
P. Pfeifer and ALL-CRAFT Team


1Departments of Physics, 2Chemistry, 3Radiology, and 4Mechanical Engineering
5International Institute of Nano and Molecular Medicine, 6University of Missouri Research Reactor
University of Missouri, Columbia, MO 65211

7General Motors, R&D Center, Warren, MI 48090
8OsComp Systems, Houston, TX 77032
9LCVN, Université Montpellier 2, 34095 Montpellier II, France
10Laboratoire Chimie Provence, Université Aix-Marseille I, 13396 Marseille, France

ICCF-18, University of Missouri—July 24, 2013

http://all-craft.missouri.edu/
Objectives, DOE/DLA-Funded Program

– Develop nano-engineered carbons for high-performance, sorption-based hydrogen storage
– Achieve high performance with high surface areas, high binding energies, and high-density adsorbed films
– Create high binding energies by boron-doping and pore network engineering
– Boron predicted to raise binding energy from 5 kJ/mol to 10-15 kJ/mol
– Function-driven materials design; 2017 DOE Hydrogen Storage Targets:
  Gravimetric storage capacity: 0.055 kg H$_2$/kg system
  Volumetric storage capacity: 0.040 kg H$_2$/liter system
– Develop prototype H$_2$ tank with storage capacity of 0.4 kg H$_2$/7 kg carbon

Objectives, SKINR Program

– Observe anomalous heat events, if any, through temperature spikes during loading of D$_2$ on Pd (foil, nanoparticles, …) at pressures 0-200 bar and temperatures 8-500 K
– Investigate dependence on surface/pore morphology (AHE of D$_2$ in lattice vs. AHE of D$_2$ in voids)
OVERVIEW: H₂ STORAGE

- Compressed Hydrogen
  - Cryo-compressed
  - Liquid Hydrogen
- Materials
- Complex hydrides
  - AlH₃
  - MgH₂
  - NaAlH₄
  - AB
  - H₃NBH₃
- Chemical hydrides
- Adsorbents
  - AC
  - MOFs
Materials for H₂ Storage

### Powder

- **Alane (AlH₃)**
  - Complex hydride
- **MgH₂**
- **NaAlH₄**
  - Complex hydride
- **Methane**
  - ~80 bar, 293 K

### MOFs: crystal density

- MOF-210
  - 80 bar, 77 K
- MOF-5
  - 80 bar, 77 K
- MOF-177
  - 80 bar, 77 K

### U. Missouri carbons: “crystal” density

- 3K-H60, 2500 m²/g
- 3K-H60 (B-doped)
  - 190 bar, 303 K
- 3K (600C)
  - 100 bar, 80 K
- 3K (600C)
  - 190 bar, 303 K
- 3K-600C
  - 100 bar, 303 K
- 3K-600C
  - 190 bar, 303 K
- MSC-30
  - 100 bar, 80 K

### Predicted 2009, 10 wt% B

- 120 bar, 298 K
- U. Missouri Phase 2 Target

### Compressed H₂

- 100 bar, 80 K

---

Produced over 100 different carbons from corncob (variable formulations) & searched for maximum storage capacity

NREL: “Missouri Hockey Puck”

Has surface area that could cover much of MU campus
**AX-21, U. Missouri: 3K-600C (0% boron), 3K-H60 (I,B) (7% boron)**

**CRYOGENIC ADSORBENTS**

3K-600C, 77-80 K, 100 bar

- **Start time to full flow (-20°C)**
- **Fill time**
- **Cycle life**
- **Volumetric storage**
- **Gravimetric storage**
- **Max operating temp.**
- **Min operating temp.**
- **Max delivery temp.**
- **Min delivery temp.**
- **Max delivery pressure**
- **Min delivery pressure**
- **System cost**
- **On board efficiency**
- **DOE 2017 revised target**

* indicates qualitative assessment.

