Enabling high performance lithium-based reactive gas capture at ambient conditions by aid of low humidity contents

Milad Asgarpour Khansary 1†, Jin Shang 1‡, Gang Li 2‡, Aamir Hanif 1ǂ, Qinfen Gu 3§, Saeed Shirazian 4⸸

1 – School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong SAR

2 – Department of Chemical Engineering, The University of Melbourne, Melbourne, Victoria 3010, Australia

3 – The Australian Synchrotron, 800 Blackburn Rd, Clayton, VIC 3168, Australia

4 – Department of Chemical Sciences, Bernal Institute, University of Limerick, Limerick, Ireland

Emails: † [miladasgarpour@ut.ac.ir](mailto:miladasgarpour@ut.ac.ir); ‡ [jinshang@cityu.edu.hk](mailto:jinshang@cityu.edu.hk); ‡ [li.g@unimelb.edu.au](mailto:li.g@unimelb.edu.au); ǂ [aamirh@cityu.edu.hk](mailto:aamirh@cityu.edu.hk); §qinfen.gu@synchrotron.org.au; ⸸ [saeed.shirazian@ul.ie](mailto:saeed.shirazian@ul.ie)

**Abstract**

It is demonstrated that lithium favorably reacts with moist gases. If such reactions may happen at ambient and STP conditions, thus it can be implemented as a high energy-economy sustainable rout for greenhouse gas control and gas capture through a reactive process and transformation of gases into solid products. This potential implementation is addressed here using density functional theory based calculations of individual reactions and temperature programmed monte-carlo calculation of competitive reactions progress when mixtures of gases are of concern. The considered constituent gases include CH4, CO2, O2, N2, and H2 and gaseous mixture include greenhouse gas polluted air, raw and pretreated natural gas, biogas as well as post combustion flue stream. The effects of adding moisture content and initial concentration of gases are investigated to evaluate the gas capture performance . We found that the gas capture at ambient and STP conditions using the lithium aided by moisture is thermodynamically favorable and would progress spontaneously. The coupled simulations of mixed gases showed that for gas pairs with significant difference in reaction rates, a perfect separation can be achieved while the dominated gas can be collected as pure gas. The optimal moisture content was determined to be XX-XX, higher than which moisture starts to play as an energy sink and halts other reactions progress. The solid products can be processed to recover gases as well as lithium which reveals its sustainability. This provides a valuable highly efficient strategy to address greenhouse gas mediation and pollution control of industrial gaseous effluents.

**Keywords**: greenhouse gas; lithium; gas capture; reactive separation;

# Introduction

Addressing the global challenge of reducing gaseous pollutant emissions from industrial activities has been a focal point of environmental research [[1](#_ENREF_1)]. Abundance of gases emitted to atmosphere such as CO2 and CH4 that have greenhouse gas effect causes global warming, and thus their capture and removal is urgently demanded [[2](#_ENREF_2)]. Among different technologies developed for such purposes [[3](#_ENREF_3)], the adsorption-based technology has attracted increasing interest among industry and academia [[4](#_ENREF_4)] as it can potentially fulfill the requirements of industrial applications as it is cost-effective, efficient, and reliable [[5](#_ENREF_5)]. In adsorptive gas capture, gases are adsorbed physically and/or chemically [[6](#_ENREF_6)] where the physicochemical properties of adsorbent dominantly determine the capture/separation performance [[7](#_ENREF_7)]. A wide range of adsorbents have been investigated and examined for gas separation as reviewed elsewhere [[8-11](#_ENREF_8)]. Excitingly, thanks to the development of computational chemistry, the efficient design of adsorbent materials for task-specific applications is possible prior to any experimental attempt [[12](#_ENREF_12)]. This in turn reduces cost and resource use by experiments [[13](#_ENREF_13)].

Reviewing literature [[14-16](#_ENREF_14)], we noted that lithium reacts favorably with some moist gases such as CO2, O2, N2, and H2. It’s reported that the exposure of moisture enhances the reactions significantly [[15](#_ENREF_15)]. In other words, the occurrence of these reactions strongly depends on the presence and content of moisture [[17](#_ENREF_17)]. The reaction between lithium and water is a fast exothermic facilitated water dissociation with a small energy barrier (2.715 kJ/mol) over a temperature range of 25-100 ℃ [[18](#_ENREF_18)]. This reaction occurs spontaneously and favorably since the low energy barrier can be easily overcome (the scaling factor for energy in molecular-scale systems corresponds to ≈1 kJ/mol over the specified temperature range [[19](#_ENREF_19)]). This reaction releases a substantial amount of energy , i.e. ≈ 430 kJ/mol. We hypothesized that upon contacting lithium to moist gases, this released energy would be available and sufficient to loosen the bonds so as to surpass the energy barrier of further reactions even at ambient conditions [[16](#_ENREF_16)]. This means that if the activation free energies of lithium-gas reactions are lower than the aforementioned energy release, those reactions can be enabled autonomously.

