

Screening Materials Relevant for Energy Technologies

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Abstract: In this short review, some recent advances are discussed in the development of computational techniques to perform large-scale screening of materials for energy-related applications. We focus on carbon capture and methane storage in different classes of nanoporous materials. We show how these screening studies can identify whether economic targets for particular processes can be reached.

Keywords: Carbon capture · Materials genome · Methane storage · Metal–organic frameworks (MOF) · Nanoporous materials

Introduction

Reducing the anthropogenic CO₂ emissions in a world that continues to increase its energy consumption is one of the most important challenges of our times.^[1,2] A long-term solution requires us to transition from fossil fuels towards a sustainable and renewable energy production. A key question is how much CO₂ will be emitted before we have reached this solution. Carbon Capture Utilization and Storage (CCUS) is one of the few, if not only, viable technologies that allows us to mitigate the CO₂ emission while we are still dependent on fossil fuels for our energy consumption.^[3]

The idea of CCUS is to separate the CO₂ from flue gases emitted by power or industrial plants and subsequently compress and store the CO₂ in geological formations.^[4] Transporting CO₂ over large distances and injecting CO₂ in geological formations is not a new idea. The oil industry has been injecting CO₂ in fields

for many years to enhance oil recovery.^[1] However, as the transportation and injection of CO₂ is an expensive operation, all the efforts have been in minimizing the CO₂ used in this process. Most of the CO₂ comes from geological formations, and special pipelines have been constructed to transport the CO₂ from these formations to the oil fields.

Since CO₂ is used in several industrial applications, one could argue that a preferential route is to convert CO₂ into useful chemicals rather than storing it. In this, one has to realize that we are producing much more CO₂ than we can possibly use. For example, 5–10 power plants are sufficient to provide all the CO₂ that is currently used.^[5] Also converting CO₂ into useful products will saturate any market as we do not use any chemical on the scale that we are producing CO₂. So for reducing CO₂ emissions it is essential to store the CO₂ where we have space.

At present, most fossil fuels (85%) are used for energy; the rest is used by the chemical industry as a source of carbon.^[3] Hence, part of the long-term solution would be to replace this source of carbon by CO₂. Therefore, developing the chemistry to capture, store and utilize CO₂ will not only be important in the short term to limit CO₂ emissions during a transition towards a sustainable energy solution, but will also be an important component to provide a sustainable source of carbon for the chemical industry.

At present, the technology exists to capture CO₂ from power plants^[6] or even directly from air.^[7,8] The main bottleneck is, however, the costs of the process.^[4,9] Capturing carbon from a power plant and the compression for the geological storage requires significant amounts of energy and therefore reduces the efficiency of a power plant by as much as 30–40%. Therefore, a considerable amount of research is focused

on reducing the costs of carbon capture. One of the promising routes is to capture CO₂ using solid adsorbents. A key research question is how the ideal material should look like to capture CO₂ as efficiently as possible. In this context, the research on Metal Organic Frameworks (MOFs) is very promising.^[10,11] MOFs are nanoporous crystalline materials consisting of organic linkers connected *via* metal centers. As we can change the linker as well as the metal, we can synthesize millions of possible materials. This makes MOFs and related materials ideal to systematically investigate which linker metal combination and what pore topology gives us the best material to capture carbon. Carbon capture is not the only application of this material; one can also envision other gas separations, storage of gases, or, with appropriate metal sites, even catalysis.^[12]

From a computational point of view, these materials give many interesting opportunities. First of all, as the materials are crystalline, the experimental crystal structure gives us an excellent starting point for computational study. Secondly, as there are many experimental studies published about these materials, there is a large amount of experimental data to compare with. Moreover, among these experimental data there are several cases in which our understanding is very limited and computational studies can help. Finally, experimentally it takes 2–6 weeks to synthesize and fully test a material for a given application. Therefore, one can only test a small fraction of all possible materials. As we will show in this short review, computational studies can help to identify the most promising materials by screening a very large number of possible materials before they have been synthesized.

This computational approach has three components. First, we need to generate databases of hypothetical materials.

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Next, we need to ensure that we predict the properties of these materials sufficiently reliably. Finally, we have to screen the databases to find the optimally performing material.

