption on the PSA performance is well illustrated by Lee et al.⁴² in their development of heat-exchange PSA. Where significant improvement was shown in the PSA performance by using a two-bed PSA system in a shell-and-tube configuration that allowed heat transfer between the two beds. The effects of heats of adsorption/desorption are further complicated by their effects on the mass transfer rates⁴³ which can be significant in rapid or kinetically controlled PSA. In the PSA system under consideration, as mentioned above, mass transfer resistance was neglected due to the relatively long cycle time.

In commercial operation of VPSA, the operating high and low pressures are normally set as 150 kPa and 50 kPa respectively for the production of O_2 via VPSA. With a pressure ratio of 3, it can be seen from Table S1 that when the feed pressure is 150 kPa, the O_2 productivity obtained using $\text{Li}_{4.2}\text{Ca}_{45.9}$ -LSX is 0.0637 $\text{tO}_2/\text{h/t-sorbent}$ compared to the throughput of 0.046 $\text{tO}_2/\text{h/t-sorbent}$ and 0.084 $\text{tO}_2/\text{h/t-sorbent}$ using Ca-LSX and Li-LSX respectively. The corresponding O_2

product purity and recovery were approximately 95% and 52%. This shows that using the $\text{Li}_{4.2}\text{Ca}_{45.9}\text{-LSX}$ sample enhanced O_2 productivity by 43% more than Ca-LSX, and only 25% lower than the productivity of Li-LSX. This is to say, in order to achieve the same O_2 productivity from using the $\text{Li}_{4.2}\text{Ca}_{45.9}\text{-LSX}$ sorbent, one only has to increase the bed size by 1.32 times (or 32%). A similar trend was observed when the feed pressure was set at 120 kPa. The use of the mixed-cation LiCa-LSX results in savings of 70% lithium. Knowing that most of the fixed investments in VPSA O_2 production industry lies in the cost of the sorbent, these results present the possibility of considerable savings in capital and operating costs, especially with the steep rise in price (driven by the demand for rechargeable batteries) of lithium. On the other hand, increasing the bed size factor would require larger vessels and larger compressors/vacuum blowers which should also be considered.

It should be noted that zeolitic sorbents used in industrial PSA/VSA processes are in the form of pellets that are formed with a clay binder, and the pelletized products need to be calcined in air at a high temperature. For example, in the improved sorbent (with high diffusion rates) of Ackley et al.⁴⁴, the Li-LSX crystals were mixed with a clay binder to form pelletized beads and the beads needed to be calcined in dry air at up to 866 K for 3 hours. Thus, for practical application of the LiCa-LSX zeolite, a modification of the sample preparation steps is required. Pelletization of Ca-LSX with a binder followed by high temperature calcination will be performed first, which is to be followed by the Li^+ ion exchange and mild calcination steps as described above. Ion exchange of zeolites in their pelletized form is practiced in laboratories⁴⁵ and, in fact, occurs in industrial wastewater treatment such as radioactive waste treatment.⁴⁶

Conclusion

Mixed-cation LiCa-LSX with less than 5% Li were prepared by sequential exchange (with Li exchange as the last step) followed by mild and short-time dehydration. Comparisons of adsorption isotherms of N₂ and O₂ and heats of adsorption data for the LiCa-LSX samples with that for pure-cation Li-LSX and Ca-LSX provided strong evidence that significant fractions of these Li⁺ cations remained on the exposed exchange sites (SIII), thereby participating in adsorption of N₂ and O₂.

The mixed-cation LiCa-LSX samples were compared against the pure-cation Ca-LSX and Li-LSX based on their performance for oxygen production by PSA, via PSA model simulation. The simulation results show that the Li_{4.2}Ca_{45.9}-LSX sorbent with only a few Li cations exchanged into the pure Ca-LSX sample, could lead to significant improvements in the PSA production of O₂. This new exchange method shows a significant advantage over earlier research where more than 70% Li cations were exchanged with pure Na-LSX.^{3,8,10,13}

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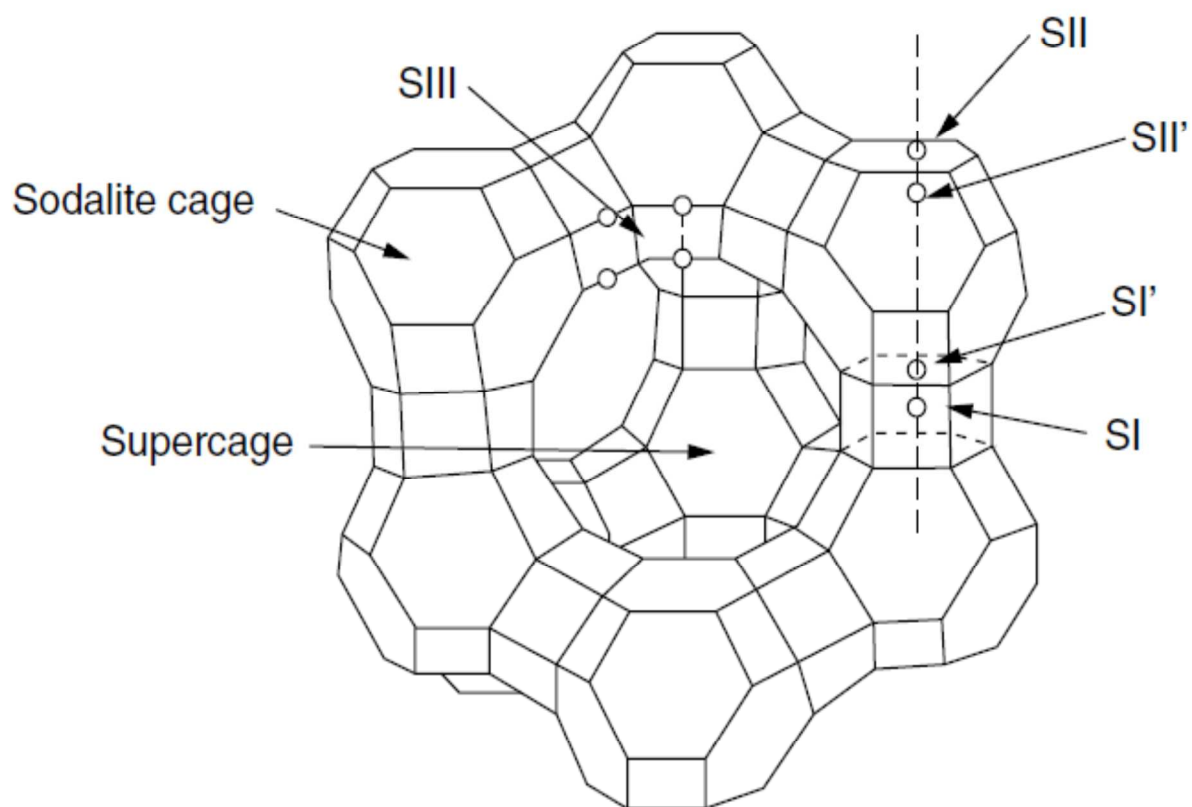


Figure 1. Unit cell of faujasite-type (X and Y) zeolites, including cation sites².

