Atomistic Mechanisms of Metal-Assisted Hydrogen Storage in Nanostructured Carbons

Nidia G. Gallego
Oak Ridge National Laboratory
May 16, 2012

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Goals

• Understanding the mechanisms of synergetic interaction in metal-doped nanostructured carbons that lead to enhanced hydrogen adsorption at near-room temperatures.
  — Identification of local atomic structures in nanoporous carbons
  — Nature of hydrogen binding sites
  — Adsorption mechanisms, energetics and dynamics of adsorbed $H_2$

• Understanding the impact of local atomic order and topological defects in disordered nanostructured carbons on their specific properties related to gas adsorption
  — Relationship between local atomic structures and large scale architecture of nanoporous carbons
  — Confinement effects on the properties of trapped molecular species
Our team: Cross-cutting expertise

- Simulation of carbon structures and modeling of adsorption
- Electron microscopy: from atomic scale to mesoscale
- In-situ characterization methods: phase behavior and dynamics of confined fluids
- Synthesis, surface modification and characterization of carbon materials: texture, atomic structure, local density, order and disorder
- Collaborations:
  - University of Tennessee
  - Spallation Neutron Source (SNS)
  - High Flux Isotope Reactor (HFIR)
Approach

• Developing realistic structural models for nanoporous carbons
  – Tight-binding molecular dynamics simulations of nanoporous carbons
  – Structural information from X-ray and neutron scattering

• Structure characterization of nanoporous carbons
  – Atomic resolution electron microscopy
  – Order/disorder characterization form X-ray and neutron scattering

• Characterization of adsorbed H$_2$ using in-situ methods
  – Phase behavior and densification of adsorbed H$_2$ (SANS)
  – Restricted dynamics of confined H$_2$ molecules (QENS)

• Understanding atomistic mechanisms of H$_2$ adsorption
  – Role of transition metals
  – Role of alkali atoms
Role of transition metals doping

✓ Demonstrated the presence of single Pd atoms stabilized in carbon structure

✓ Together with earlier results, this leads to the possibility of multiple mechanisms for enhance H₂ uptake in Pd-doped activated carbon fibers:
  ✓ Destabilization of Pd hydride and release of H atoms to carbon
  ✓ Spillover of H atoms and bonding to dangling bonds of unsaturated C atoms
  ✓ Kubas-type bonding of multiple H₂ molecules to single Pd atoms

van Benthem et al. *Carbon* **49** (2011) 4059-4073
Role of alkali metals doping

- Demonstrated higher H$_2$ uptake on ultramicroporous carbon (UMC) compared with other carbons in equal conditions.
- Hypothesized that alkali metal traces cause enhanced uptake through polarization-induced physisorption.
- Adsorption is slow and desorption shows hysteresis.
- Physical mixing with Pd black accelerates adsorption but has no effect on desorption.

- Enhanced uptake found on other alkali-doped (K, Li) carbons confirms the hypothesis of polarization-induced physisorption.
- Adsorption energy was higher on K-doped carbon (15 - 23 kJ/mol) compared with the same carbon with no K doping (14 – 16 kJ/mol).
- Adsorption energy on K- and Li- doped carbons is in the range considered optimal for practical H$_2$ storage.

Bhat et al, Carbon 48 (2010) 2361-2364
Saha et al, Langmuir (2012) dx.doi.org/10.102/la3002948
Effect of physically-mixing Pd

- Physically mixing with 10 wt % Pd black causes a small increase in H₂ uptake.
- Adsorption kinetics was much faster after addition of Pd.
- Desorption rates were not changed.

Summary on the role of metals

**Pd-doped carbon**

- Enhanced uptake caused by polarization – induced physisorption on K+
- Slow adsorption rates

**K-doped carbon**

- Strong binding on K+ causes hysteresis on desorption

**K-doped carbon physically mixed with Pd particles**

- Pd particles accelerate adsorption
- Pd particles have no effect on desorption
- NO REVERSE SPILLOVER

**HYDROGEN CAPACITY DEPENDS CRITICALLY ON CARBON PROPERTIES**
Superdensification of adsorbed $H_2$

- Used high-pressure in-situ small angle neutron scattering (SANS) to estimate the density of $H_2$ trapped in nanopores as a function of pore size and external $H_2$ pressure.

