Practical methods for hydrogen storage are still a major bottleneck in the realization of an energy economy based on hydrogen as an energy carrier. Storage within solid-state clathrate hydrates and in the clathrate hydrate of tetrahydrofuran (THF) was recently reported [1,2], and in the latter case, stabilization by THF was claimed to reduce the operation pressures by orders of magnitude close to room temperature.

Here we use in-situ neutron diffraction to show that - in contrast to previous reports [1,2] - hydrogen (deuterium) occupies its small cages only for 30% at 274K and 90.5 Bar.

Such D₂ load is equivalent to 0.27 wt.% of stored H₂. In addition we show that a surplus of D₂O results in the formation of additional D₂O ice Ih rather than a sub-stoichiometric clathrate stabilized by loaded hydrogen as was reported in [2]. Structure-refinement shows THF-d₈ to be dynamically disordered, while it fills each of the large cages of THF-d₈-17D₂O stoichiometrically. Our results (measured over temperatures between 282K and 8K) show that the clathrate hydrate takes up hydrogen rapidly at pressures of 60-90 Bar at ~270K. Above ~220K the H-storage characteristics have similarities with surface-adsorption materials such as nanoporous zeolites and metal organic frameworks but at lower temperatures adsorption rates slow down due to reduced D₂ diffusion between the small cages.

Conclusions

At pressures up to 100 Bar, that may be considered above the upper limit relevant for hydrogen storage inside materials, the hydrogen occupation in the small cages of the THF clathrate hydrate reaches values of ~0.3, and not 2 as proposed in [1,2]. No ‘tuning’ of the THF concentration in favour of hydrogen uptake in the large cages but rather phase separation between clathrate and ice is observed, in contrast to [2]. Perhaps surprisingly the hydrogen loading can be accomplished on relatively short timescales when small crystals are used at ~270K.