Moist-pretreated lithium for high-performance reactive gas separation: focus on natural gas upgrading

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**Abstract**

For efficient gas capture and separation at ambient temperatures, a moist-pretreated lithium is introduced as a reactive adsorbent and its separation performance is examined for different gas mixtures (CH4, CO2, O2, N2, and H2), especially natural gas upgrading practice. For evaluation of the proposed adsorbent, we used density functional theory calculations as well as temperature programmed kinetic Monte Carlo calculations. Contribution of different mechanisms for the gas capture was examined, including diffusion, sorption, adsorption, and reaction, where it was found that gas capture is governed by reaction only. In contrast to common adsorbents, the gas capture mechanism follows the reaction between gases and species generated due to pre-exposure of lithium to moisture. The gases are transformed into solid products which can be post-processed to recover the gas and regenerate the adsorbent. The proposed separation is thermodynamically favorable and would progresses spontaneously. It is shown that for several gas mixtures containing methane, a perfect selectivity can be achieved where a pure methane gas stream leaves the reaction chamber and the other gaseous components are transformed to corresponding solid products.

**Keywords**: Gas separation; lithium; computational chemistry; reaction kinetics

# Introduction

Addressing the global challenge of reducing gaseous pollutants emissions from industrial activities demands the development of efficient gas separation and purification technologies [[1](#_ENREF_1)]. Important gas separation practices include acid gases and impurities removal and capture of H2, CO2, O2, N2, etc. from different sources, such as raw/pretreated natural gas, post-combustion flue gas, biogas etc. [[2](#_ENREF_2), [3](#_ENREF_3)]. Among various practices, N2 removal from pretreated natural gas streams, which mainly contains N2 and CH4, is of great interest to achieve a high purity CH4 stream as methane is regarded as a source of clean energy that generates much lower harmful emissions than coal [[4](#_ENREF_4)]. Such practice is one of the most challenging gas separation applications [[5-7](#_ENREF_5)] due to the similar physical chemistry properties between these two molecules. In addition, industrial applications require separation techniques to be cost-effective, efficient, and reliable [[8](#_ENREF_8)]. Accordingly, adsorption-based technologies have attracted increasing interest among other contemporary used ones, such as cryogenic distillation and membrane-based separations [[9](#_ENREF_9)].

In adsorptive gas separation, gases are selectively adsorbed, either physically or chemically, onto the surface of adsorbents which can be subsequently regenerated using different methods to recover pure components [[10](#_ENREF_10)]. Based on the separation practice of interest, the adsorptive gas separation can be referred to as either bulk separation (involves adsorption of >>10% w.t. from a gas stream) or bulk purification (involves adsorption of <10% w.t. from a gas stream) [[8](#_ENREF_8)].

In adsorptive gas separation, the physicochemical properties of adsorbent, including surface area, porosity, texture, and active sites capable of imparting strong interactions with gases (adsorbate), collectively determine the performance of the adsorbent, reflected by adsorption selectivity, capacity, and kinetics toward target gases [[11](#_ENREF_11)]. Among these performance parameters, selectivity plays the dominant role in determining the separation efficiency. The demand of for high-performance adsorbents have fueled a continuous exploration of various materials including metal-organic frameworks, zeolites, carbon nanotubes, etc. [[12-15](#_ENREF_12)]. Marathe et al. [[16](#_ENREF_16)] reported the desirable N2/CH4 separation (263.15 - 303.15 K) by strontium-exchanged Engelhard titanium silicate (Sr-ETS-4). Olajossy et al. [[17](#_ENREF_17)] used solid potassium hydroxide and activated carbon to reach a methane recovery efficiency of 86–91%. Cansado et al. [[18](#_ENREF_18)] prepared a series of carbon molecular sieves (CMSs) for the adsorptive purification of gas mixtures containing O2/N2 and CO2/CH4 where they used cork oak (Quercus suber L.) and recycled granulated PET for adsorbent preparations. The CMSs exhibit relatively high but similar adsorption capacities toward each component (up to 20 mmol/g) and thus lead to undesirable selectivities. Belmabkhout et al. [[19](#_ENREF_19)] measured adsorption of nitrogen, argon, methane, and oxygen on four activated carbons (Centaur, BPL, F30/470, and WS42) and on one molecular sieve. While the highest adsorption capacities were determined to be less than 5 mmol/g, they showed that methane is always preferably adsorbed. Watson et al. [[20](#_ENREF_20)] measured adsorption of nitrogen and methane on a commercial carbon molecular sieve (Shirasagi MSC 3K-161) at temperatures between 115 to 323 K and pressures up to 5 MPa and obtained similar adsorption capacity of both gases. Zhang et al. [[21](#_ENREF_21)] measured adsorption of N2 and CH4 on MIL-101 and reported a selectivity of N2 over CH4 of around 3. The adsorption capacity of Activated Carbon JX101 for H2, N2, CH4, and CO2 was measured by Wu et al. [[22](#_ENREF_22)] where the highest achievable value of each gases was around 10 mmol/g. The adsorption capacity of a series of ion exchanged silicoaluminophosphates (SAPO-34) with different cations (Ag+, Mg2+, Ca2+, Sr2+, Ti3+, and Ce3+) were examined for separation of N2/CH4 showing up to 3 mmol/g of studied gases [[23](#_ENREF_23)]. Literature survey implies that CH4/N2 equilibrium selectivity on most adsorbents is below 5 [[7](#_ENREF_7)]. In search of superior adsorbents capable of imparting substantially elevated N2-over-CH4 selectivity, the use of moist-pretreated lithium as a reactive adsorbent for gases (CH4, CO2, O2, N2, and H2) at ambient temperatures by screening temperature range 25 ℃ < T < 100 ℃ is addressed here.