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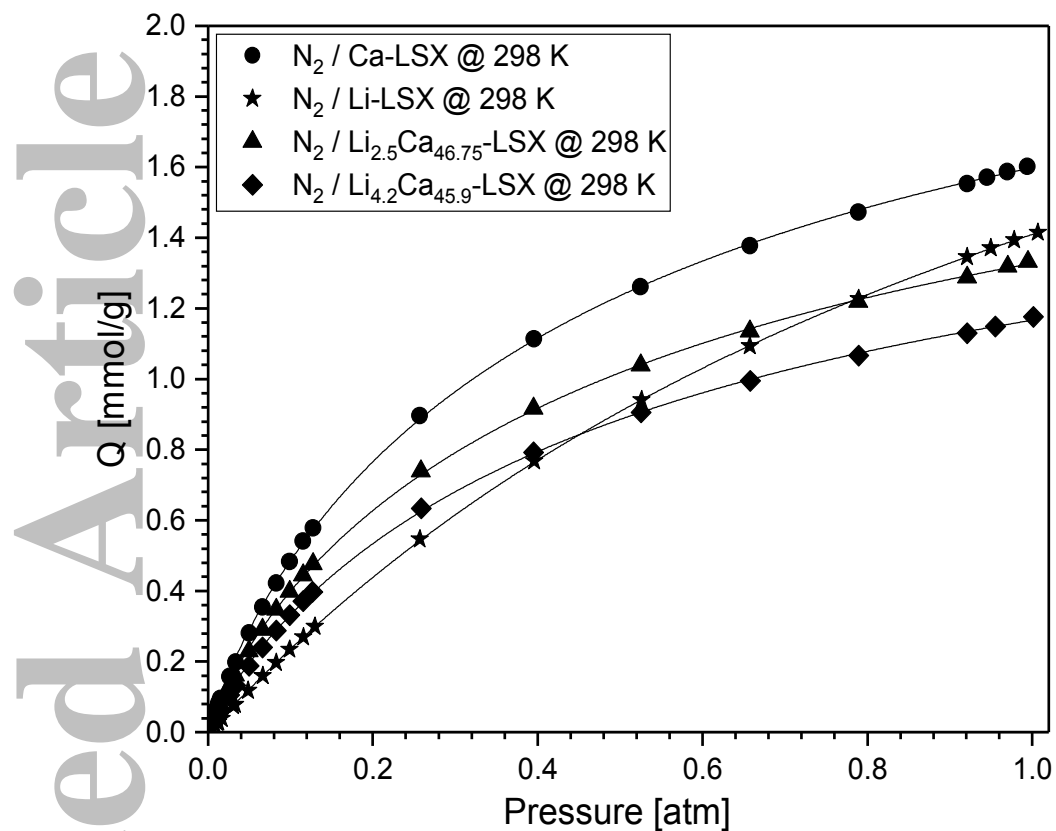


Figure 2. Experimental adsorption isotherms of N₂ at 298 K and 101 kPa on representative sorbents.

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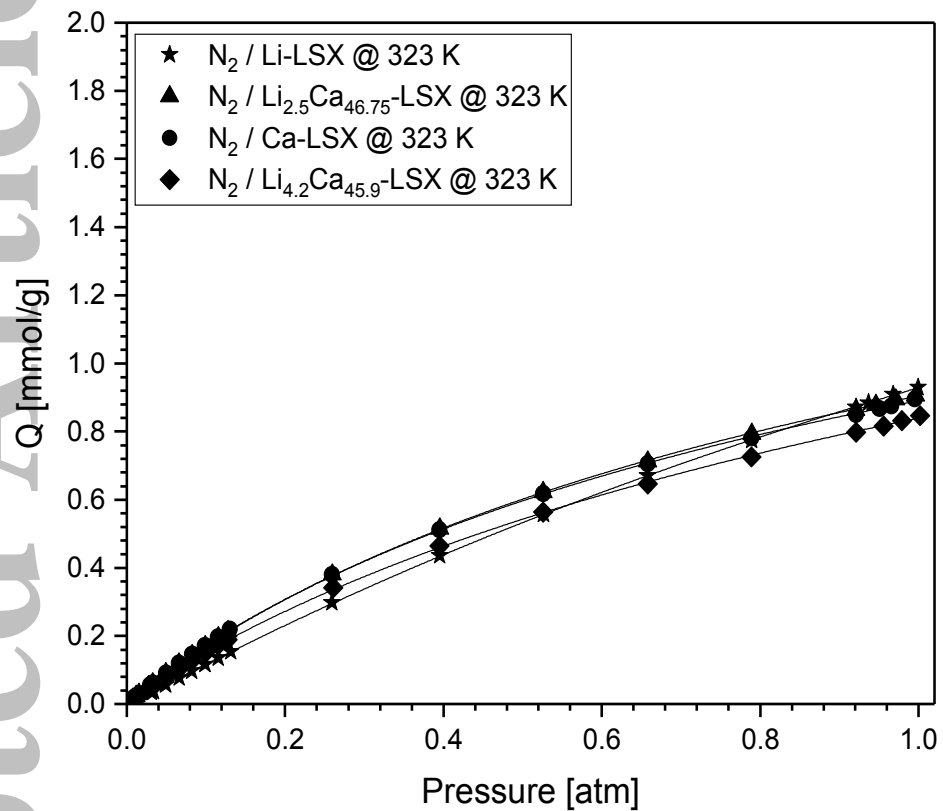


Figure 3. Experimental adsorption isotherms of N₂ at 323 K and 101 kPa on representative sorbents.

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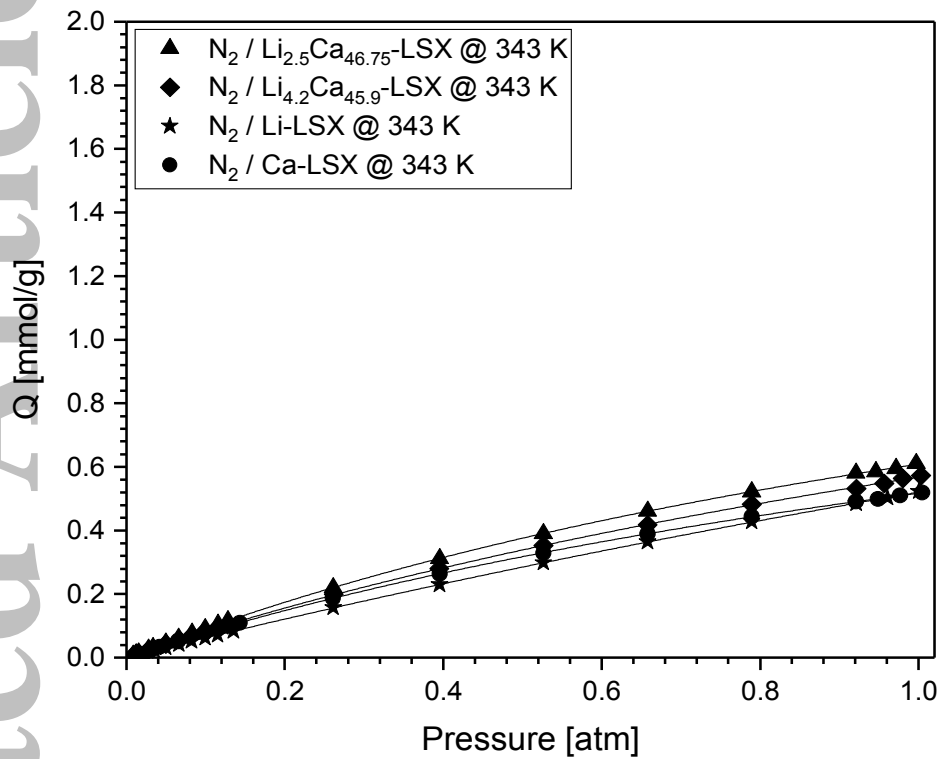


