HYDROGEN – CARBON INTERACTIONS

A BRIEF LITERATURE SURVEY

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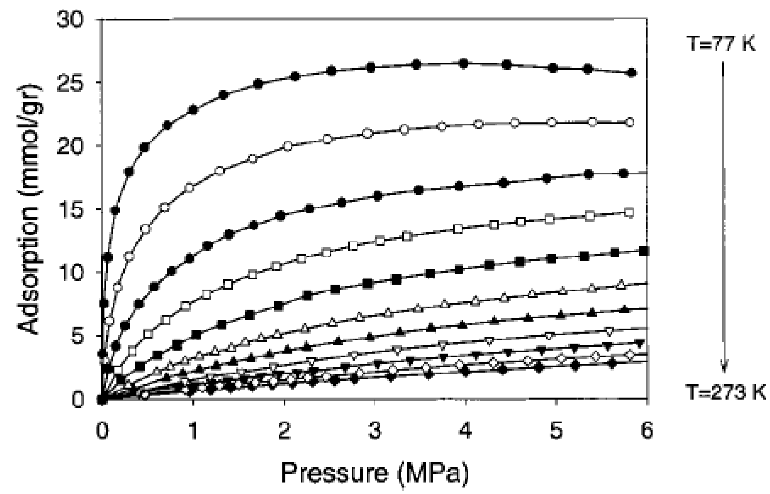
Workshop on Tritium Control and Capture in Salt-Cooled and Fusion Reactors

Salt Lake City, October 27-28, 2015

Hydrogen retention mechanisms

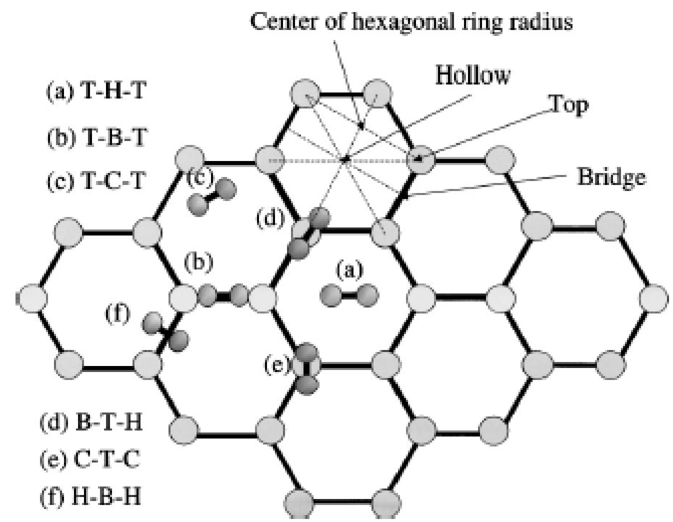
- Molecular H2 physisorption on porous carbons
  - Significant at cryogenic temperatures
  - Decreases with increase of temperature
  - Well documented from prior work on H2 storage
- Atomic H chemisorption
  - Lower saturation capacity
  - Not as much investigated as physisorption
  - Temperature dependence may be sensitive to structural factors and state of the surface
- Molecular H2 trapping / solubility
  - Mixed mechanism (molecular diffusion / chemisorption)
  - Sensitive to structural factors, irradiation



Benard, Chahine, *Langmuir* **173** (2001) 1950

Theory and modeling

- DFT calculations:
  - Dissociative chemisorption of H2 on armchair sites requires high activation energy
  - Dissociative chemisorption on zig-zag sites is easier (no activation)
  - H atom chemisorption on basal planes requires pocking of a C atom from its planar position and requires activation energy
  - The crucial step is H2 dissociation which is energetically demanding



Dino et al. Surf Sci Nanotech 2 (2004) 77; Solid State Commun 132 (2004) 713

H retention on graphite

- Retention and diffusion of H2 on isotropic graphite from Toyo Tanso
  - At 1000 C and 1 bar, H2 uptake leads to loading of up 20-600 ppm (based on pressure drop)
  - Diffusion and trapping in the graphite structure
  - Two types of trapping sites proposed (based on thermodesorption data)
  - Enhanced trapping on defective and irradiated graphite