The idea of using moist-pretreated lithium originates from the observation of lithium reactivities with some moist gases [[24](#_ENREF_24), [25](#_ENREF_25)]. For gases such as CO2, O2, N2, and H2, it’s been observed that at dry conditions and moderate temperatures (45 ℃ < T < 186 ℃), no considerable reaction could occur between lithium and each of these gases [[25](#_ENREF_25)]. However, it’s reported that the exposure of moisture enhances the reactions significantly [[25](#_ENREF_25)]. Such reactions produce solid products with different physicochemical properties and appearance. The products include red/purple solid lithium nitride, odorless white powder lithium carbonate, and white solid lithium oxide due to the reaction of lithium with nitrogen, carbon dioxide, and oxygen, respectively [[24](#_ENREF_24)]. The occurrence of these reactions strongly depends on the presence and concentration of moisture, suggesting that moisture should play a key role in enabling such reactions. The mechanism was recently reported [[26](#_ENREF_26)]. Specifically, we revealed that the reaction between lithium and water is an exothermic and facilitated water dissociation reaction by investigating water interactions on lithium surface over a temperature range of 25-100 ℃. This reaction occurs spontaneously and favorably since the small energy barrier (2.715 kJ/mol) can be easily overcome given the scaling factor for energy in molecular-scale systems with a large number of molecules at ambient temperature range of 25-100 °C corresponds to ≈1 kJ/mol [[27](#_ENREF_27)]. Depending on the amount of exposed moisture, this reaction produces hydrogen, lithium hydride, and lithium hydroxide as well as releases energy (≈ 430 kJ/mol). For full moisture coverage, which implies immersing lithium particles in a bath of water in practice, the products would be lithium hydroxide and water surrounded lithium hydroxide as well as hydrogen (lithium oxide may also be observed) [[24](#_ENREF_24)]. For low moisture coverage, implying spraying water over lithium surface in practice, the major products would be lithium hydroxide and hydrogen while lithium hydride is also generated, the amount of which has a reciprocal dependency with the moisture concentration [[26](#_ENREF_26)]. Such an observation of lithium reactivity is absent for other gases interacting with lithium. This means that when lithium is exposed to a gas in the presence of moisture, the aforementioned water dissociation precedes and generates the auxiliary species and energy to enable further reaction with the gas. The species present upon dissociation should be responsible for further reactions observed for lithium and moist gases where the released energy from water dissociation should be able to supply the energy needed to overcome the energy barrier of the reactions. To confirm this hypothesis, it is needed to determine the activation free energies of reaction of each gas with pure lithium and with each species generated by lithium-water dissociative reaction. Once confirmed, for gas capture we should contact lithium with moisture to generate moist-treated lithium which is then contacted to gases for reactive capture. Such a practice removes the safety and maintenance issues of using moist gas as the presence of moisture in gas stream transportation equipment such as compressors causes the corrosion risks [[28](#_ENREF_28)]. Thus, pre-exposure of lithium to moisture is proposed to remove the need of humid/moist gas stream as well as strike requirements for lithium storage. Thus, we propose that lithium is first exposed to moisture to produce moist-pretreated lithium followed by contacting with gas/gases of interest for selective reactive separation.

There is an important difference between (*i*) exposing gas/gases to moist treated lithium and (*ii*) exposing moist gas/gases to lithium. In case *ii*, the energy release upon water dissociation would be available to supply the energy needs of reactions of other present gases with substrate, while in case *i*, this energy will be lost and won’t be accessible efficiently. This implies that a small external heating will be required for practical application of moist-pretreated lithium. Hopefully, such external heating shouldn’t be considerable as we determined the low temperature demanded by reaction kinetics. The low temperature well meets the energy-economy needs in industrial and practical applications which demands an adsorption process to be able to operate at near-ambient temperatures (25-100 ℃). Thus, moist-pretreated lithium should meet all these requirements.

To elucidate the potential of moist-pretreated lithium as a reactive adsorbent for different gas separation practices, we report a reaction analysis between lithium and gases, lithium hydride and gases, and lithium hydroxide and gases, because the moist-pretreated lithium might be a mixture of these species [[26](#_ENREF_26)]. Note that proportion of these species depends on the extent of pre-exposure of lithium to moisture (moist pretreatment step). While hydrogen and lithium hydroxide productions are proportional to the moisture content, the lithium hydride showed a non-proportional dependency [[26](#_ENREF_26)]. The activation free energies were determined using density functional theory (DFT) calculations and compared with the aforementioned scaling factor energy. These results were then used to determine reaction rate constants employing the transition state theory of chemical reactions. While comparison of reaction rate constants may provide a general overview of how fast and competitively the reactions proceed, for a practical analysis of adsorptive separation where feed stream is a gas mixture, the collective and combined effects of gases in mixture need to be addressed. To avoid exhaustive computational costs related to mixed gas reactivity, based on the determined reactivity of gases, a reaction network was constructed using a temperature programmed calculation kinetic Monte Carlo method (TPC-kMC). The reaction network was applied for two main gas separation scenarios including (i) binary N2/CH4 gas and (ii) pretreated natural gas mixture containing nitrogen, methane, carbon dioxide, and moisture [[7](#_ENREF_7)].

This paper is organized as follows: First, the theoretical methods are presented. Second, the reactivity results are summarized and discussed followed by their implementation in temperature programmed calculation kinetic Monte Carlo method. The TPC-kMC results are analyzed for each gas mixture studied. The possible binary mixtures that can be processed using the proposed approach are presented. In appendixes, we provide additional analysis done through the course of process network determination and construction as it was thought that physical sorption (non-binding) and diffusion of gases in moist-pretreated lithium may have some contributions.

# Theoretical section

## General considerations

For theoretical process modeling of gas adsorption and separation using an adsorbent, contributions of different mechanisms need to be considered. When a gas is exposed to an adsorbent surface, it may (i) react with adsorbent, (ii) diffuse into the gaps, pores and microstructural defects in adsorbent, (iii) adsorbed onto the surface of adsorbent and, (iv) sorbed into the adsorbent due to close contact and interactions with adsorbent atoms in combination with #ii, etc. Thus, we considered that when exposing moist-pretreated lithium substrate to gases, the gases may diffuse/sorb into the gaps or porosity of substrate and/or react with substrate. Accordingly, a series of sorption and diffusivity simulations were performed. We found that sorption and diffusion do not play a considerable role compared with reaction and thus excluded sorption and diffusion from modeling. The corresponding results are nevertheless reported in appendix. The reactions play the dominant role and are therefore focused in this study. For reactivity analysis, we used density functional theory (DFT) calculations. To examine the performance and potential of the proposed adsorbent, the analysis of mixture gas streams is needed, for which temperature programmed calculation kinetic Monte Carlo method was employed to reduce the computational costs.

