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Lithium-Doped Metal-Organic Frameworks for Reversible H₂ Storage at Ambient Temperature

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The use of hydrogen as a future energy carrier is an essential part of future energy strategies; however, application as an energy carrier in vehicles and portable electronics is limited by problems with hydrogen storage.¹ Two major strategies being pursued toward hydrogen storage for fuel cell applications are dissociative adsorption (DA) and associated adsorption (AA) of hydrogen.

DA is the mode for metal alloys, which dissolve the H atoms separately in the matrix breaking the H–H bond. These systems tend to suffer from large barriers in dissociating the H–H bond in storing the hydrogen and large barriers in reassociating the H atoms to desorb H₂ for input to the fuel cell. In contrast AA binds the H₂ as a molecule, reducing the rate problems with adsorbing or desorbing. But here the challenge has been to obtain sufficiently strong bonding to molecular H₂ to achieve the target of 6.0 wt % H₂ near room temperature with pressures ≤100 bar.²

A recent major advance in AA systems is the development of metal-organic frameworks (MOFs), which are crystalline materials composed of metal oxide and organic units.³ At 60 bar and 77 K, IRMOF-1 stores 5.0 wt % of H₂ and MOF-177 stores 7.5 wt %.^{3h} However, their H₂ uptake capability decreases dramatically near room temperature to ~0.5 wt %, far too low for practical use. Although the H₂ storage capability at room temperature can be increased to 1.8 wt % at 298 K and 100 bar by hydrogen spillover techniques,³ⁱ the current materials do not meet the 2010 DOE (Department of Energy) criteria for use in transportation (6.0 wt % in the temperature range of –30 to 80 °C).²

We report here that Li-doped MOFs significantly improve H₂ uptake capacity near ambient conditions. Indeed, we predict that at –30 °C and 100 bar the Li–MOF-C30 leads gravimetric H₂ uptake of 6.0 wt %, reaching (barely) the 2010 DOE target.

Figure 1 illustrates the metal (Zn) oxide secondary building unit and the organic carboxylate links of the MOFs investigated here. We considered systems based on a cubic lattice with optimized lattice parameters of 26.025 for MOF-C6, 30.252 for MOF-C10, 34.374 for MOF-C16, 38.652 for MOF-C22, and 42.824 Å for MOF-C30, which are in good agreement (within 0.7%) of available experimental lattice parameters.^{3h}

Starting with these structures, we used quantum mechanics (QM) calculations (X3LYP flavor of DFT)⁴ to predict the structure for Li atoms bound to aromatic organic linkers with up to nine fused rings. We find that Li atoms prefer to bind at the centers of the hexagonal aromatic rings, but Li atoms on adjacent aromatic rings are on opposite sides. To predict the strength of binding H₂ to these structures we used the results for QM calculations [high quality second-order Møller–Plesset (MP2) at the quadruple- ζ QZVPP and triple- ζ TZVPP basis sets]⁵ to calculate the van der Waals interaction between H₂ and the metal-oxide clusters and between H₂ and the organic linkers.

These QM results were used to determine the nonbond H–C, H–O, and H–Zn interactions in the final force field (FF). The FF leads to structures and energies in very good agreement with the

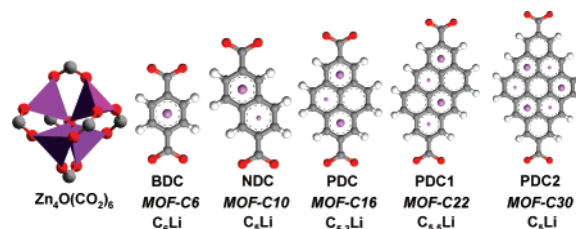


Figure 1. Li-doped MOFs. In each case the Zn₄O(CO₂)₆ connector couples to six aromatic linkers through the O–C–O common to each linker. The MOFs are named according to the number of aromatic carbon atoms. The large violet atoms in the linkers represent Li atoms above the linkers while small violet Li atoms lie below the linkers. The C_xLi ratio considers only aromatic carbon atoms.

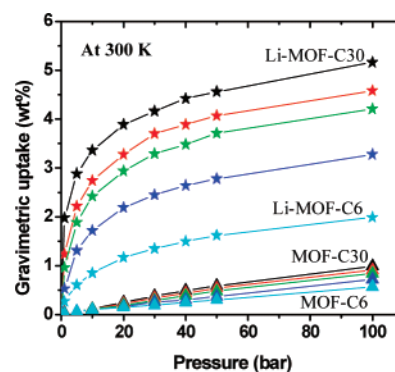


Figure 2. Predicted H₂ adsorption isotherms in gravimetric units (wt %) at 300 K for MOF (triangles) and Li–MOF (stars) systems using Zn₄O(CO₂)₆ connectors. Note that Li–MOF-C30 achieves over 5 wt % at 100 bar. The color code is MOF-C6 = cyan, MOF-C10 = blue, MOF-C16 = green, MOF-C22 = red, and MOF-C30 = black.

QM data. The FF parameters and comparison to QM are in the Supporting Information (SI).

With this first-principles-derived FF, we used grand canonical ensemble Monte Carlo (GCMC) simulations⁶ to calculate the H₂ uptake behavior of the Li-MOFs. This determines the equilibrium loading of H₂ as a function of pressures and temperature, as shown in Figure 2. To eliminate boundary effects, we use an infinite three-dimensionally periodic cell containing four independent sheets each with 32 Zn atoms. Additional calculation details are included in the SI.