Advanced Nanoporous Materials

An exciting feature of these novel advanced nanoporous materials is their chemical and geometrical tuneability. For example, for materials like metal-organic frameworks (MOFs)^[13–15] or porous polymer networks (PPNs),^[16] millions of different materials can be envisioned by combining different molecular building blocks (Fig. 1). In practice, we can only make and test a small set of all possible materials. Computational research focuses on developing computational tools that allow us to explore this vast space of materials and identify those that are optimal for a given application.^[17,18]

The computational approach starts with generating a large number of hypothetical materials. To ensure that these materials can potentially be synthesized, the starting point is usually the chemistry that is involved in the known materials. The computational approaches that have been used by the various groups can be very different. First, it is important to realize that as the number of combinations of building blocks is nearly infinite, it is impossible to enumerate all possible structures. Therefore, the aim is to ensure that a representative set of materials is being generated. Wilmer *et al.*^[19] compiled a set of metal units and bridging organic linkers known from experimental MOF structures. Novel structures were generated by linker functionalization and by combining these building blocks. In this way Wilmer *et al.* generated over 130,000 hypothetical MOF structures. Martin *et al.*^[20] used as a starting point a database of commercially available molecules and identified those molecules that could be used as a linker. Martin *et al.*^[20] further used this strategy to generate analogues of MOF-5 structures and hypothetical PPN materials.^[21] Deem and coworkers^[22,23] generated hypothetical zeolite structures by enumerating different zeolite topologies. Since ZIFs are a class of MOFs that have the same pore topologies as zeolites, Lin *et al.*^[24] used Deem's zeolite database to generate a corresponding ZIF database through chemical substitution. In Fig. 2, examples of the different materials are shown.

In addition to these hypothetical materials, databases have also been compiled for materials that have already been synthesized. For most of these materials the crystal structure is deposited in the Cambridge Structural Database.^[25] However, quite a

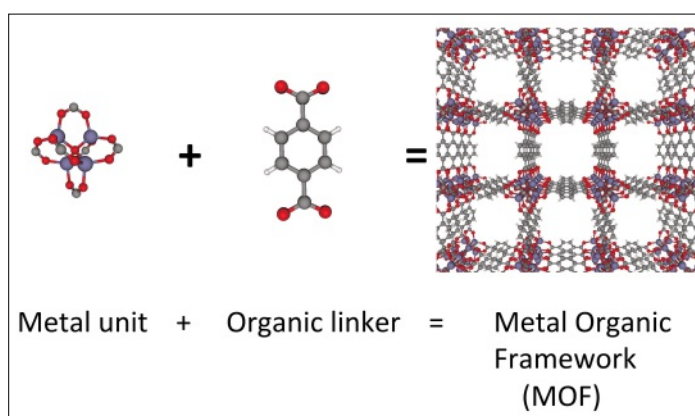


Fig. 1. By combining different molecular building blocks, we can obtain a very large number of different materials. For example, metal units are combined with organic linkers to form a metal-organic framework (MOF). Figure by Cory Simon.