## Methods

In reactivity analysis, we attempted to determine the reaction rate constants and activation free energies. For this purpose, we used transition state theory of chemical reactions formulated by Wigner, Eyring, Polanyi and Evans (WEPE) [[29-31](#_ENREF_29)]. It is worthy to mention that the use of transition state theory or the statistical mechanical treatment of free energy instead of Arrhenius model is advised [[32](#_ENREF_32)]. This is because, the activation free energy (*∆G*) is temperature dependent practically, while in the Arrhenius model it is assumed to be temperature independent and treated as a fitting parameter [[33](#_ENREF_33)]. However, temperature may affect the share of different transition states in reaction progress which may result in a different reaction path [[34](#_ENREF_34)]. In fact, apart from the minimum path, there are other paths passing transition states that may be involved in reaction with different activation energies. The reaction rate constant formulated by WEPE [[29-31](#_ENREF_29)] is given as where *kB* is Boltzmann’s constant (1.38064852×10-23 J.K-1), *h* is Planck’s constant (6.626069934×10-34 J.s), *R* is universal gas constant (8.3144598 J.K-1.mol-1), *T* is temperature in Kelvin [[35-37](#_ENREF_35)]. This means that rate constant is related to free energy of activation as  indicating that a higher *∆G* corresponds to a lower *k* and a slower progress [[31](#_ENREF_31)]. For the calculation of *∆G*, a vibrational analysis of first principles calculations [[38](#_ENREF_38)] was used here. For this purpose, we utilized the DMol3 package [[39](#_ENREF_39)]. For relaxation of all considered materials, a geometry optimization and energy minimization step was considered. In these steps, the generalized-gradient approximations (GGA) and becke-lee-yang-parr (BLYP) density functional theory (DFT) were employed [[40](#_ENREF_40)] including Hamiltonian, d-polarization function (DND) level of theory to enhance self-consistent field (SCF) calculations convergence [[41](#_ENREF_41), [42](#_ENREF_42)]. Numerically, the convergence tolerances are: displacement = 10-5 Å, energy = 10-4 kJ/mol, force = 0.001 kJ/mol·Å, self-consistent field criteria = 10-6. Also, solvation effects were considered using COnductor-like Screening MOdel (COSMO) [[43](#_ENREF_43)]. The free energy of each structure from reactant to next transition state structure toward the products were calculated using the Dmol3 package. The activation *∆G* of overall reaction was calculated as net summation of these obtained free energies up to the transition state which has the highest energy. These calculations are performed for (i) lithium-gas, (ii) lithium hydroxide-gas, and (iii) lithium hydride-gas cases as the moist-pretreated lithium may contains all of these compounds.

For gas separation from mixed gas feed, then, these reactions were coupled using a temperature programmed kinetic Monte Carlo calculations (TPC-kMC) [[44](#_ENREF_44)].

TPC-kMC is a discrete event simulation implemented in the Kinetix package [[39](#_ENREF_39)] calculating property changes based on the kinetic data introduced. Using TPC-kMC, it is possible to study the collective effect of these reactions when a feed stream of mixed gases is processed. Also, the effect of operating conditions can be assessed in TPC-kMC calculations by varying the input temperature/pressure dependent parameters. The constructed process network includes all the reactions listed in Table 1 with corresponding reaction rate constants for all considered temperatures. For TPC-kMC calculations at each temperature of interest, the corresponding sub-process in process network was activated only. For TPC-kMC, there’s a need to construct a substrate. For all TPC-kMC calculations, we used a grid of 2048×2048 sites. To create a substrate corresponding to moist participated lithium, we first performed a TPC-kMC run for a substrate of pure lithium where only reactions of lithium and water were activated in process network. In this step, all of the 2048×2048 sites in the substrate grid were assigned to lithium corresponding to the pristine lithium. The run time corresponds to the exposure time of moisture to the lithium substrate. Reviewing the literature [[24](#_ENREF_24)], it was concluded that for different gases, lithium reactivity with moist gases is highest at low moisture content and decreases as moisture content increases. In addition, the lithium reactivity was observed even in the case of short exposure to air humidity [[25](#_ENREF_25)]. Having this information, we considered a short moist pre-exposure step of 10 s. This actually involves introducing 1 water molecule (site) per 25 adsorbent (Li) atoms (sites), which corresponds to a moisture concentration of ≈ 15 w.t.%. The final configuration of this TPC-kMC run contains lithium, lithium hydride, and lithium hydroxide. This configuration was then used as initial configuration of each mixed gas TPC-kMC run. For each mixed gas analysis of interest, the corresponding reaction sub-processes in process network was enabled and the calculations were performed for an operating period of 24 hours (24×60 minutes) in the operating conditions (temperature and pressure) of interest for each studied scenario. The considered scenarios include (i) binary N2/CH4 gas and (ii) pretreated natural gas mixture containing nitrogen, methane, carbon dioxide, and moisture [[7](#_ENREF_7)].

# Results and discussion

First the calculated activation free energies are reported and discussed. Then, TPC-MC results for mixed and binary gas simulations are presented and discussed.

## Results of reactivity analysis

### Activation ∆*G* for lithium and moist-pretreated lithium with various gases

The reaction between Li and moisture was studied in a recent paper [[26](#_ENREF_26)]. The activation ∆*G* of plausible reactions of lithium, lithium hydride, as well as lithium hydroxide with CH4, CO2, O2, N2, and H2, respectively, are summarized in Table 1. At low temperatures (25-100 ℃), a slight temperature dependency was observed so the values in Table 1 are averaged over aforementioned temperature range. Clearly, lithium almost does not react with the gases at ambient temperatures (without external heating or energy supply) because the ∆*G* values are much larger than the aforementioned scaling factor. When lithium is exposed to moisture, a considerable amount of energy is released as calculated to be ≈ 430 kJ/mol [[26](#_ENREF_26)]. Comparing this energy release with the calculated activation ∆*G*s , it can be concluded that it affords to overcome the ∆*G* for most of the reactions leading to observation of reactions upon contacting lithium with moist gases, as observed in literatures [[24](#_ENREF_24), [25](#_ENREF_25)]. Also, as discussed before [[26](#_ENREF_26)], the activation ∆*G* of moisture reaction with lithium is 2.715 kJ/mol meaning that this reaction is so fast that it overwhelms all plausible reactions with any other gases in the case of lithium contact with moist gases. This guarantees the presence of lithium hydride and lithium hydroxide as well as energy release. Thus, it can be concluded that the produced lithium hydride and lithium hydroxide are responsible for the observed reaction with different gases.