These observations indicate that exposure of lithium to gas in presence of moisture can be introduced as a gas capture technique to address greenhouse gas emissions, such as gas capture from air, natural gas, biogas as well as post combustion flue gas streams. To address such a potential, an inevitable and essential step is the determination of optimal moisture content due to multi-fold role of moisture. At high contents, moisture starts to play as an energy sink and therefore halts other reactions progress. As a side, required energy to maintain progress of reactions autonomous is supplied by the energy release upon the water dissociation on lithium (if there’s no external heating) which itself strongly related to moisture content [[17](#_ENREF_17), [18](#_ENREF_18)]. Thus, to verify feasibility of proposed method, the processable gaseous mixtures and the moisture content need to be addressed and optimized to guarantee high efficiency. This verification was performed via density functional theory (DFT) based calculations and a modified temperature programmed calculation kinetic Monte-Carlo method (TPC-kMC) as illustrated in following sections.

# Theoretical section

## Methods

To track the amount of captured gases, the reactivity data including reaction rates are needed. The reaction rates can be determined using transition state theory of chemical reactions [[20-22](#_ENREF_20)]. Based on this theory, reaction rate constant can be calcutaed using , 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 [[23-25](#_ENREF_23)]. [22](#_ENREF_22" \o "Manthe, 2011 #1011) [22](#_ENREF_22" \o "Manthe, 2011 #1011)These calculations have been carried out using a vibrational analysis of first principles calculations [[27](#_ENREF_27)] as implemented in the DMol3 package [[28](#_ENREF_28)] and reported in a recent contribution [[16](#_ENREF_16)]. Having these reactivity data available, the next step is the construction of reaction network in TPC-kMC method [[29](#_ENREF_29)] which is used to predict the progress of gas capture from gaseous mixtures. [[30](#_ENREF_30)][[31](#_ENREF_31), [32](#_ENREF_32)][[33](#_ENREF_33)]TPC-kMC is a discrete event simulation implemented in the Kinetix package [[28](#_ENREF_28)] 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 gas mixture is of interest. TPC-kMC grants the occurrence possibility/probability to all introduced events/reactions and then examines the progress and evolution of events/reactions as a competition. TPC-kMC calculations initially require to construct (i) the events/reactions network and (ii) the substrate structure. For the present work, the constructed process network includes all possible reactions (25 overall reactions where for each reaction, individual reactant consumption and product production rates comprise an individual sub-process) with corresponding reaction rate constants. For TPC-kMC calculations for each gas capture case study, the corresponding sub-processes in process network are activated only.

For substrate structure, we used a grid of 2048×2048 sites (= total gird points of 4,194,304) where each site accommodates one particle. It shows the simplicity and efficiency of TPC-kMC that enables the analysis of such a large system of particles. Conventionally the grid sites are all assigned as voids [[29](#_ENREF_29)]. To investigate the effects of gas concentrations as well as to determine the optimal moisture content of the gas stream and even the adsorbent size/amount, we introduced an artificial allocation step to fill and load desirable initial quantity of particles in substrate grid to reflect the mixture of under study as illustrated in following paragraphs.

The initially generated grid of 2048×2048 sites is divided into three main populations, i.e., (i) adsorbent particles, (ii) gas molecules particles, and (iii) extra empty space (void) particles. Note that we used “population” instead of “zone” or etc. as in labeling/assignment of particles to compounds, the amount of particles can be controlled, but the orientation/location of particle on the grid is selected randomly. Population *iii* is considered to account for controlling mass continuity due to different stoichiometric coefficients of different reactants/products in reactions. It comprises 5% of total initial grid corresponding to *Niii*=209,715 particles. Population *ii* enables us to include different initial concentration of gases/reactants as well as moisture where the ratio of “*particles assigned to a gas/reactant/moisture to total particles available in the population*” reflects the mole fraction of that gas/reactant/moisture in the mixture initial composition. This population is composed of 70% of total initial grid corresponding to *Nii*= 2,936,012 particles. The number of particles assigned to each compound depends on the case study of concern, i.e., gas capture from air, raw and pretreated natural gas, biogas as well as post combustion flue gas streams. Population *i* enables us to account for the effect of adsorbent size (quantity) which can be reflected into the simulations by varying the number of particles assigned to adsorbent. A total of 25% of total initial grid is assigned to this population corresponding to *Ni*=1,048,576 particles, which itself reflects the highest amount of adsorbent we can consider by this allocation. For smaller amount of adsorbent, we partially fill sites in this population.