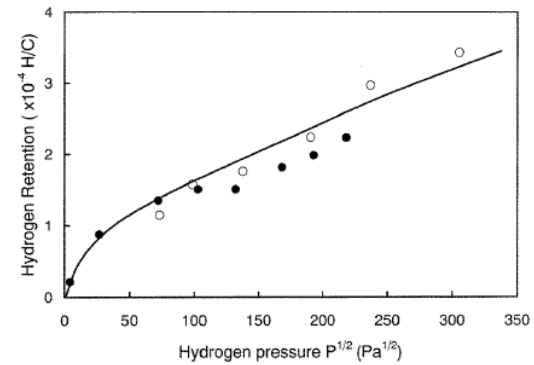


Fig. 3. Pressure dependence of hydrogen retention in graphite measured by absorption experiment (solid circles) and desorption experiment (open circles) [6] (sample: ISO-880U (absorption), ISO-88 (desorption), temperature: 1273 K) (ISO-880U is purified sample of ISO-88).

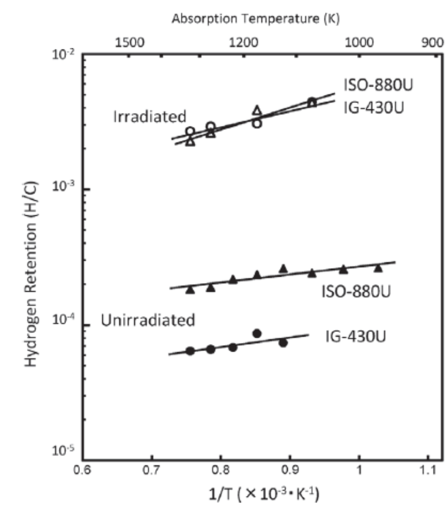


Fig. 2. Temperature dependence of hydrogen retention in graphite before and after neutron irradiation (irradiation fluence: 3.9 × 10^{23} n/m^2 (0.047 dpa), absorption temperature: 1273 K, equilibrium pressure: ~10 kPa).

Atsumi, Phys Scripta T103 (2003) 77; J. Alloys Compounds 356-357 (2003) 705

Trapping sites in graphite

- Two types of trapping sites
  - Dangling bonds at crystallite edges (2.6 eV)
  - Interstitial sites inside crystallites (4.4 eV)
  - The prevalence of each type of sites varies with irradiation fluence

Atsumi, J, Nucl. Mater. 313-316 (2003) 543

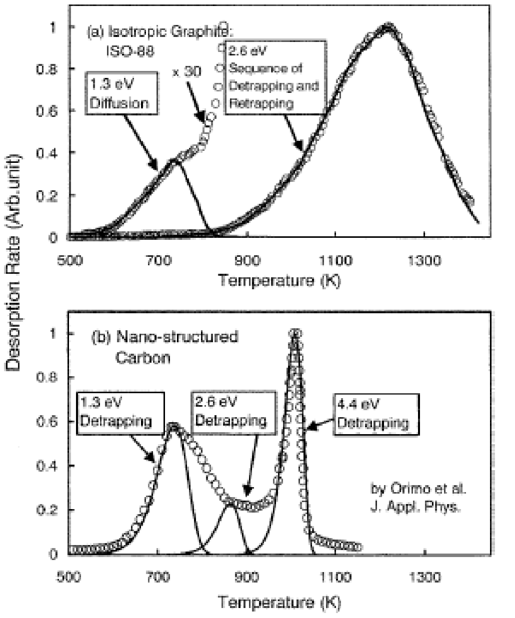


Fig. 4. Deuterium desorption spectra and the curve fittings for isotropic graphite (ISO-88: (a)) [6] and nano-structured carbon milled in hydrogen atmosphere [31] (heating rate: 10 K/min).