Our simulations show that the H₂ uptake of the MOF-C6 at 77 K and 1 bar is 1.28 wt % which compares well with the experimental results of 1.32 wt %, while for MOF-C10 at 77 K and 1 bar we calculate 1.62 wt % which compares well with experiment, 1.50 wt %.^{3e} We calculate that MOF-C6 has 4.17 wt % at a pressure of 20 bar and 77 K (experimental value of ~4.6)^{3h} and 4.89 wt % at a pressure of 50 bar and 77 K (experimental result of ~5.0 wt %).^{3h} In addition, at 300 K our simulation predicts that MOF-C6 has 0.35 wt % at 60 bar (experimental value of 0.45 wt %)^{3j} and MOF-C10 has 0.3 wt % at 30 bar (experimental value

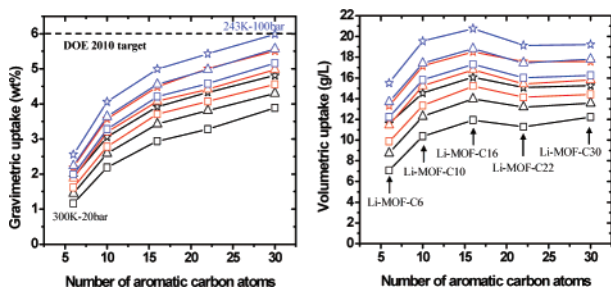


Figure 3. Predicted H_2 uptake for Li-MOFs as a function of temperature and pressures. Note that the DOE target of 6 wt % is achieved at 243 K and 100 bar for Li-MOF-30. Here the symbol code is 243 K = star, 273 K = triangle, and 300 K = square and black = 20 bar, red = 50 bar, and blue = 100 bar.

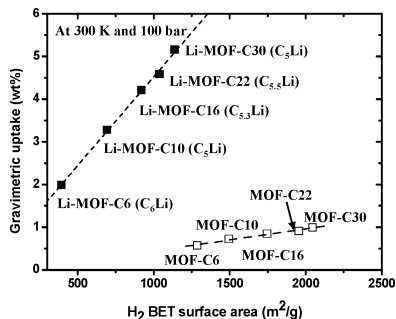


Figure 4. Gravimetric H_2 uptake at 300 K and 100 bar plotted against H_2 BET surface area for MOF and Li-MOF systems. This shows that both surface area and the ratio of Li to C are important for high performance. Figure S2 of the SI shows that the Connolly surface leads to ~ 3 times the BET area.

of 0.4 wt %).^{3j} These results validate our FF and GCMC techniques. However, at 300 K, these pure MOFs lead to low H_2 uptake of < 1 wt % even at 100 bar (Figure 2), which is far too small for practical use.

For the Li-doped MOF system, we predict significantly improved H_2 storage at room temperature (Figure 2). Thus at 300 K we calculate that Li-MOF-C30 binds 3.89 wt % H_2 at 20 bar pressure, which goes up to 4.56 wt % at a pressure of 50 bar. This is the highest room-temperature reversible hydrogen-storage capacity yet reported. It is an order of magnitude higher than for pure MOF-C30 (0.25 and 0.56 wt % for 20 and 50 bar, respectively) and MOF-C6 (0.15 and 0.30 wt % for 20 and 50 bar, respectively). Even at 1 bar and 300 K, Li-MOF-C30 stores 1.98 wt % H_2 .

Figure 3 shows H_2 uptake for Li-doped MOFs at various temperature and pressure conditions. For all temperatures and pressures, Li-doped MOF-C30 has the highest gravimetric H_2 uptake. For example, at a pressure of 100 bar, Li-MOF-C30 has 5.16 wt % (300K), 5.57 wt % (273K), and 5.99 wt % (243 K), which reaches the 2010 DOE target of 6.0 wt %. The best volumetric H_2 uptake at a pressure of > 50 bar is found for the MOF-C16 system. At 100 bar, it stores H_2 of 17.31 g/L (300 K), 18.83 g/L (273 K), and 20.76 g/L (243 K).

We also calculated the H_2 uptake as a function of surface area of the MOFs (Figure 4). This H_2 BET (Brunauer, Emmett, Teller) surface area was calculated from our H_2 adsorption isotherms at 300 K for Li-doped MOFs and at 77 K for pure MOFs, assuming the diameter (0.351 nm)⁷ of solid H_2 . These BET surface areas are

compared with the Connolly surface areas in the SI, where we see that the BET is 58% smaller, but with a linear relationship (area Connolly = 1.28 area BET + 1888.94). For both pure MOF and Li-doped MOF systems, there is a linear correspondence of H_2 uptake with surface area but with a slope that increases with the ratio of Li to C. In particular, the Li concentration is the dominant factor for high H_2 uptake near room temperature.

For the pure MOFs, the H_2 molecule binds weakly with both the metal oxide clusters and the aromatic linkers with binding energies of 1.5 and 0.9 kcal/mol, respectively. This leads to significant H_2 uptake in pure MOF systems only at temperature of 77 K and lower. However, for Li-MOF the high electron affinity of the aromatic sp^2 carbon framework promotes separation of the charge, making the Li positive (acidic), providing strong stabilization of molecular H_2 .⁸ Here we obtain effective binding energies of 4.0 kcal/mol, enhancing high-temperature H_2 uptake.

Summarizing, our first-principles based simulations show that Li-MOF systems can reach the 2010 DOE target of 6.0 wt % gravimetric at -30 °C and 100 bar. Even at 300 K, Li-MOF-30 leads to 5.2 wt % at 100 bar. This suggests that the doping of MOF with electropositive metals is a promising strategy for practical hydrogen storage.

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Supporting Information Available: Detailed computational methods, H_2 adsorption (total and excess) isotherms for Li-doped MOFs at 273 and 300 K, a plot of BET surface area versus Connolly surface area, and the distribution of H_2 in the Li-MOF-C30 at 243 K and 100 bar. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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