To allocate each population with the corresponding composing compound, in particular population *i* and *ii*, we defined artificial allocation events/reactions as “\* → *c*”, where \* stands for void in the initial grid and *c* stands for loaded particle which can be gas, moisture or lithium depending on the population of interest. For this artificial allocation reaction, the run time of TPC-kMC is arbitrary as it’s not a real reaction and the number of loaded particles *pi* over time *t* can be related to the corresponding artificial rate (*ki*) as *pi*=*ki*×*t*. For population *ii*, *pi* can be determined for each composing compound of gas as *pi*= *Nii*×*xi*, where *xi* is the given mole fraction of each compound and *Nii*=2,936,012 reflects the total number of particles that can be accommodated in this population. For population *i*, i.e., adsorbent, the same relationship can be used to related the number of loaded particles to the corresponding rate constant as used in population *ii*. In this population, the number of loaded adsorbent particles (*pi*) reflects the size of adsorbent included in simulation as *pi*= *Ni*×*xF* where *xF* is the percentage of zone *ii* filled and implies the size of adsorbent when *xF*=1 is the largest adsorbent size that can be considered which accommodates *Ni*=1,048,576 particles. The loaded grid is then used as initial configuration in TPC-kMC simulations. considered datasetrelated reactions

## Datasets

The gas capture concerning single gases as well as mixed gases are considered as listed in Table 1. The single constitute gases include CO2, O2, N2, and H2. The gas capture concerning mixed gases include raw and pre-treated natural gas, post combustion flue gas, biogas as well as greenhouse gas polluted air. For single and mixture gas datasets, addition of up to 25 % mole fraction of moisture (corresponding to a relative humidity (*RH*) of ≈ 80 % as *RH* (%) = 3.1995 × *x* (%) - 8×10-5) in gas mixture is analyzed. The mixed gases can reflect the processable gas concentrations by this capturing method. Available single gas studies addressing lithium reaction and selected gases in presence of moisture are noted here to verify simulation results [[14](#_ENREF_14)]. However, there’s no experimental data available for mixture gas simulations to be compared to.

Table 1. Considered single and mixture gas data

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample type** | **Condition** | **Sample code** | **Components mole fraction (%)** | | | | | |
|  |  |  | **CH4** | **N2** | **CO2** | **O2** | **H2** | **H2O** 3 |
| Single gas | STP | CH4 | 100 | - | - | - | - | - |
| N2 | - | 100 | - | - | - | - |
| CO2 | - | - | 100 | - | - | - |
| O2 | - | - | - | 100 | - | - |
| H2 | - | - | - | - | 100 |  |
|  |  |  |  |  |  |  |  |  |
| Natural gas1 | STP | RG-1 [[34](#_ENREF_34)] | 97.495 (*85.898*) 2 | 1.007 | 1.498 | - | - | - |
| GU-1 [[34](#_ENREF_34)] | 85.431 (*81.299*) 2 | 13.575 | 0.994 | - | - | - |
| GU-2 [[34](#_ENREF_34)] | 86.705 (*81.203*) 2 | 5.703 | 7.592 | - | - | - |
| NIST-1 [[34](#_ENREF_34)] | 99.142 (*96.58*) 2 | 0.269 | 0.589 | - | - | - |
| NIST-2 [[34](#_ENREF_34)] | 96.4 (*90.644*) 2 | 3.134 | 0.466 | - | - | - |
|  |  |  |  |  |  |  |  |  |
| Pretreated natural gas | T = 25 ℃, P = 8 MPa | PNG-1 [[35](#_ENREF_35)] | 95.999983541 | 4 | 3.22716×10-7 | - | - | 1.61358×10-5 |
|  |  |  |  |  |  |  |  |  |
| Post combustion | STP | PCG-1 [[36](#_ENREF_36)] | - | 85 | 15 | - | - | - |
|  |  |  |  |  |  |  |  |  |
| Biogas | STP | BG-1 [[37](#_ENREF_37)] | 50 | - | 50 | - | - | - |
|  |  |  |  |  |  |  |  |  |
| Atmospheric air | STP | AAG-1 [[38](#_ENREF_38)] | (-)4 | (78.084)4 | (360ppm)4 | (20.946)4 | (0.5ppm)4 | (-)4 |
|  |  |  |  |  |  |  |  |  |
| **Notes:**  1 – natural gas contains a number of hydrocarbons heavier than methane, however, due to absence of reactivity data of such compounds, methane is considered as the sole present hydrocarbon.  2 – numbers in parenthesis show the composition of methane without note # 1.  3 – the water content in gas mixture itself, prior to addition of any moisture.  4 – dry unpolluted atmospheric air composition retrieved from ref. [[38](#_ENREF_38)], due to absence of reactivity data of other compounds, those are ignored and not reported. | | | | | | | | |

# Results and discussion

## Summary of reactivity data

In Table 2, the minimum activation *∆G*s for the individual gas reactions with lithium in presence of moisture are listed with a comparison of their relative magnitude as well as the corresponding rate constant ratios. Noting to the released energy due to the fast and immediate reaction of water and lithium (≈ 430 kJ/mol) [[18](#_ENREF_18)], it is evident why the presence of water enables the reaction of lithium with gases as obverted in literature [[14](#_ENREF_14), [15](#_ENREF_15)]. In fact, this released energy is sufficient to overcome the energy barrier and then such reactions occur in moist environment. However, as high contents of moisture plays as a heat/energy sink, the use of low moisture contents is advised [[16-18](#_ENREF_16)].