- Thermodesorption of H2 trapped in isotropic graphite is similar to that from graphite mechanically milled in a hydrogen atmosphere

Orimo, J Appl Phys 90 (2001) 1545

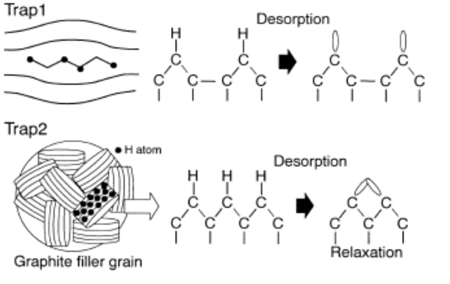


Fig. 3. Schematic illustration of the proposed model on hydrogen trapping in a graphite material. The chemical bond model was referred from Ref. [18].

- The nature of trapping sites in graphite is still debated

Miyabe, J Appl. Phys. 104 (2008) 044311

Deuterium in graphite

- D2 thermodesorption from isotropic graphite exposed to D2 at various temperatures
  - Solubility is proportional with $P^{1/2}$
  - Three main desorption peaks
  - Evidence of various trapping sites
  - Very small CD4 desorption was found

Atsumi, J, Nucl. Mater. 155-157 (1988) 241

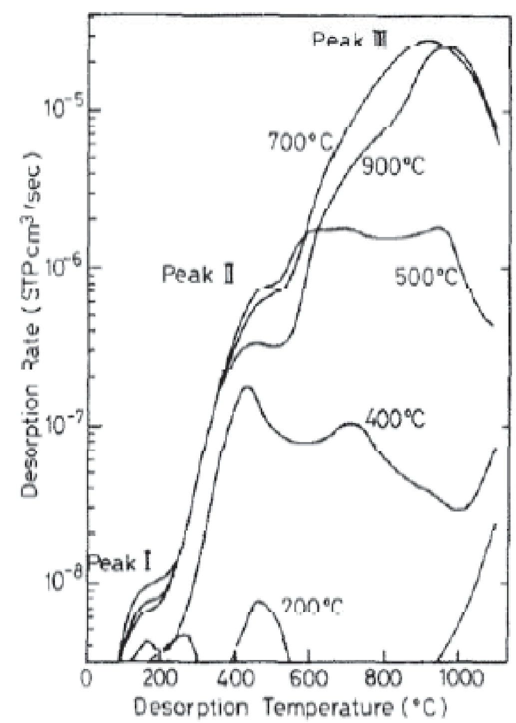


Fig. 2. Thermal desorption curves of deuterium for graphite exposed to D_2 at various temperatures (60 kPa, 5 h).

Tritium in graphite and PyC

- Diffusion and solubility in PyC
  - T2 diffusion in PyC is much lower than in metals, and activation energy is high, suggesting chemical bonding
  - D2 solubility in PyC suggests a dissociative mechanism (varies with $P^{1/2}$)
  - PyC suggested as an effective barrier for T implantation in fusion reactors

Causey, Carbon 17 (1949) 323

- Retention of D+ and T+ ions in POCO graphite
  - Plasma exposure to 100 eV ions below 500 K causes fast saturation
  - Between 500-1000 K diffusion along pore surfaces occurs deep in the sample
  - Above 1000 K the isotopes penetrate graphite and decorate high energy traps

Causey, J Vac Sci Technol 4 (1986) 1189

Thermal release of tritium

- Thermal release of T2 from irradiated graphite
  - T2 is released as HT, and also as HTO (if oxidation occurred)
  - The release temperature increases with the increase of neutron fluence received by graphite