Figure 4. Experimental adsorption isotherms of N₂ at 343 K and 101 kPa on representative sorbents.

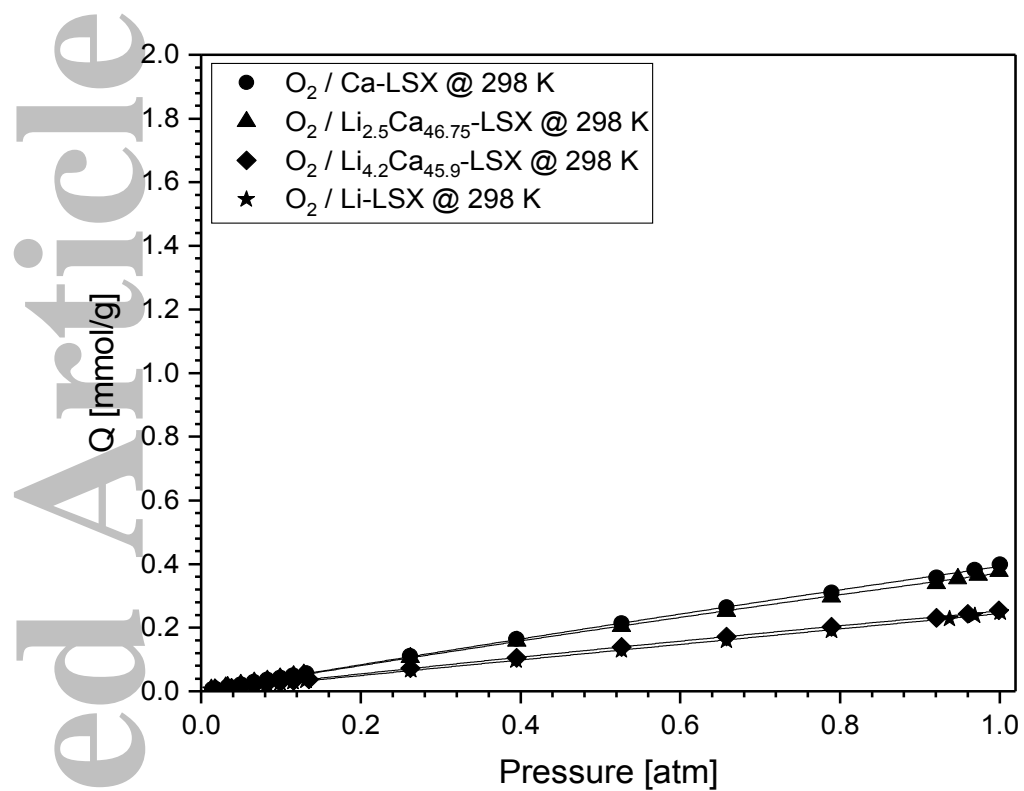


Figure 5. Experimental adsorption isotherms of O₂ at 298 K and 101 kPa on representative sorbents.

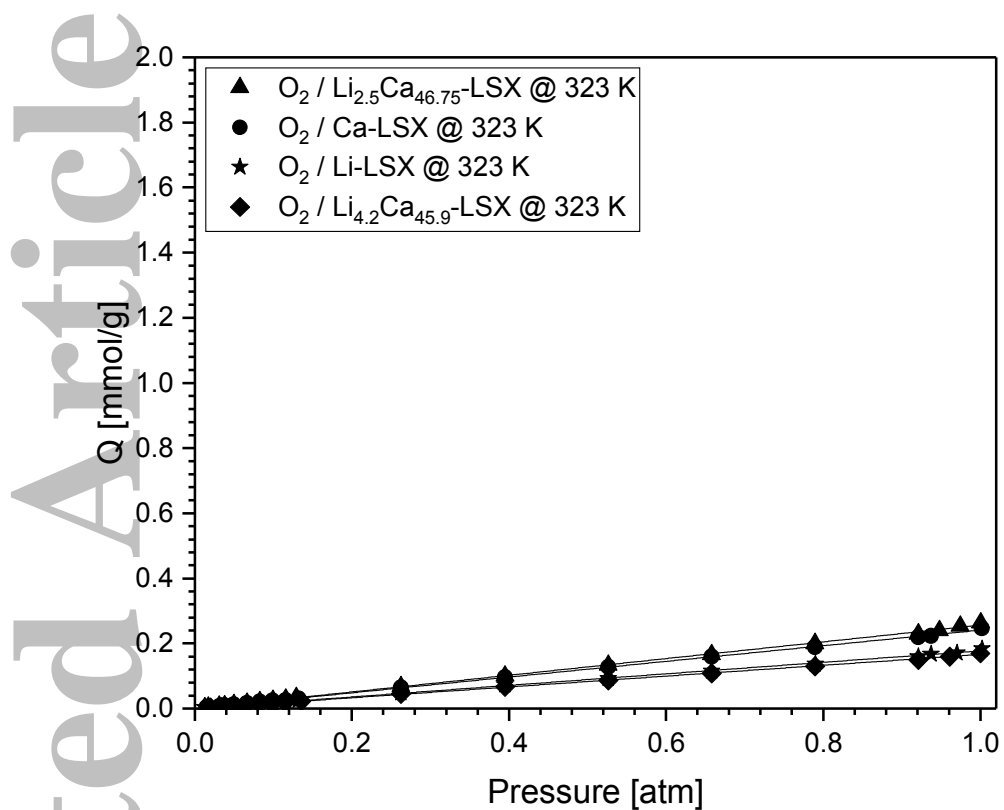


Figure 6. Experimental adsorption isotherms of O₂ at 323 K and 101 kPa on representative sorbents.