Table 2. Comparison of kinetic competition in A/B gas separation using moist lithium [[16](#_ENREF_16)]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **∆*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** |  |  |  |  | - |

The data listed in Table 2 also can be used for a preliminary examination of the capture/separation from binary gas mixtures as well as binary gas pair separation and purification applications. Such pairs include CO2/N2, CO2/H2, CO2/CH4, H2/N2, H2/CH4, and O2/N2. Based on the results, it can be concluded that as a rule of thumb, since reaction kinetics govern the share and progress of capture and removal of each gas in considered pair, one may expect that for pair A/B, almost perfect separation can be achieved when *kA* >> *kB* holds. For instance, the bulk purification of gas streams containing methane and any of the studied gases is the most achievable application as methane reactions overwhelmed by others. In such conditions, methane will be collected at outlet as a pure gas. As the activation ∆*G* of methane is much higher than that of other gases, it 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 lithium in moist environment when other gases are present. This behavior is of importance as it implies that processing a gas mixture containing methane will keep methane ends up to pure methane stream while others are transformed to corresponding lithium containing solid products.

The captured gases in form of reactions products (solid mixtures) can be processed in many ways based on the characteristics of present products [[16](#_ENREF_16), [39](#_ENREF_39)]. For instance, exposing lithium to CO2 greenhouse gas polluted air, the lithium peroxide is produced due to oxygen reaction with lithium. This lithium peroxide can initiate a reaction with CO2 gas and produce lithium carbonate as 2Li2O2 + 2CO2 → 2Li2CO3 + O2 [[40](#_ENREF_40)]. This reaction is the working principal of air purifiers in spacecraft to produce oxygen [[41](#_ENREF_41)] and as it is a reversible reaction, it also has been used to establish lithium–air batteries [[42](#_ENREF_42)]. Lithium carbonate has applications in the processing of metal oxides and also treatment of bipolar disorder [[43](#_ENREF_43)]. 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 [[41](#_ENREF_41)].

## Gas capture analyses

For single and mixture gas case studies, only the single gas calculations could be verified by the available literature [[14](#_ENREF_14), [15](#_ENREF_15)]. It needs to be noted that no experimental is data available for mixture gas simulations to be compared to, which is due to the fact that the proposed application of lithium as reactive gas capture material is new.

### Single gas capture

### Mixture gas capture

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# Conclusion

The potential use of lithium for reactive gas capture and storage over ambient temperature range by the aid of low moisture contents is examined. A modified temperature programmed kinetic monte-carlo method developed and used utilizing density functional theory based determined reactivity data. Parameters such as gas concentrations, adsorbent amount/size and moisture content were examined. It is shown that lithium reaction with gases in a moist environment provides an energy-economy sustainable rout to address the greenhouse gas control practices and air pollution challenges as well as gas storage from industrial gas production and explorations units. In addition, this proposal suggests that gas separation and purification can be achievable with significant recovery and selectivity for gas pairs when the reaction kinetics of the two pairs is highly comparable such as binaries containing methane.

**Supporting Information**

The constructed library in Dassault Systemes Materials Studio can be accessed using following link <https://sites.google.com/site/miladasgarpour>/resource.

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Reviewing the literature [[14](#_ENREF_14)], it was concluded that for different gases, lithium reactivity with moist gases is highest at low moisture content and decreases as moisture content increases.

It can be seen that the water concentration decreases as the process proceeds due to the small activation ∆*G* of reaction between Li and H2O which enables it to immediately produce LiOH, LiH, and gaseous hydrogen [[14](#_ENREF_14)]. No significant change in the concentration of methane was observed, which can be related to the high activation ∆*G* requirements and/or relatively lower activation ∆*G* of other species. This is highly desirable for the separation-view of the present work. Considering products, lithium carbonate (Li2CO3) and lithium nitride (Li3N) are major products from which carbon dioxide and nitrogen can be retrieved either by heating to decompose or charge transfer [[41](#_ENREF_41)]. Variations in the concentrations of lithium hydrate (LiH) and lithium hydroxide (LiOH) were observed, which is related to their contribution in different reactions and the progress of reactions. Other products are of minor quantity including lithium oxide (Li2O) and lithium peroxide (Li2O2).

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