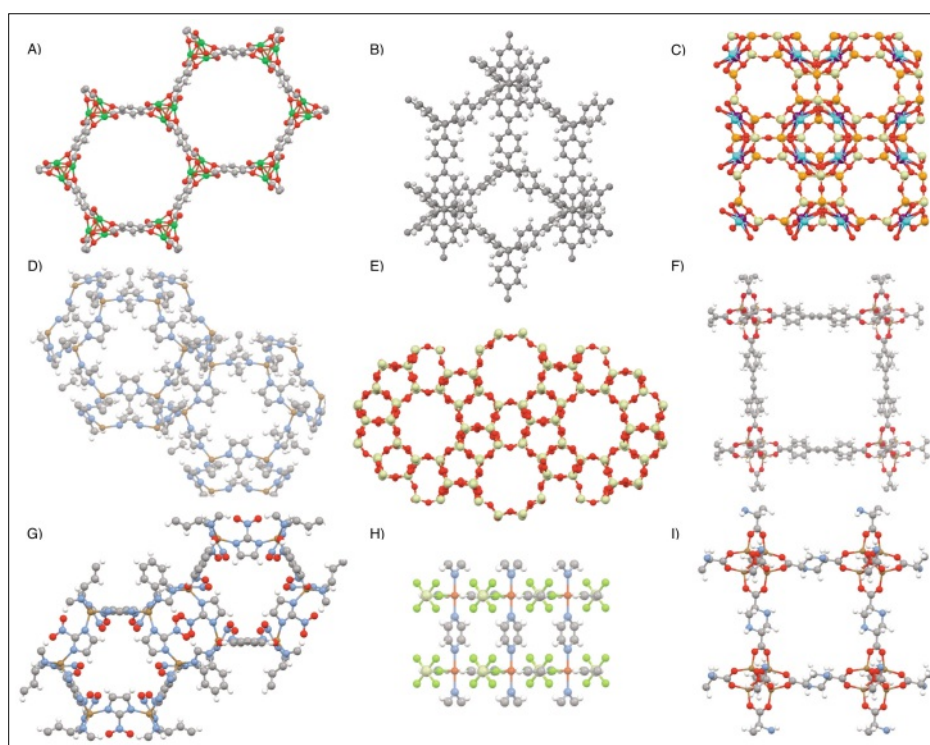


Fig. 2. Representative selection of structures for the different classes of material: (A) Mg-MOF-74, (B) PPN-6, (C) CaA, (D) ZIF-8, (E) MFI, (F) HMOF-2368, (G) ZIF-78, (H) SIFSIX-3-Cu, and (I) HMOF-992. Atoms and bonds are illustrated as ball and sticks. Color-code for the atoms: red: oxygen, light yellow: silicon, grey: carbon, white: hydrogen, blue: nitrogen, green: magnesium, brown: zinc, orange: aluminium, cyan: calcium, purple: sodium, yellow: fluorine, rust-color: copper. Figure by Johanna Huck.

number of these structures contain solvent molecules and other impurities, which makes it difficult to compare the properties of these structures with those of the hypothetical structures. To make such a comparison possible, computational methods have been developed to automatically remove these impurities from these structures.^[26]

Predicting Adsorption Properties

If we know the crystal structure of the material, we can use molecular simulation techniques to predict the behavior of adsorbed molecules in the pores of these materials. Adsorption isotherms are obtained from grand-canonical Monte Carlo simula-

tions and transport properties usually from molecular dynamics.^[27] Both methods assume that we know the interactions of the atoms of the adsorbed molecules with the atoms of the nanoporous materials.

The development of force fields that describe these interactions is an important field of research in which significant progress has been made.^[28–30] Fig. 3 shows some typical examples of adsorption isotherms that have been computed with these force fields for different gasses in materials for which experimental data is available. Comparison shows that for most materials we obtain a very reasonable agreement with experimental data. As hypothetical materials involve the same atoms as materials for which we could compare our simulations with experiments, but with

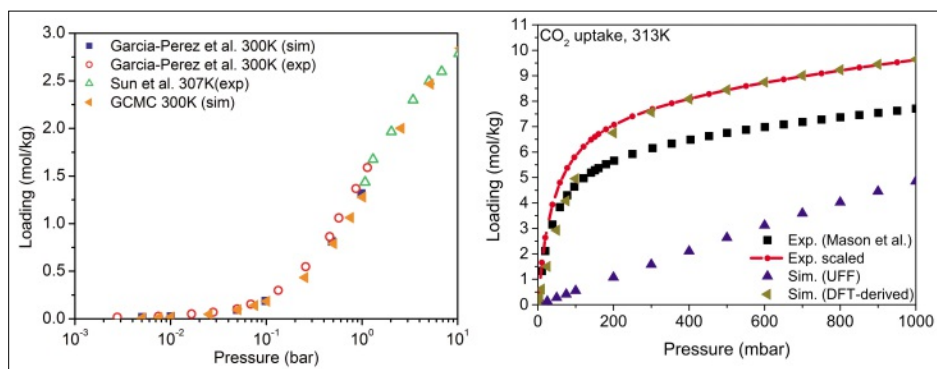


Fig. 3. Comparison of some experimental isotherms with the results of molecular simulations. The left figure gives the isotherm of CO₂ in the zeolite silicalite and the right figure CO₂ in the MOF Mg-MOF-74, Figures by Li-Chiang Lin based on data from refs. [24] and [29].

different crystal structures, we can use the same force fields and simulation methods to predict the thermodynamic properties with some confidence.

As the number of materials for which we need to compute adsorption properties can be large, it is important to use efficient simulation techniques. For this we have developed special algorithms that use graphic processor units (GPU).^[31,32] These GPU differ from the conventional CPU as they are very fast, but have a limited memory and instruction set, which requires changes in the algorithm. If one is able to use GPUs optimally the speed-up can be two orders of magnitude, which reduces the time for the calculation of an isotherm from two days on a CPU to a few minutes on a GPU.

Examples of Large-scale Screening

To illustrate how we can use these libraries to address some practical questions, we discuss two applications: nanoporous materials for carbon capture and methane storage.

An important step in the screening of materials is to develop a metric to rank the different materials. From a practical point of view the most important criteria is often costs; the material that allows us to capture CO₂ from flue gasses and sequester CO₂ in geological formations with the least costs will most likely be the material of choice. However, at an early stage of research it is difficult to include costs. Costs are, of course, important if we were to build a new carbon capture plant tomorrow; this would require us to compare the current price of, say, the amine solutions, which are commodity chemicals, used in the current technologies with the costs of a novel metal-organic framework, which is only synthesized on a laboratory scale. And in this comparison the price of MOFs will be astronomically high. However, if MOFs were to be used on the same scale

as amine solutions, the economy of scale would drive the price down significantly unless we are using metals that are very rare.^[33] Irrespective of the cost of the chemical, one also needs to ensure that the costs associated with the CCS process are minimized. A convenient way to express this is to use the parasitic energy, which is defined as the loss of electricity caused by the addition of the CCS process to an existing power plant.^[24,34] The best material minimizes these losses.