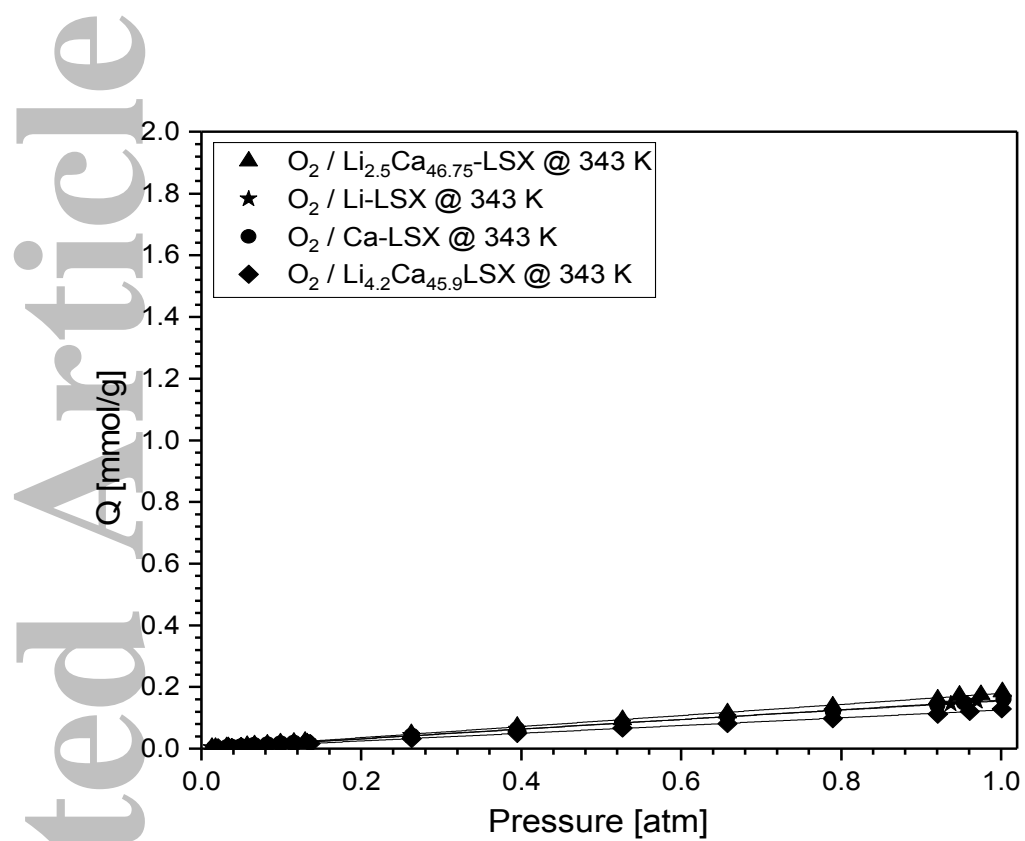


Figure 7. Experimental adsorption isotherms of O₂ at 343 K and 101 kPa on representative sorbents.

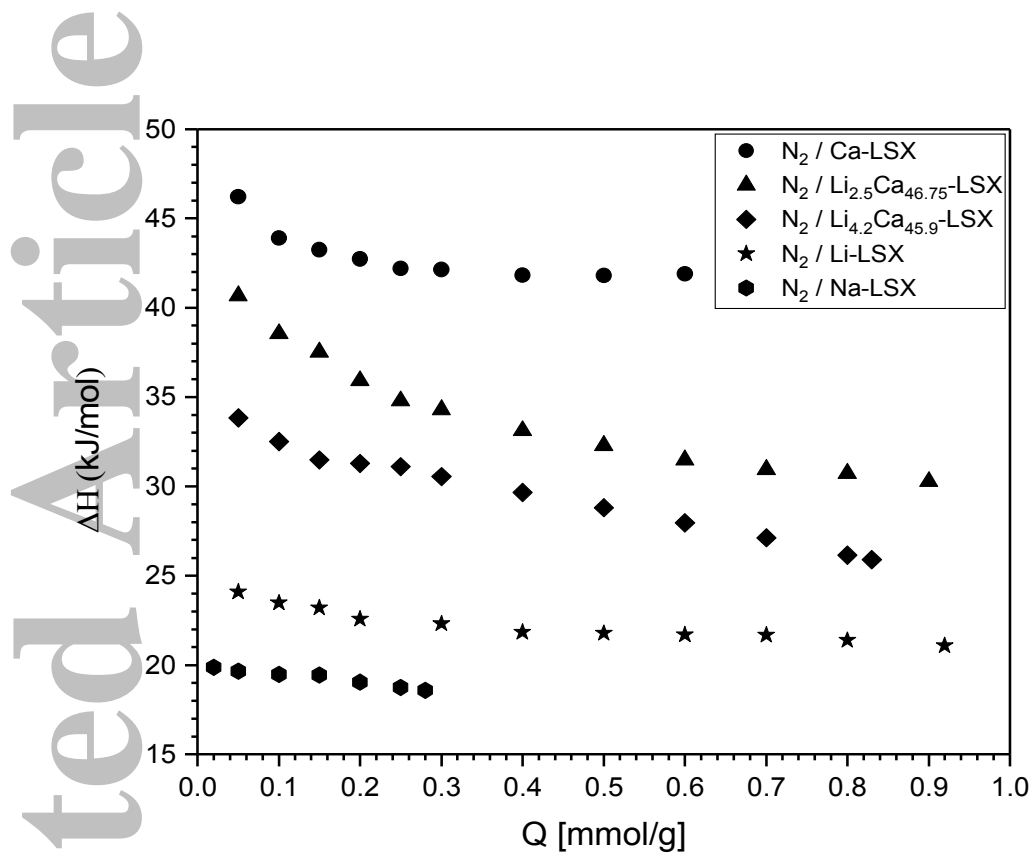


Figure 8. N_2 Heats of Adsorption on various sorbents.

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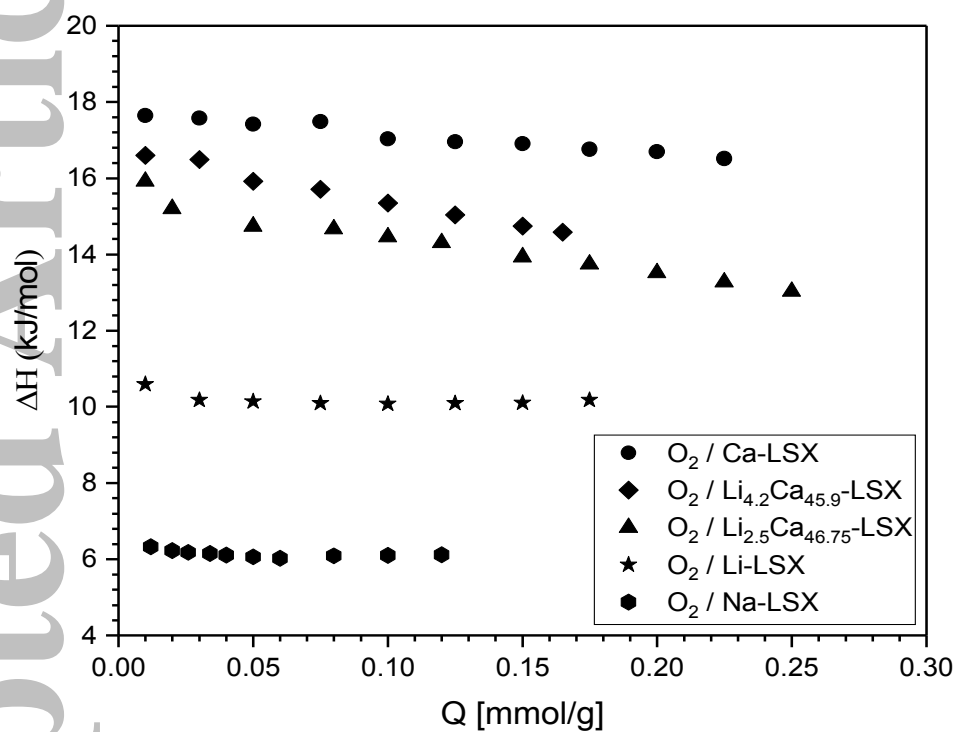