Table 1. Computed activation ∆*G*

|  |  |
| --- | --- |
| **Reaction** | **activation** ∆*G* **(kJ/mol)** |
| **Dry Li + gases** | |
| 2Li + H2 → 2LiH | 53.93 |
| 6Li + N2 → 2Li3N | 87.19 |
| 4Li + O2 → 2Li2O + Li2O2 | 75.97 |
| 10Li + 3CO2 → Li2CO3 + 3Li2O + Li2C2 | 117.18 |
| 2Li + 2CH4 → Li2C2 + 4H2 | 105.76 |
| **LiH + gases** | |
| LiH + H2 → LiH + H2a | 2.19 |
| 6LiH + N2 → 2Li3N + 3H2 | 13.42 |
| 3LiH + N2 → Li3N + NH3 | 96.37 |
| 2LiH + O2 → 2LiOH | 18.34 |
| 10LiH + 3CO2 → Li2CO3 + 3Li2O + Li2C2 + 5H2 | 97.82 |
| 2LiH + 2CH4 → Li2C2 + 5H2 | 218.71 |
| **LiOH + gases** |  |
| 2LiOH + H2 → LiOH + LiH + H2O | 86.94 |
| 3LiOH + N2 → Li3N + N(OH)3 | 327.57 |
| 4LiOH + O2→ 2Li2O2 + 2H2O | 17.94 |
| 2LiOH + CO2 → Li2CO3 + H2O | 19.67 |
| 2LiOH + 2CH4 → Li2C2 + 2H2O + 3H2 | 213.93 |
| **Other reactions** | |
| Li + OH → LiOHb | 0.41 |
| Li + H → LiHb | 3.82 |
| LiH + LiOH → Li2O + H2 | 21.17 |
| Li2O + CO2 → Li2CO3 | 174.95 |
| Li2O + H2O → 2LiOH | 149.37 |
| aIt’s actually a proton exchange and does not change the population of corresponding reactants/products.  bfrom water dissociation on lithium surface [[26](#_ENREF_26)] | |

In following paragraphs, we focus on the analysis of results obtained in reactivity analysis of moist pre-treated lithium and gases. As convened, we simulated reaction of binary systems containing lithium and gases, lithium hydroxide and gases as well as lithium hydride and gases. Thus, to discuss the reactivity of each gas with moist lithium, we address the activation ∆*G*s of all composing binary systems simultaneously.

### The reaction of moist-pretreated Li with nitrogen

For the analysis of nitrogen reactivity with moist-pretreated lithium, the activation ∆*G*s for (i) 6Li + N2 → 2Li3N (87.19 kJ/mol), (ii) 6LiH + N2 → 2Li3N + 3H2 (13.42 kJ/mol), (iii) 3LiH + N2 → Li3N + NH3 (96.37 kJ/mol) and (iv) 3LiOH + N2 → Li3N + N(OH)3 (327.57 kJ/mol) need to be considered. Although that the available energy (≈ 430 kJ/mol) is much higher than each of these activation ∆*G*s, it doesn’t guarantee that all these reactions would occur altogether. As it can be seen, reaction *ii* has the lowest ∆*G* which means that it much favorably initiates and progresses at least *e*6 times faster than the other reactions as we have . Noting that reactions *ii* and *iii*, both consume LiH, a comparison of activation ∆*G*s shows equivalent reaction rate constants where reaction *ii* overwhelms reaction *iii*. Note that reaction *iii* indicates the potential production of NH3 by contacting moist lithium with N2 if required energy is provided which is highlighted elsewhere [[45](#_ENREF_45)]. This means that either no or negligible amount of NH3 and higher amount of hydrogen must be observed in products. This is actually true with reference to experimental observations where hydrogen gas is identified [[24](#_ENREF_24), [25](#_ENREF_25)]. Considering the aforementioned arrangements for moist pretreatment step (i.e., short exposure time = low moisture content), it can be concluded that reactions *ii* and *iii* are competing to consume a limited amount/source of lithium hydride. Thus, after a time, upon depletion of lithium hydride, the reaction would progress through reaction *i* as this reaction is fast and thermo-kinetically favorable rather than reaction *iv* to progress. This assumption can be verified by the fact that in experimental observations, N(OH)3 was not observed in products [[24](#_ENREF_24), [25](#_ENREF_25)]. Experimental analysis of products validates the presence of lithium nitride as solid product and hydrogen as system pressure changes [[24](#_ENREF_24)].

### The reaction of moist-pretreated Li with oxygen

For the analysis of oxygen reactivity with moist-pretreated lithium, the activation ∆*G*s for (i) 4Li + O2 → 2Li2O + Li2O2 (75.97 kJ/mol), (ii) 2LiH + O2 → 2LiOH (18.34 kJ/mol) and (iii) 4LiOH + O2 → 2Li2O2 + 2H2O (17.94 kJ/mol) need to be considered. The reactions *ii* and *iii* are anticipated to progress with approximately the same rate as their activation ∆*G*s are comparable. It seems that reaction *ii* provides the reactant for complete progress of reaction *iii* as it produces lithium hydroxide which can be consumed in reaction *iii*. It is anticipated that reaction *i* would also proceed but in lower scale (approx. *e*4 slower) in comparison with reactions *ii* and *iii*. In a reported experimental observation of such a reaction, the major product is Li2O2 although that Li2O is also observed [[24](#_ENREF_24), [25](#_ENREF_25)]. This practically means that reaction *iii* progress more than reaction *i* which are mainly responsible for production of Li2O2 and Li2O respectively. Thus, the calculated results in this study rationalize such observations.

### The reaction of moist-pretreated Li with carbon dioxide

For the analysis of carbon dioxide reactivity with moist-pretreated lithium, the activation ∆*G*s for (i) 10Li + 3CO2 → Li2CO3 + 3Li2O + Li2C2 (117.18 kJ/mol), (ii) 10LiH + 3CO2 → Li2CO3 + 3Li2O + Li2C2 + 5H2 (97.82 kJ/mol) and (iii) 2LiOH + CO2 → Li2CO3 + H2O (19.67 kJ/mol) need to be considered. The activation ∆*G*s show that reaction *iii* overwhelms other reactions as it has the lowest value and progresses as least *e*5.7 faster than the other two reactions. Noting to the fast rate of this reaction and acknowledging that the experimentally observed product of carbon dioxide reaction with lithium in the presence moisture is mainly Li2CO3, it can be concluded that the other two reactions would have no chance to proceed to a considerable extent. In lithium combustion studies, it was reported that when temperature is increased (higher than 180 ℃), Li2O and other products can be observed [[24](#_ENREF_24), [25](#_ENREF_25)]. This can be explained using the calculations reported here as higher temperatures provide higher thermal energies to overcome the activation ∆*G*s for reaction *i* and *ii*. However, high temperatures should be avoided to reduce the cost of heating for an adsorptive separation unit to operate provided that the reactant gases are received at low temperatures. Theoretically we concluded that a reaction involving carbon dioxide would produce Li2CO3 which can be verified according to experimental observations [[24](#_ENREF_24), [25](#_ENREF_25)].