A simple CCS process using solid adsorbents has two steps: in the first step, CO₂ is selectively adsorbed and, when the material is saturated, it needs to be regenerated. The captured CO₂ is subsequently compressed for geological storage. The energy required for this process has three components: (1) energy to heat the material, (2) energy to supply the heat of desorption (equal to the heat of adsorption), and (3) energy required to pressurize CO₂

to 150 bar, which is a standard requirement for transport and storage. We then assume that the energy for this process is taken directly from the power plant. Steam to heat the material and electricity for the compression. As this energy cannot be used for generating electricity, the efficiency of the power plant will decrease. This loss is defined as the parasitic energy and for every material we optimize the operating conditions to minimize this parasitic energy. This minimum parasitic energy for a given material is then used as a metric to compare different materials.

Fig. 4 shows the results of a screening study for zeolites and ZIFs.^[24,34] This study shows that materials can be synthesized that significantly reduce the parasitic energy compared to the conventional, amine-based technology. It is also interesting to investigate what makes a material optimal for carbon capture. Lin *et al.*^[24] showed that it is important to have a material that has a reasonable selectivity with respect to N₂. In addition, the material has to have an optimal binding energy for CO₂; not too weak to ensure that the material will adsorb CO₂ at the pressure of interest, but not too strong otherwise the regeneration step will require too much energy. The best material has the highest density of these optimal adsorption sites.

These nanoporous materials are not only of interest for carbon capture. Another potential application for these nanoporous materials is methane storage for vehicles. The recent increase in the supply of natural gas has initiated research to investigate whether methane can replace gasoline in cars.^[35] As methane has a much lower energy density, we have to compress (com-

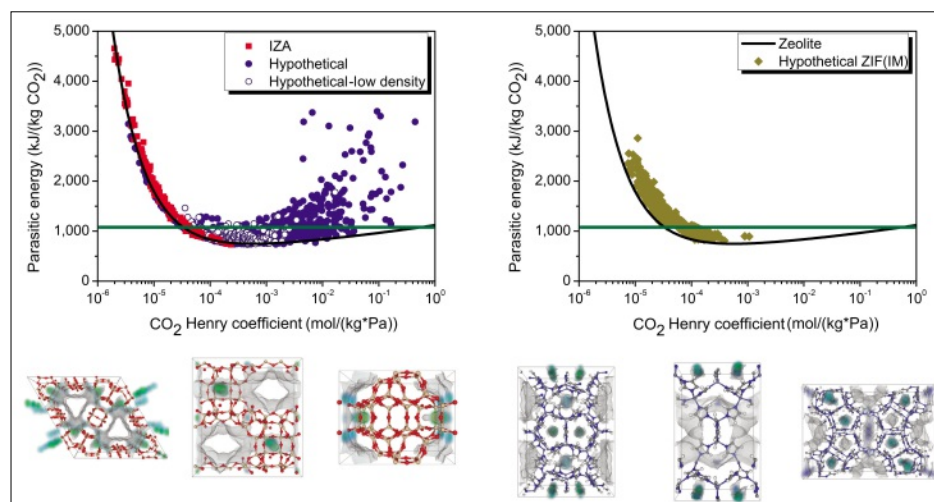


Fig. 4. Parasitic energy as a function of the Henry coefficient of CO₂ for all silica zeolite structures (left) and ZIFs (right). In the left top figure we compare the IZA zeolite structures (red squares) with the predicted zeolite structures (blue circles). The green line gives the parasitic energy of the monoethanolamine (MEA) technology, which is the current standard. The black line is the minimal parasitic energy observed for a given value of the Henry coefficient in the all-silica structures. The bottom figure shows some examples of the top performing structures. Figure reproduced with permission from Lin *et al.*, ref. [24].

pressed natural gas or CNG) or liquefy (liquefied natural gas or LNG) methane to arrive at an energy density that is comparable to gasoline. Liquefied natural gas (LNG) involves, however, an energy-intensive process of cooling methane to a liquid. This cooling requires expensive liquefaction equipment. Also, the cryogenic fuel tanks required to store LNG in a vehicle are bulky and expensive. Compressed natural gas (CNG) involves compression to approximately 250 bar, which requires costly compressors at refilling stations. Also, to withstand these large pressures, CNG fuel tanks must be cylindrical or spherical to evenly distribute stress and as a result these tanks will occupy a relatively large space in the vehicle.^[36]