Saeki, J Nucl Mater 99 (1981) 1019

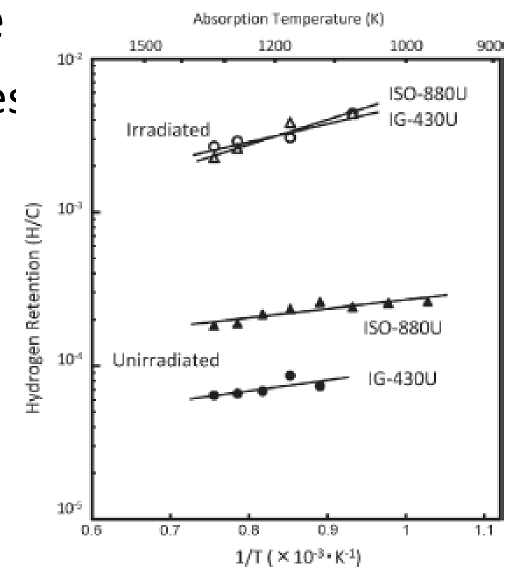
- Thermal release of T2 implanted in fine grain isotropic graphite
  - Detrapping o implanted T starts at ~ 600 K, reaches maximum rate at 1100-1400 K, and is 95% completed at 1600 K
  - On single type of trapping sites was observrved
  - High T retention up to high temperature suggests that graphite will retain T inventory after exposure to energetic T ions

Sawicki, J. Nucl Mater 162-164 (1989) 1019

Factors affecting H trapping

- Hydrogen trapping in neutron irradiated graphite
  - Neutron irradiation creates high energy trapping sites
  - H atoms diffusivity is 1-2 orders of magnitude lower after irradiation at only 0.047 dpa
  - Irradiation and subsequent annealing of graphite changes substantially the absorption rates

Atsumi, J Nucl Mater 386-388 (2009) 379; ibid 390-391 (2009) 581



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- Hydrogen retention in graphite irradiated at high temperature
  - Irradiation causes damage in graphite structure
  - H retention is significantly reduced at high temperature

Yoshida, J. Nucl. Mater 386-388 (2009) 841

Hydrogen thermodesorption

- Thermodesorption spectroscopy from H-implanted graphite
  - Thermodesorption spectroscopy can be used to characterize the energy strength of trapping sites

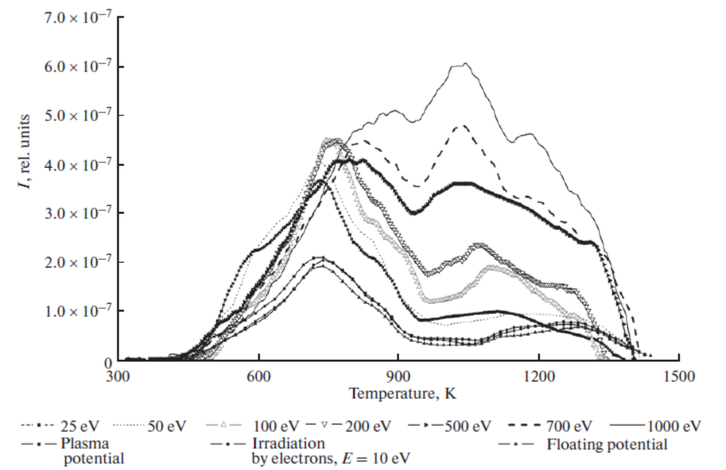

Fig. 2. Spectra of hydrogen desorption from MPG-8 graphite irradiated by different-energy ions and electrons.

Airapetov, J Surf Investigation 4 (2010) 537-571

- Modeling H2 thermodesorption from H+ implanted graphite
  - Study showed the effect of graphite porosity and crystallite size on the number and types of trapping sites

Liu, Nucl Instruments Methods Phys Rev B 269 (2011) 431

Other works

- Modeling of reactive-diffusive transport of hydrogen after ion implantation
  - Release and retention of H in porous graphite depends on the graphite internal structure and on the energy and flux of incident ion beam

Rai, J Nucl Mater 374 (2008) 304

- Hydrogen isotopes permeations through carbon materials
  - Measurements of gas pressure driven permeation of isotopes

Spitsyn, J Nucl. Mater 390-391 (2009) 701

Perspectives

- Physisorption on high surface area, porous carbons is far more efficient than chemisorption on graphite
  - Requires cryogenic temperatures
  - Can be used in conjunction with a sweep gas (He) to separate T2 from T2/He mixtures
- Retention by carbon elements in contact with the molten salt (pebbles) will be difficult to control given the irradiation effects on carbon
- Salt corrosion effects on carbon (pebbles) will change the hydrogen retention properties