### The reaction of moist-pretreated Li with methane

For the analysis of methane reactivity with moist-pretreated lithium, the activation ∆*G*s for (i) 2Li + 2CH4 → Li2C2 + 4H2 (105.76 kJ/mol), (ii) 2LiH + 2CH4 → Li2C2 + 5H2 (218.71 kJ/mol) and (iii) 2LiOH + 2CH4 → Li2C2 + 2H2O + 3H2 (213.93 kJ/mol) need to be considered. The activation ∆*G*s show that these reactions are highly energy demanding. Considering the activation ∆*G*s, it can be seen that the activation ∆*G*s for lithium hydroxide and lithium hydride are twice higher than that obtained for pure/dry lithium. This means that providing sufficient energy may cause the reaction between lithium and methane to occur even in dry conditions which will progress slowly however. The activation ∆*G* of methane is much higher than that of other gases which suggests that methane must undergo and involve in a highly intensive competition to find access to and react with substrate. This in turn means that we may anticipate practically negligible reaction for exposure of methane to moist-pretreated Li. Such a conclusion is verified using the TPC-MC calculations and the results are present and considered in next sections. This behavior is of importance as it implies that processing a gas mixture containing methane will keep methane untreated by adsorbent.

### The reaction of moist-pretreated Li with hydrogen

For the analysis of hydrogen reactivity with moist-pretreated lithium, the activation ∆*G* for (i) 2Li + H2 → 2LiH (53.93 kJ/mol), (ii) LiH + H2 → LiH + H2 (2.19 kJ/mol) and (iii) 2LiOH + H2 → LiOH + LiH + H2O (86.94 kJ/mol) need to be considered. The activation ∆*G* show that these reactions would occur and progress readily. The reaction *ii* is actually a proton transfer and doesn’t change the population of reactants/products. The major product of these reactions is lithium hydroxide which was observed in the experimental studies [[24](#_ENREF_24), [25](#_ENREF_25)]. This is actually because the generated LiH in reaction i will undergo a reaction with produced moisture in reaction iii and generates LiOH [[46](#_ENREF_46)] leading to higher content of LiOH in final product.

## Temperature Programmed Calculation-Monte Carlo results

As mentioned, we performed the TPC-MC calculations for two cases; (i) pretreated natural gas and (ii) binary N2/CH4 gas.

The considered pretreated natural gas mixture (*per 1 mol gas mixture*) contains 0.04 mole nitrogen, 3.22716×10-9 mole carbon dioxide, 1.61358×10-7 mole moisture and 0.95999983541 mole methane at ambient temperature (25 ℃) and pressure of 8 MPa [[7](#_ENREF_7)]. Using corresponding reactions data in the TPC-MC constructed network, calculations were performed at aforementioned operating conditions and the concentration curves are reported in Fig. 1 (left).

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|  |

Fig. 1. Computed concentration changes; (left) at T = 25 °C and P = 8 MPa for a pretreated natural gas mixture contains 0.04 mole nitrogen, 3.22716×10-9 mole carbon dioxide, 1.61358×10-7 mole moisture and 0.95999983541 mole methane, (right) binary mixture of methane and nitrogen containing 10 mol.% N2 at 35 °C and 101.325 kPa

The slight amount of moisture is consumed immediately. It can be seen readily that a pure methane stream will leave the reaction chamber while other gases are captured in the form of solid products. After 1 hour of operation, the separation completes. To achieve the simulation results and expectations in practice, we need to consider some factors in experiments. In TPC-kMC simulations all adsorbents are readily available to contact the gases, while in practice the external surface of adsorbent pile is available and following the occurrence of reactions, a layer will be formed on the external surface which reduces the accessibility of underlying adsorbents and acts as a mass transfer resistance. To resolve that, in experiments, it is needed that the adsorbent particles (i) grinded and powdered and (ii) the chamber be equipped with a mixer or stirrer.

For separation of N2/CH4 from binary mixture using moisture pretreated lithium, a TPC-MC calculations were performed and the results are shown in Fig. 1 (right). For this binary pair separation, methane would not compete with nitrogen as it can be readily seen that reaction kinetics are *kN2*/*kCH4* ≈ *e*16. In addition, as there’s no other gas present to compete with nitrogen to access moist-pretreated lithium, nitrogen reaction proceeds completely. This implies that an infinite selective separation of N2/CH4 can be achieved. It needs to be noted that the difference in these reaction kinetics is that such a behavior retains over ambient temperature range, so the infinite selectivity would still stand. However, an increase in temperature slightly increases reaction rates and shortens the separation time. A pure methane gas stream can be collected at gas outlet while nitrogen is transformed to solid lithium nitride. Using limited amount of substrate (less than the stoichiometric demanded amount), one may expect that at the end of process, the remaining solids must be mainly products. One of main usage of Li3N is ammonia production [[47](#_ENREF_47)] which finds wide applications in pharmaceutical and many commercial cleaning products. By exposing the product to extra moisture, lithium nitride reacts with moisture to produce lithium hydroxide and ammonia.