**U. Missouri:**
Projected from experimental values

**AX-21:**
Hydrogen storage engineering center of excellence. *Anton, et al.,* 2010-2011. The gravimetric and volumetric storage capacity of material AX-21 decreased by ~62% and ~44% respectively when including the complete storage system.
GAS ADSORPTION

Excess: 1
Absolute: 1 + 2
Total amount: 1 + 2 + 3

Gibbs Excess

Distance From Surface

Gas Concentration

Adsorbed phase
Gas phase

Pressure (bar)

\( g \text{H}_2/\text{kg carbon} \)
Density distribution for participating pores, with carbon volume represented by grey walls (GCMC)

**Temperature: 80 K**

Second layer formation for pores between 10-20 Å

Experimental pore size distribution from N\textsubscript{2} adsorption at 77 K
Lines represent the numerical simulation fits:
3K: 50% H13 + 50% H20 (Hxx: slit pore of width xx Å)
MSC-30: 50% H8 + 50% H30

Bimodal model correctly predicts:
- Grav. excess adsorption
- Grav. storage capacity
- Isotherms at 80 K
- Isotherms at 303 K
MU ADSORBENTS

MU carbons vs. conventional/commercial carbons

Cryogenic (80 K)

30% improvement at 100 bar

Room temperature (303 K)

20% improvement at 100 bar

- MU carbon optimized for hydrogen adsorption: nanospace engineering (quantitative control over surface areas, porosities, sub-nm (<1 nm) and supra-nm (1-5 nm) pore volumes)

- MU carbon outperform MSC-30 by 20% at 100 bar and 303 K and 30% at 100 bar and 80 K

- Additional improvement by boron doping (upcoming slides).
MU ADSORBENTS

H₂ storage capacity of MU carbons

**Cryogenic (80 K)**

- Gravimetric storage capacity of 10 wt% and 2.0 wt% at 80 K and 303 K, respectively, at 100 bar

- Gravimetric storage capacity of 12 wt% and 3.3 wt% at 80 K and 303 K, respectively, at 200 bar

- Volumetric storage capacity of 54 and 63 g/L at 100 and 190 bar, respectively, and 80 K, exceeds 2015 DOE target.

**Room temperature (303 K)**

- Gravimetric storage capacity of 10 wt% and 2.0 wt% at 80 K and 303 K, respectively, at 100 bar

- Gravimetric storage capacity of 12 wt% and 3.3 wt% at 80 K and 303 K, respectively, at 200 bar

- Volumetric storage capacity of 54 and 63 g/L at 100 and 190 bar, respectively, and 80 K, exceeds 2015 DOE target.
The activation mechanism by potassium hydroxide is a complicated process and consists of several simultaneous/consecutive chemical reactions.

2KOH → K₂O + H₂O  
C + H₂O → CO + H₂  
CO + H₂O → CO₂ + H₂  
CO₂ + K₂O → K₂CO₃  

Above 700°C

K₂O + H₂ → 2K + H₂O  
K₂O + C → 2K + CO

**Oxidation of carbon** by oxygen produces carbon monoxide and carbon dioxide

- **Penetration of metallic potassium into the carbon lattice**
- Expansion of the lattice by the intercalated potassium
- Rapid removal of the intercalate from the carbon sheet

High specific surface areas (up to 3000 m²/g), porosities, sub-nm (<1 nm) and supra-nm (1-5 nm) pore volumes are controlled by a combination of KOH concentration and activation temperature

Romanos et al., Nanotechnology 23, 015401 (2012)
Objective: Increasing binding energy of $\text{H}_2$ on carbon by functionalization of surface with boron:

- Binding energy of $\text{H}_2$ on graphite: 5 kJ/mol
- Binding energy of $\text{H}_2$ on B-substituted carbon: 10-15 kJ/mol (electron donation from H2 to electron-deficient B; computations Firlej et al., 2009; Kuchta et al., 2010)
- Increase in binding energy extends far beyond (~0.7nm) immediate neighborhood of B-atom
- Computed H2 ads. isotherms (GCMC) on B:C = 10 wt% predict (Firlej et al., 2009; Kuchta et al., 2010):
  - $\text{H}_2$: adsorbent = 5 wt% at room temp. and 100 bar,
  - $\text{H}_2$: adsorbent = 12 wt% at liq. N$_2$ temp. and 100 bar
Technical Accomplishments

B-doped 3K-H60(I,A), 8.9 wt% B

- H₂ excess adsorption per unit surface area (areal excess adsorption, AEA) depends only on how strongly surface binds H₂, not on surface area or pore volume. **40% increase in AEA at 200 bar:** high binding energies on majority of surface sites

- Enthalpy of adsorption, \( \Delta H \), increased from 6 kJ/mol (0.0 wt% B) to 10 kJ/mol (8.9 wt% B)

- Film thickness \( t \) from \( \Delta H \) analysis: \( t = 0.6 \text{ nm at } 303 \text{ K} \) (AMR 2010: \( t = 0.4 \text{ nm at } 77 \text{ K} \)
Technical Accomplishments

Density of adsorbed H₂ film and non-adsorbed H₂ gas in pore space, at 77-80 K:

- Density exceeds that of liquid H₂ at 20 K
- Critical temperature of H₂: 33 K
- Liquid-like film at temperatures above liquid-gas critical point!
- “Adsorption-induced liquefaction at supercritical temperatures”

![Graph showing stored density vs. pressure for different materials: MSC-30, 3K-0046, HS:0B-20, 3K-600C. The graph illustrates the density of liquid H₂ at 20 K and 1 bar.]