Figure 9. O_2 Heats of Adsorption on various sorbents.

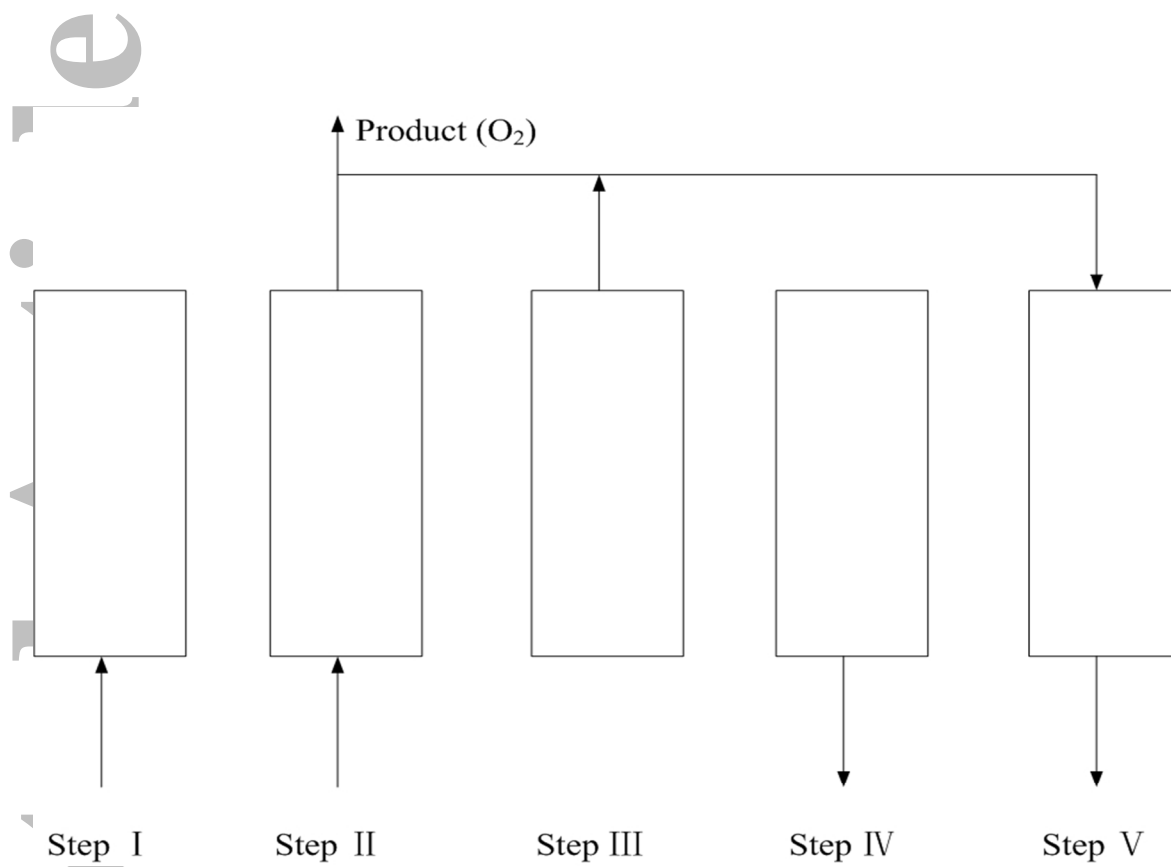


Figure 10. PSA cycle configuration.

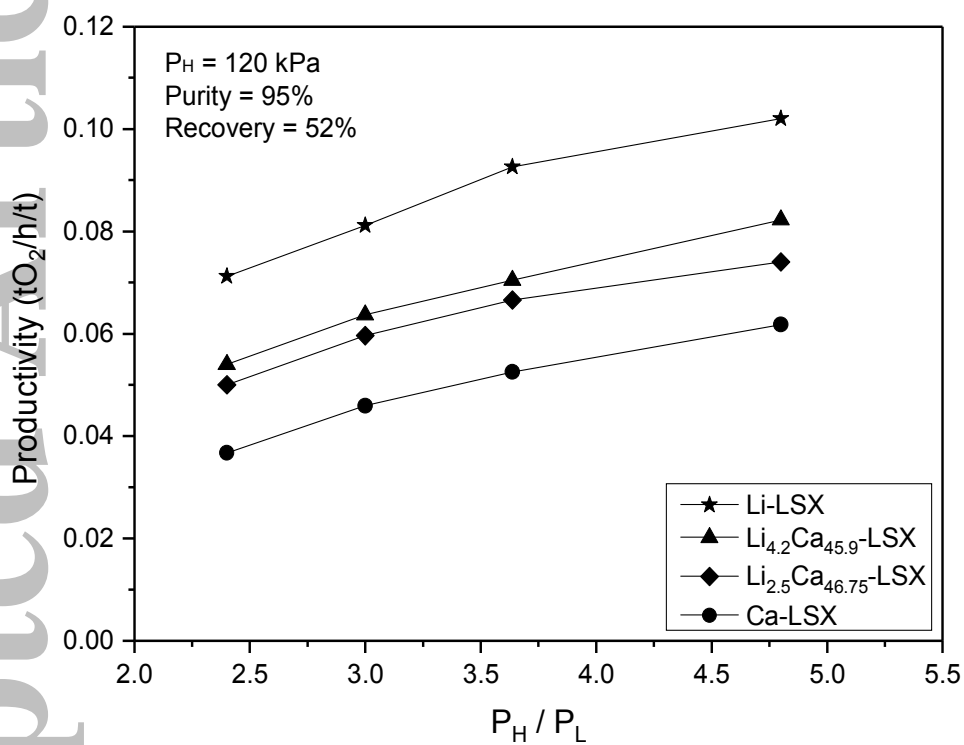


Figure 11. Comparison of O₂ Productivity at 120 kPa pressure.