It is worthy to compare this perfect separation with reports in literature. It’s shown that carbon molecular sieve (CMS) membranes may reach moderate N2/CH4 selectivity of 7.7 barrers (1 barrer = 10–10 cm3(STP)·cm/(cm2·s·cmHg)), and suffer from low N2 permeability [[48](#_ENREF_48)]. SAPO-34 membranes for N2/CH4 separation showed separation selectivities up to 12 [[49](#_ENREF_49)] however they need challenging synthesizing procedure [[50](#_ENREF_50), [51](#_ENREF_51)]. Various type of metal-organic framework (MOFs) have been analyzed for CH4/N2 separation and exhibited high preference to CH4 over N2; however, the need of toxic and costly materials, long preparation time and harsh synthesis conditions are the main challenges for the use of MOFs [[14](#_ENREF_14), [15](#_ENREF_15)]. A review of various adsorbents for CH4 and N2 is compiled elsewhere [[7](#_ENREF_7)] (table 8 therein) which shows CH4/N2 equilibrium selectivity in most of adsorbents is limited to 5. For a coal mine methane (CMM) mixture sample (N2/CH4 = 30/70 mol.%), a hybrid process of membrane and hydrate formation units was proposed in literature [[52](#_ENREF_52)] which showed CH4 recovery of 46%. This process suffers from the use of secondary materials, i.e., cyclopentane as promoter for gas hydrate crystallization, unpractical operating conditions (283.4 K and at 2-3 MPa), and also common issues in membrane gas separation [[53](#_ENREF_53)] sub-unit. The state of the art technology for N2 removal from natural gas is cryogenic distillation [[7](#_ENREF_7)]. This process is highly energy intensive to achieve low temperatures [[7](#_ENREF_7)]. A CH4/N2 selectivity of about five was reported in literature [[54](#_ENREF_54)] which exceeds that of MFI and NaX zeolites which are traditionally used adsorbents [[55](#_ENREF_55)]. The superiority of proposed method for N2/CH4 separation is obvious.

## Evaluating the proposed method for other binary gas pairs

The performance of proposed separation process was examined for different binary gas pairs. Such pairs include CO2/N2, CO2/H2, CO2/CH4, H2/N2, H2/CH4, and O2/N2. As a rule of thumb, since reaction kinetics governs the share and progress of capture and removal of each gas in a considered pair, one may expect that for pair A/B, an almost perfect separation can be achieved when *kA* >> *kB* holds. Such comparison is summarized in Table 2 using the data of Table 1.

Table 2. Comparison of kinetic competition in A/B gas separation using moist lithium

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **∆*Gmin* =** | 2.19 | 13.42 | 18.14 | 19.67 | 105.76 |
|  | **∆*GB*/∆*GA* (*kA*/*kB*)** | | | | |
| **↓ A / B→** | **H2** | **N2** | **O2** | **CO2** | **CH4** |
| **H2** | - | 6.13 (*458.45*) | 8.28 (*3956.46*) | 8.98 (*7956.42*) | 48.29 (*9.4×1020*) |
| **N2** |  | - | 1.35 (*3.86*) | 1.47 (*4.33*) | 7.88 (*2645.92*) |
| **O2** |  |  | - | 1.08 (*2.95*) | 5.83 (*340.42*) |
| **CO2** |  |  |  | - | 5.38 (*216.31*) |
| **CH4** |  |  |  |  | - |

Based on the results, the bulk separation of gas streams containing methane and any of the studied gases is the readily achievable application of proposed separation process. In such conditions, methane will be collected at outlet unreacted as a pure gas. Extra amount of moist lithium should guarantee a pure methane stream at outlet as it provides the reactants for other gases to react and being captured. It is worthy to remind that the solid products, depending on other gases contained in the bulk gas stream, may contain lithium nitride, lithium carbonate, lithium oxide, lithium hydroxide, lithium hydride, lithium peroxide, etc. Such solid mixtures can be processed in many ways based on the characteristics of present products [[56](#_ENREF_56)]. For generality of discussion, we assume that all possible products are present. The possible lithium peroxide in the mixture can be converted to lithium carbonate by exposing the products to additional carbon dioxide which initiates the reaction 2Li2O2 + 2CO2 → 2Li2CO3 + O2 [[57](#_ENREF_57)]. This reaction is the working principal of air purifiers in spacecraft to produce oxygen [[58](#_ENREF_58)] and as it is a reversible reaction, it has been used to establish lithium–air batteries [[59](#_ENREF_59)]. This step would transform lithium peroxide to lithium carbonate and produces oxygen which can also consume any unreacted substrate if exits. In such a case, from results listed in Table 1 and also discussion of oxygen reactivity with the absorbent, it can be readily seen that lithium peroxide and lithium hydroxide would be generated where lithium peroxide undergoes the aforementioned reaction with carbon dioxide. The generated lithium hydroxide may also react with exposed carbon dioxide atmosphere to produce lithium carbonate and moisture [[60](#_ENREF_60)]. One may expect that this step longs for a while as the competition between carbon dioxide and oxygen to consume such unreacted substrate is equal according to the data shown in Table 1 and Table 2. A long exposure to carbon dioxide assures that lithium hydroxide and lithium peroxide would not be present in products anymore. At the same time, lithium oxide may also be converted to lithium carbonate provided that external heating is added to induce the corresponding reaction as Li2O + CO2 → Li2CO3 [[61](#_ENREF_61)]. Such a heating would be favorable as it removes the slight amount of moisture produced by these reactions. Thus, the remaining would be a solid mixture of lithium nitride and lithium carbonate. The charge transfer or difference between decomposition temperatures of lithium nitride (≈ 800 ℃) and lithium carbonate (≈ 1300 ℃) can be considered for nitrogen, carbon dioxide, and lithium recovery [[58](#_ENREF_58)]. Other routes may be explored as different characteristics may be considered for the processing purpose of obtained mixtures.

The gas pair separations of practical interest, i.e., CO2/N2, CO2/H2, CO2/CH4, H2/N2, H2/CH4, and O2/N2 are achievable. For CO2/N2 pair separation which is of interest in post-combustion gas processing at power plants [[62](#_ENREF_62)], the separation of N2 as solid Li3N, and CO2 as solid Li2CO3. As the reaction rate of nitrogen is much higher than that of carbon dioxide, it is expected that the amount of products produced follows the order Li3N > Li2CO3. For CO2/H2 pair separation, the separation of CO2 as solid Li2CO3 is achievable where hydrogen reaction acts as an enhancement on perfect progress of carbon dioxide reaction as it provides the required reactants and species. For CO2/CH4 pair separation which is of interest in CO2 separation from offshore natural gas [[63](#_ENREF_63)], the separation of the separation of CO2 as solid Li2CO3 is achievable. The outlet stream would be almost a pure CH4 gas. For H2/N2 pair separation, the separation of N2 as solid Li3N is achievable. Depending on the amount of nitrogen in feed stream, the products of hydrogen reaction with moist-pretreated Li would be used by reacting to nitrogen to produce more Li3N. For H2/CH4 pair separation, the separation of hydrogen in the form of LiOH and slight amount of LiH can be expected. However, we cannot consider it as an actual separation of hydrogen but due to the overwhelming reaction of hydrogen in comparison to methane, it can be assumed that methane will be remained unreacted. In this practice, the outlet stream would be pure methane while hydrogen is reacted and consumed by moist-pretreated Li. For O2/N2 pair separation, the separation of N2 as solid Li3N, O2 as solid Li2O and Li2O2 where the amount of products produced follows the order Li3N > Li2O > Li2O2 is achievable. These results shows that proposed system can be used for a wide range of separation practices.

