HYDROGEN – CARBON INTERACTIONS

A BRIEF LITERATURE SURVEY

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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

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

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

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
  

- 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

- The nature of trapping sites in graphite is still debated
  
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

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

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


- Thermal release of T2 implanted in fine grain isotropic graphite
  - Detrapping of 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 observed
  - High T retention up to high temperature suggests that graphite will retain T inventory after exposure to energetic T ions

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


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

Hydrogen thermodesorption

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


- 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
    

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