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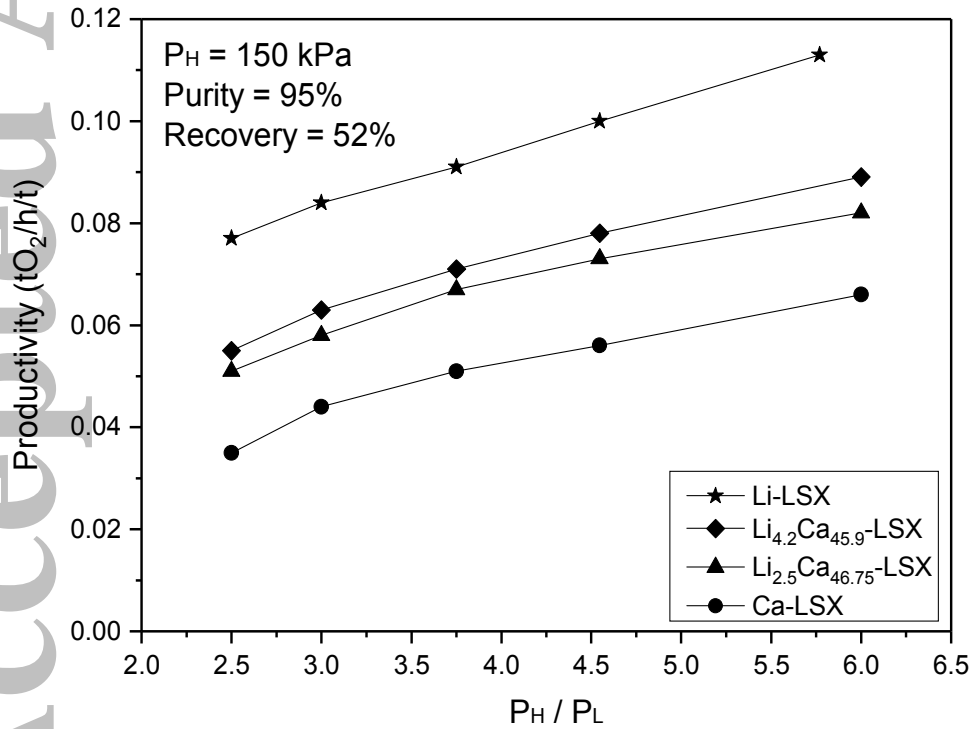


Figure 12. Comparison of O₂ Productivity at 150 kPa pressure.

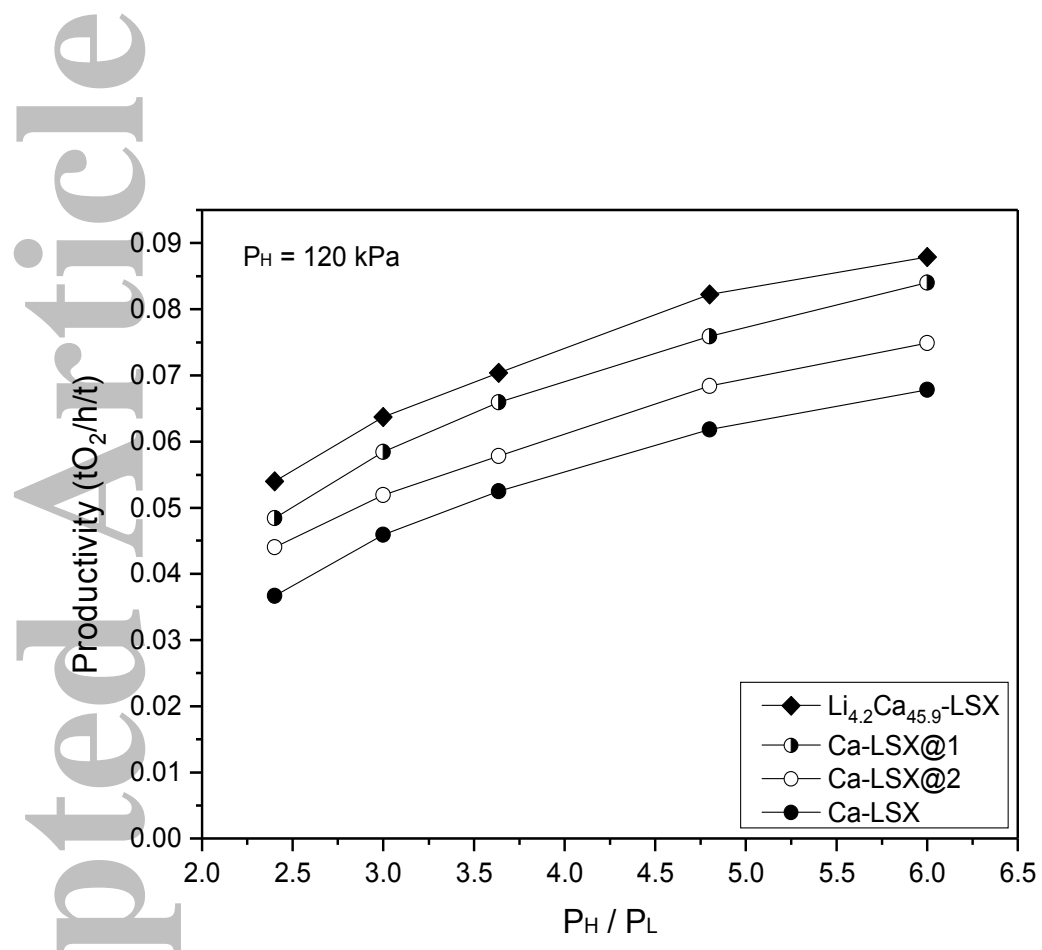


Figure 13. Effect of N₂ heats of adsorption and O₂ isotherm on O₂ productivity.

Table 1. Cation Site Occupancies in Dehydrated X Zeolites (Maximum = 96 Monovalent Cations per unit Cell for Si/Al = 1)

Zeolite	Al/Unit Cell	Sites				
		I	I'	II	II'	III
Li-LSX ²⁵	95.8		27.2	33.9		32.4
Li-LSX ²⁶	96		33	34		29
Na-X (13X) ²⁷	81	3.8	32.3	30.8		7.9
K-X ²⁸	87	9	13	26		38
Ca-X ²⁹	86	7.5	17.3	17.3	9.0	

Table 2. Composition of Various Represented Sorbents

Zeolite	Mole Ratio			
	Si/Al	Li/Al	Ca/Al	Na/Al
Na-LSX	1.005	-	-	0.995
Ca-LSX	1.005	-	0.991	-
Li _{2.5} Ca _{46.75} -LSX	1.005	0.025	0.467	-
Li _{4.2} Ca _{45.9} -LSX	1.005	0.042	0.459	-

Table 3. Temperature-Dependent Parameters of Langmuir-Freundlich Isotherm of N₂ and O₂