- At room temperature and 200 bar $H_2$, the hydrogen density in narrow pores (9 Å) approaches the density of liquid hydrogen.

- Densification factors are much higher at low pressures and gradually weaken at higher pressures.

- This demonstrates the advantage of adsorptive storage over compressed storage.

Restricted mobility of confined H\textsubscript{2}

- Used quasi-elastic neutron scattering (QENS) to probe the dynamics of H\textsubscript{2} confined in carbon nanopores.

- Hydrogen became mobile at temperatures some 8-11 K above the melting point of bulk H\textsubscript{2} (13 K).

- After becoming mobile, diffusion occurs by the solid-like mechanism with activation energies close to those of solid H\textsubscript{2}.

Role of quantum confinement in diffusion

✓ Usual isotope effect would suggest that $D_{D_2} < D_{H_2}$ due to doubled mass of molecule.

✓ Quantum de Broglie wavelength of $D_2$ is significantly smaller than that of $H_2$ because $D_2$ is heavier.

✓ Under the same conditions, $D_2$ shows higher mobility.

✓ The restricted mobility of $H_2$ is caused by extreme confinement and strong quantum effects at low temperatures.

De Broglie wave-length  $\lambda_T = \hbar / \sqrt{\mu k_B T}$

Preliminary results (2012)
Order vs. disorder in carbons

- Nanoporous carbons have 2D structures with short range order.
- Local folds and cusps limit lateral coherence to only 8-10 Å.
- Graphene layers are stacked closely but with minimal interlayer atomic correlation.
- Local atomic density is only 20% lower than in graphite.

Electron microscopy: short graphene layers with random orientation

Neutron scattering and pair distribution function (PDF) analysis: short range 2D order

Effect of carbon density

- Tight-binding simulations give realistic local structures.
- Carbon structures depend on both density and quenching rate.
- Structures are primarily 3-fold bonded.
- Pore volumes increase rapidly for densities less than 1.7 g/cm³.

Peng, Morris, Carbon 50 (2012) 1394-1406
New computational approach allows rapid adsorption calculations for given carbon structures.

- First systematic
- Uptake rises with decreasing carbon density
- Opposite of trend for heat of adsorption (ranging from 12-23 kJ/mol).
- Small pores absorb strongly, but there are few such pores in dense materials.

Regions with $E_{ads} < -10$ kJ/mol in simulated carbon structure with density 1.25 g/cm$^3$. 

Peng, Morris, Carbon 50 (2012) 1394-1406
Conclusion

✓ The main contribution to hydrogen uptake capacity of metal-modified carbons is physisorption on the porous carbon support, which is strongly dependent on the properties of the porous carbon support.

✓ Metal additions enhance the uptake through different mechanisms (spillover, Kubas binding, chemisorption, polarization) but their effect is secondary to physisorption on the carbon support.

✓ Narrow pores in carbon have favorable heat of adsorption (12-22 kJ/mol) and induce extreme densification of adsorbed hydrogen, approaching the density of liquid hydrogen at room temperature.

✓ Increasing the heat of adsorption by increasing carbon density does not necessarily increase the hydrogen uptake.

✓ The volume available for adsorption in narrow pores is as important as the heat of adsorption for hydrogen storage in nanoporous carbons.
Future plans

We will focus on understanding the impact of local atomic order and topological defects in disordered nanoporous carbons on their specific properties determined by the presence of a large fraction of atoms exposed at interfaces.

✓ How do local atomic structures at the nanoscale relate to the mesoscale architecture in carbons of various origins, and how do they determine measurable texture properties (pore distribution, surface area)?

✓ How do local structures affect interactions with gases and how does confinement change the phase behavior and properties of trapped molecular species?