Density of liquid H₂ at 20 K and 1 bar
Technical Accomplishments

10-liter Hydrogen Sorption Instrument

Capacity: 10.6 L
Pressure: 0-100 bar
Temp.: 194-303 K
Flow rate range: (0-400 Ln/min H₂)

- 10-liter system capable of non-equilibrium measurements (pressure temperature, flow rate)
- Gives information about heat management and sample/tank kinetics
Technical Accomplishments

10-liter Hydrogen Sorption Instrument

- 10-liter system validated, including sorbent homogeneity
- Gravimetric storage (total) capacity of bulk material is higher than that of individual carbon grains because porosity is higher
Able to fill the tank to 95% capacity in 3.3 minutes, 303 K; no heat exchanger

Gravimetric storage capacity will increase 5% with improved outgassing procedure
Excess Heat Measurements
EXCESS HEAT MEASUREMENTS

- Heat released during adsorption of H\textsubscript{2} on high-surface-area carbon (2 mg H\textsubscript{2} on 100 mg C at 1.5 bar) is 5 J and gives temperature spike of 6 K

- Expect: heat released during anomalous heat event (D\textsubscript{2} on 100 mg Pd) \(~5\) kJ and huge temperature spike

- Thus: instrumentation to detect pressure-controlled anomalous heat events is in place
The palladium is a palladium foil (99.95% palladium). The data was measured at 100 °C. 988.4 mg was used.

Loading as function of pressure

\[
\text{(0.70 g H)/(100 g Pd)} = 0.73 \text{ H atom : Pd atom}
\]

Temp. rises as \( \text{H}_2 \) absorbs after opening of valve

Press. drops as \( \text{H}_2 \) absorbs after opening of valve
Hydrogen on Pd Foil

30 °C

![Graph showing the relationship between pressure (bar) and mol H/mol Pd.](image)
HYDROGEN ON PALLADIUM

- At 30 ºC: Observed loading of > 0.8 H atom/Pd atom on SKINR Pd sample, at 200 bar
- No anomalous heat event observed during 20 h
- At –240 ºC or lower: \( \text{H}_2 \) exists as liquid and loading near 1.0 H atom/Pd atom as static property is expected
DEUTERIUM ON PALLADIUM/SWCNT

- SKINR samples: Pd/Single-Wall-Carbon-Nanotube/Pd sandwiches
- Sample #2: 82.56 mg Pd + 0.62 mg C; volume: 0.0072 cm$^3$
- Sample #3: 77.91 mg Pd + 0.64 mg C; volume: 0.0068 cm$^3$

- At 30 ºC: Observed loading of > 0.8 D atom/Pd atom at 100 bar
- Loading significantly different on the two samples
- No anomalous heat event observed during 20 h
LOW-TEMPERATURE INSTRUMENT

• High-precision, custom-built instrument

• Temperature range: 8-293 K (–265 - 20 ºC) using closed-cycle helium refrigerator

• Temperature stability: ± 0.01 K
  Pressure range: 0-200 bar
  Gases: H₂, D₂, He, …
  Sample size: 0.5-2 g

• Hydrogen shock of 60 bar on evacuated carbon sample at 35 K: heat released during adsorption gives prominent temperature spike even though sample cell by design has large thermal mass; adsorption equilibrium is reached in less than 10 min and temperature stability is better than 0.01 K

• Will build calorimeter around dosing and sample cell
Conclusion

– Can measure $T$, $P$ as function of $t$ for 77-750 K and 0-200 bar
– Can easily see events of $\sim 5$ J (peak in $T$ vs $t$ signal)
– Events of 5 kJ will give huge peak in $T$ vs $t$
– Can do semi-quantitative calorimetry
– Can determine loading of Pd, Ni, … from sorption isotherm (0-200 bar), at any fixed $T = 77-750$ K
– Will be able to load Pd, Ni, … at 0-200 bar & 8-500 K
– Typical sample size 100-200 mg
– Promising for Pd, Ni, … nanoparticles on any support