Sorbent	Sorbate	k ₁ (mmol/g)	k ₂ (K)	k ₃ (atm ⁻¹)	k ₄ (K)	n	ΔH (kJ/mol)
Li-LSX	O ₂	0.4798	636.6	0.00948	500	1.08168	9.17
Li-LSX	N ₂	1.84559	139.68	2.19×10 ⁻⁴	2484.2	1.033	21.79
Ca-LSX	O ₂	0.01448	1385.97	0.12788	207.35	1.152	12
Ca-LSX	N ₂	0.2623	646.75	6.88×10 ⁻⁶	3785.11	0.931	43.39
Li _{2.5} Ca _{46.75} -LSX	O ₂	1.89933	145.55	6.20294×10 ⁻⁴	1609.13	1.021	15.63
Li _{2.5} Ca _{46.75} -LSX	N ₂	1.31846	104.23	1.9726×10 ⁻⁵	3489.63	0.958	31.47
Li _{4.2} Ca _{45.9} -LSX	O ₂	2.20255	179.35	4.02105×10 ⁻⁴	1525.38	0.992	15.09
Li _{4.2} Ca _{45.9} -LSX	N ₂	0.98863	149.34	4.67445×10 ⁻⁵	3243.35	0.999	28.72

Table 4. Adsorption Bed Characteristics and Operating Conditions for PSA Simulations

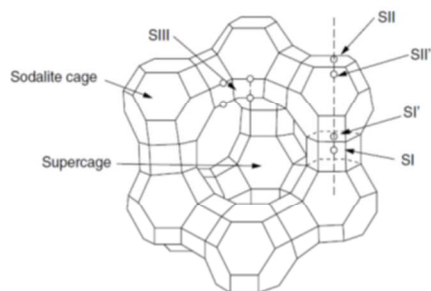
Bed length	2.5 m
Diameter of sorbent	1.0 m
Bed external porosity	0.4
Bed density	720 kg/m ³
Heat capacity of gases	28.72 J/mol/K
Heat capacity of sorbent	1.17 kJ/kg/K
Ambient temperature	298 K
Feed gas temperature	298 K
Feed gas composition	78% N ₂ , 22% O ₂
Axial dispersion coefficient (D _{ax})	5×10 ⁻⁵ m ² /s
Effective heat conductive	0.2 w/m/K

Table 5. Effects of N₂ heats of adsorption and O₂ adsorption capacity on PSA performance.

Sorbent	P _H (kPa)	P _{CD} (kPa)	P _L (kPa)	U _H (m/s)	U _L (m/s)	O ₂ Product Purity (%)	O ₂ Product Purity (%)	Product Productivity (tO ₂ /h/t)
	120	75	20	1.21	3.05	94.744	52.289	0.084
	120	80	25	1.13	2.27	94.995	51.903	0.0759
Ca-LSX@1	120	80	33	0.99	1.59	95.238	52.146	0.0659
(See Text)	120	85	40	0.92	1.21	95.307	51.992	0.0584

	120	90	50	0.802	0.85	94.971	51.821	0.0484
	120	75	20	1.04	2.8	94.959	52.426	0.0749
	120	80	25	0.99	2.1	95.225	52.718	0.0684
Ca-LSX@2	120	80	33	0.87	1.45	95.255	52.464	0.0578
(See Text)	120	85	40	0.835	1.13	95.316	52.293	0.0519
	120	90	50	0.765	0.83	95.118	51.955	0.044

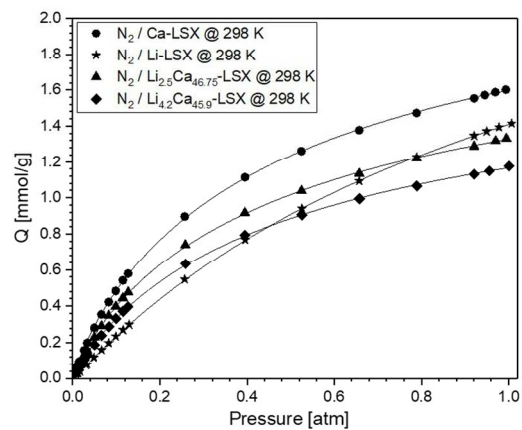
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Unit cell of faujasite-type (X and Y) zeolites, including cation sites.

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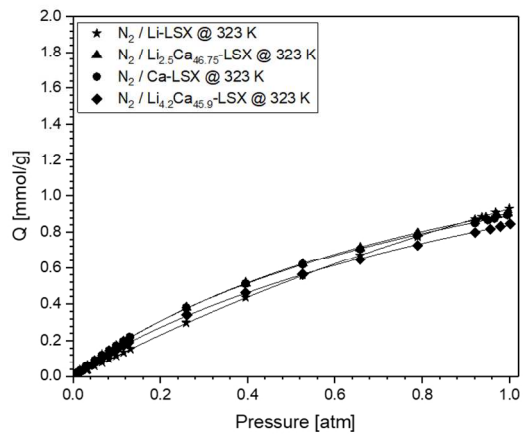
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Experimental adsorption isotherms of N₂ at 298 K and 101 kPa on representative sorbents.

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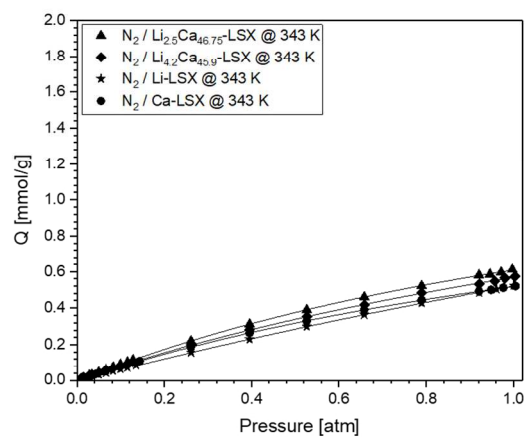
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Experimental adsorption isotherms of N₂ at 323 K and 101 kPa on representative sorbents.

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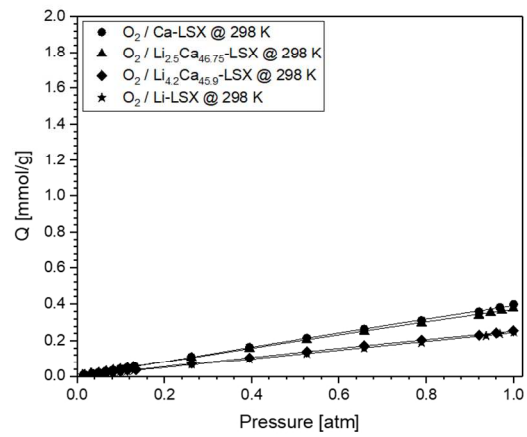
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Experimental adsorption isotherms of N₂ at 343 K and 101 kPa on representative sorbents.