# Conclusion

We proposed the use of moist-pretreated lithium as adsorbent for high performance reactive/adsorptive gas separation. The contribution of different mechanisms, including diffusion, sorption, adsorption, and reaction was investigated by modeling gases contacting with moist-pretreated lithium. Our results showed that sorption, adsorption, or diffusion does not play an important role and the contributions of all these three mechanisms in the process can be ignored. The reaction mechanism governs the reactive gas adsorption and separation. Reaction rates were determined to analyze the pace of reaction competitions in the process of separation of binary or multicomponent gas mixtures. It was shown that for N2/CH4 as well as other binary gas mixture containing methane, a pure methane gas stream can be obtained provided that slightly more than stoichiometric demanded moist-pretreated lithium is used. It is also demonstrated that a series of gas pairs, i.e., CO2/N2, CO2/H2, CO2/CH4, H2/N2, H2/CH4, and O2/N2, highly selective separations are achievable using our proposed Li reactive adsorbent.

# Appendixes

## Appendix A: Preliminary diffusivity/sorption simulation results

The share of diffusion and sorption of gases into the adsorbent microstructure need to be analyzed to determine its possible share in gas separation performance.

To determine diffusion/dispersion of gases (*D*) in crystal gaps (distance/window between two neighboring Li atom) and internal pores, the mean square displacement (MSD) data were calculated [[64](#_ENREF_64)]. MSD is related to *D* as  where *Nα* is the number of diffusive atoms in the system, angular bracket indicates that averaging must be performed over all choices of time origin within a dynamics trajectory and *ri* denotes the position vector of atom *α* [[65](#_ENREF_65)]. For each gas, we constructed cells containing 5 molecules of gas loaded into a supercell composed of 2×5×5 (thickness × width × length) repetition of unit cell of Li, LiH and LiOH. Unit cells are based on the data retrieved from Ref. [[66](#_ENREF_66)] and [[67](#_ENREF_67)] for Li (5 Li atoms per cell, corresponding to a total of 250 atoms in supercell), Ref. [[68](#_ENREF_68)] for LiH (6 Li atoms, 6 H atoms, corresponding to a total of 600 atoms in supercell) and Ref. [[69](#_ENREF_69)] for LiOH (10 Li atoms, 4 O atoms, 4 H atoms, corresponding to a total of 900 atoms in supercell). The supercells were relaxed using a geometry optimization and energy minimization step as mentioned in previous paragraphs. The relaxed structure then further relaxed for 75 fs by performing molecular dynamics (MD) calculations in NPT (constant number of molecules, pressure and temperature) ensemble followed by 75 fs MD calculations in NVE (constant number of molecules, volume and energy) ensemble using Forcite package [[39](#_ENREF_39)]. Then, the displacement of gas molecules was tracked and using aforementioned relationship was converted to *D*. For binary *A*/*B* gas pairs of interest, as well as the mixture of all considered gases, the same approach followed with this modification that cells contain 5 molecules of each gas. The results, averaged over studied operating condition, are shown in Fig. 2. Small diffusivity is obtained for all cells. The diffusivity of moisture and hydrogen is higher than that of oxygen, methane, carbon dioxide, and nitrogen. In Li, the diffusion of moisture and hydrogen inside the Li crystal may provide the chance to react with Li atoms located inside the crystal. Gases such as oxygen, methane, carbon dioxide, and nitrogen mostly would collide onto the Li crystal and then bounced back. Referring to the gases kinetic diameters [[70-72](#_ENREF_70)], it can be seen that oxygen (3.46 Å), methane (3.8 Å), carbon dioxide (3.30 Å) and nitrogen (3.64 Å), all have larger kinetic diameters than the displacement between two neighboring lithium atoms in lithium crystal structure (3.04 Å) [[66](#_ENREF_66)] (for hydrogen and water, kinetic diameter is 2.89 Å and 2.65 Å respectively). The relative dimension may imply that these compounds cannot penetrate into lithium crystal gaps in considerable quantity and therefore have lower share of lithium surfaces. On the other hand, hydrogen and water would be able to access interior surface of lithium crystal due to their small dimensions. It can be seen that diffusivity of gases in LiH and LiOH is much lower than that of Li which can be related to crystal structures following the same way used for explaining observation in Li. In LiH crystal, lithium and hydrogen atoms are packed much tighter than the Li crystal so that there’s no effective gap for gases to penetrate into. In LiH crystal, the displacement/gap in crystal is 2.04 Å [[68](#_ENREF_68)]. In LiOH also, the largest gap is 2.00 Å [[69](#_ENREF_69)]. Actually, low diffusivities would not have negative effect on the performance/outcome of proposed reaction-separation system where reactivity is the emphasized.

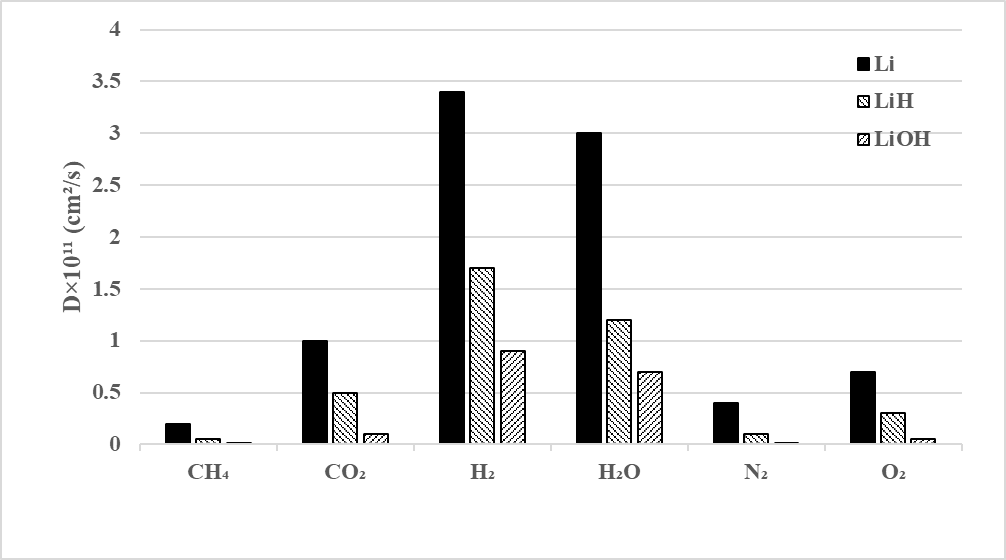


Fig. 2. Diffusivity data of gases in Li, LiH and LiOH; values are averaged over studied operating conditions