An alternative approach is to fill the tank with nanoporous materials.^[37] Because of the interactions of methane with the walls, methane will adsorb with a higher density in the pores of these materials. The idea is to use the chemical tuneability of these materials to achieve an energy density similar to CNG, but at such a lower storage pressure that we can use thinner-walled fuel tanks, which, like the gasoline tanks can be placed more conveniently in a vehicle. Further, the compressors to achieve this more moderate pressure in adsorbed natural gas technology are cheaper than those required for CNG, making for cheaper refill stations and possibly enabling at-home refueling.

The Advanced Research Projects Agency-Energy (ARPA-E) of the US Department of Energy has set a research target: one volume of adsorbent material should deliver 315 volumes of methane at STP (standard temperature and pressure) to the engine using a storage pressure of 65 bar at ambient temperature. This represents a slightly higher energy density than CNG, to compensate for packing losses, as a tank cannot be perfectly packed with a

single crystal. To account for these packing losses, the target energy density is set to 125% of energy density of CNG.

Fig. 5 shows the result of a screening to see whether different nanoporous materials can meet the ARPA-E target.^[38] The figure shows the deliverable capacity as a function of the density of the material. If the density of the material is low, we do not have any adsorption sites for methane. If the density of the material is high, the pore volume is so small that only a few methane molecules will adsorb. If we look at the optimal density, we see that we can reach an energy density of 70% of the ARPA-E target but, unfortunately, none of the materials reach the ARPA-E target. So the result of this screening study is that we most likely won't find a material based on the current chemistry that reaches this target.

Outlook

The idea of screening large databases for different applications is part of what has become known as the Materials Genome Initiative. This initiative comes from the White House as an effort to reduce the development time from research to practical applications.^[17,39] The name Materials Genome reflects a similarity with biology where combining different amino acids leads to a nearly infinite number of proteins; a combination of building blocks gives a infinite number of possible materials. However, to fully explore the potential of all possible materials, we simply lack the resources. It is in practice impossible to screen all possible materials experimentally and in this context computational methods are being developed to prescreen materials such that the experimental efforts can focus on the most promising materials.

The two examples that have been dis-

cussed, materials for carbon capture and materials methane storage are examples of this effort. The question we have been trying to address is whether it is worth the experimental effort to develop materials given a particular economic target.

One can envision that similar computational strategies can be developed for a large range of problems. In Sion, the experimental effort will extend toward novel materials for CO₂ utilization. Also, here the number of possible materials can be practically infinite and computational techniques will have to be developed to screen these materials. Similar studies can be envisioned for H₂ storage and generation.

Acknowledgement

The author would like to thank the members of his group for their contribution to the research on which part of this review is based. In addition the author would like to thank Johanna Huck, Cory Simon and Li-Chiang Lin for making their figure available.

Received: March 26, 2015

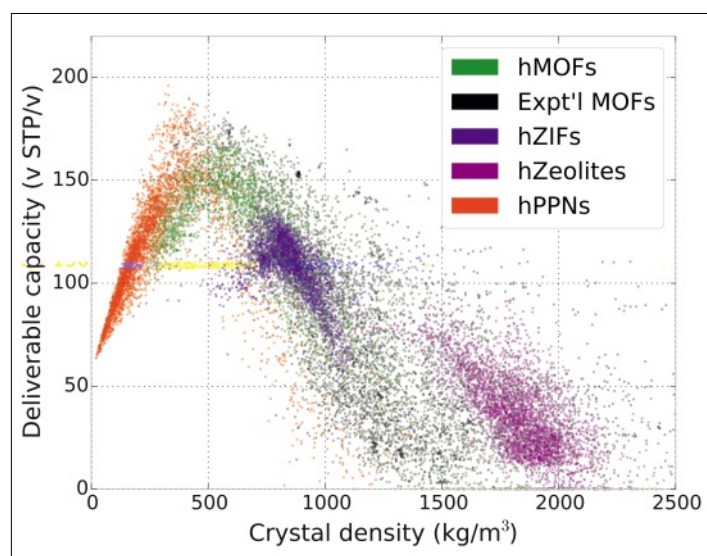


Fig. 5. Deliverable capacity for different materials as a function of the crystal density. The ARPA-e target of 315 is well above the maximum deliverable capacity we have found in our screening study. All figures, the materials are color-coded according to class. Data from Simon *et al.*, ref. [38]. Figure by Cory Simon.

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