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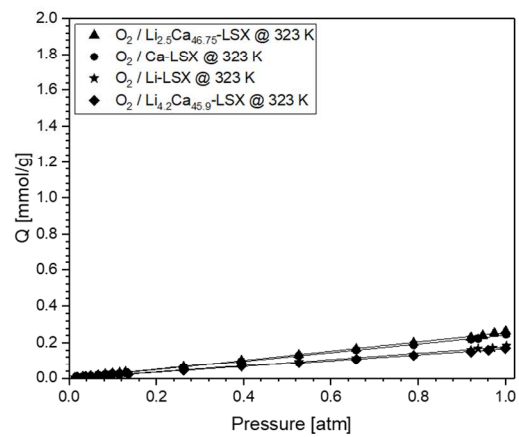
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Experimental adsorption isotherms of O₂ at 298 K and 101 kPa on representative sorbents.

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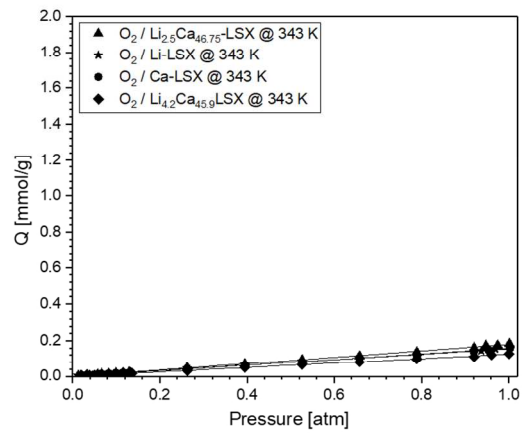
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Experimental adsorption isotherms of O₂ at 323 K and 101 kPa on representative sorbents.

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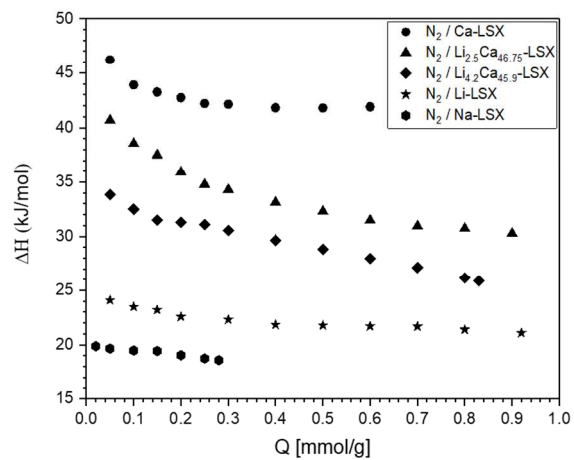
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Experimental adsorption isotherms of O_2 at 343 K and 101 kPa on representative sorbents.

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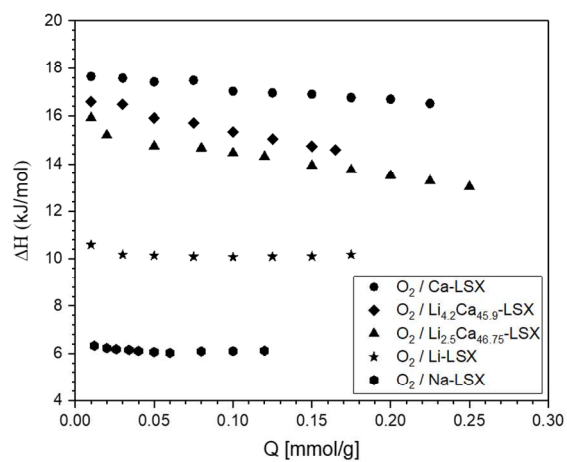
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N_2 Heats of Adsorption on various sorbents.

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O₂ Heats of Adsorption on various sorbents.

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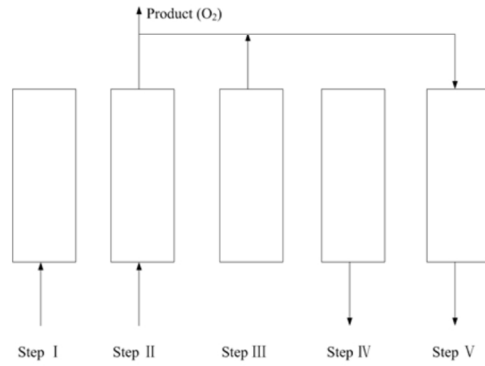


Figure 10. PSA cycle configuration.

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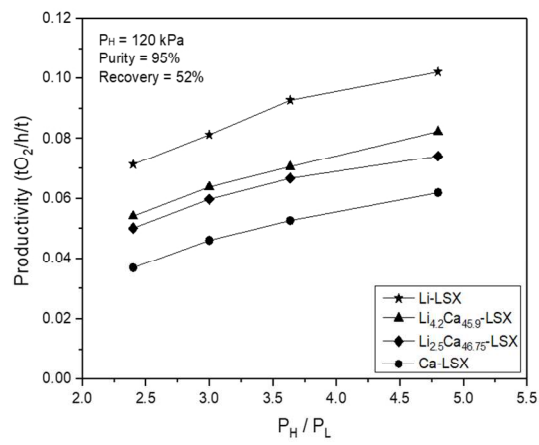


Figure 11. Comparison of O₂ Productivity at 1.2 atm pressure.

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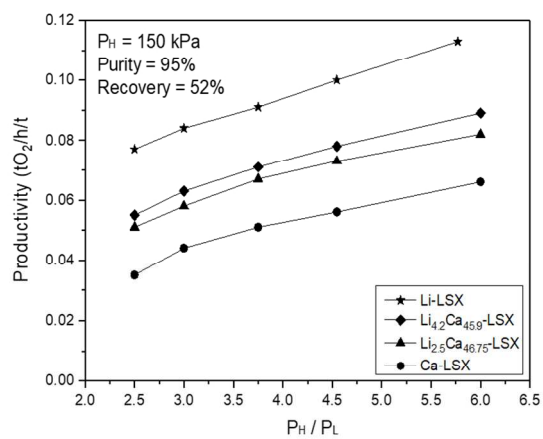


Figure 12. Comparison of O₂ Productivity at 1.5 atm pressure.

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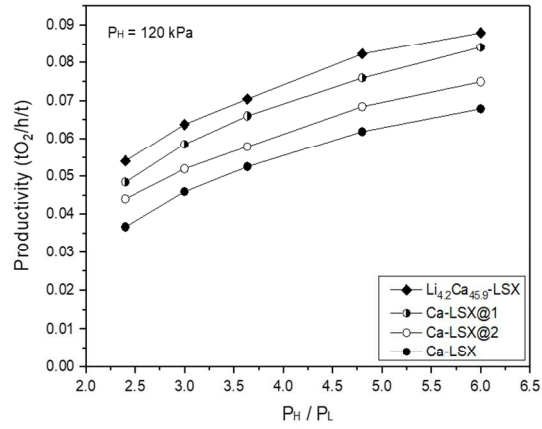


Figure 13. Effect of N_2 heats of adsorption and O_2 isotherm on O_2 productivity.

357x182mm (96 x 96 DPI)

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