To investigate sorption/adsorption [[44](#_ENREF_44)], the configurational bias Monte Carlo technique [[73](#_ENREF_73)] was used according to a simulated annealing schedule [[74](#_ENREF_74)]. In this technique, candidate pairs are sampled from a canonical ensemble and each configuration *i* could have a probability  [[75](#_ENREF_75)] where *kB* is the Boltzmann constant (1.38064852×10-23 *J*/*K*) and *T* is the absolute temperature (Kelvin), *C* is an arbitrary constant and *Ei* is the total energy of configuration *i*. This total energy of configuration is given as a sum of (1) intermolecular energy between the adsorbent/adsorbate, (2) interaction energy between the adsorbent and adsorbate molecules, and (3) total intramolecular energy of the adsorbate/adsorbent molecules. The adsorption locator and sorption packages [[39](#_ENREF_39)] were used for calculations. The results are reported in Fig. 3. For sorption, calculations showed no effective presence of gases inside the crystals. It can be observed that hydrogen and water (moisture) are captured physically in small amounts. The sorption results are coherence with diffusivity calculations as the last is a requisite for the first one. The stability or trapping ability of lateral surface is shown in terms of the detachment energies (dEad/dNi) of gas compounds. This energy is the energy needed to remove one attached molecule from surface [[44](#_ENREF_44)]. This energy shows how strongly a molecule of one gas compound is attracted by crystal lateral surface which itself demonstrates how selectively and practically crystal surface may interact through its lateral surface with gas compounds [[76](#_ENREF_76)]. The detachment energy of water is considerably higher than other compounds demonstrating strong interaction of water and crystal surface which can be related to polarity of this molecule which lacks in the other molecules and also can be linked to the wettability of water for crystal surface [[77](#_ENREF_77)].

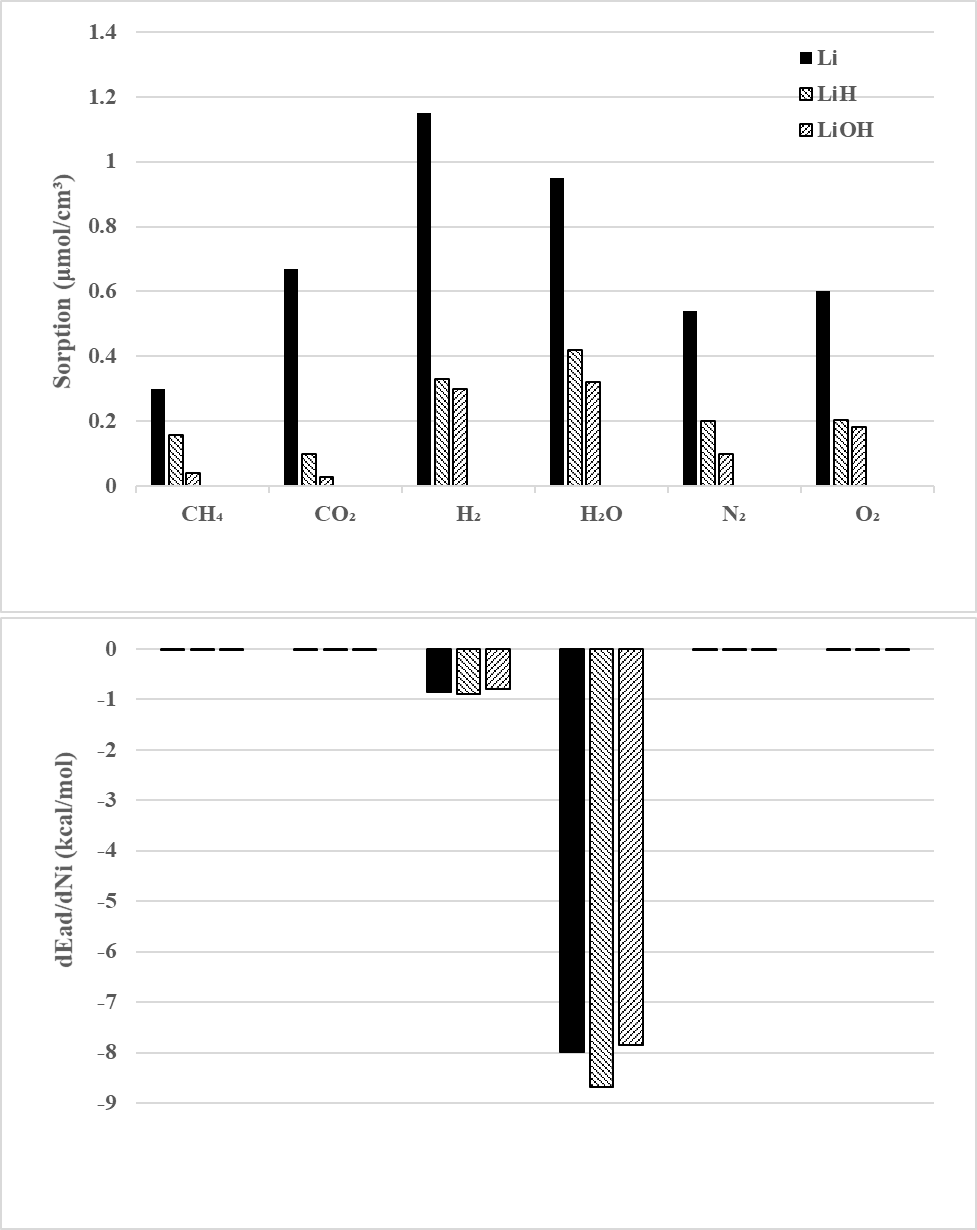


Fig. 3. Sorption results in Li, LiH and LiOH

**Declarations of interest**: none

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