

2009 DOE Hydrogen Program Review

Hydrogen Storage by Spillover

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Project ID: ST_24_Yang

Overview

Timeline

- Project start date: FY05
- Project end date: FY10
- Percent complete: 80%

Budget

- Total project funding
 - DOE share: \$1,275,355
 - Contractor share: \$369,046
- Funding received in FY08: \$237,000
- Funding for FY09: \$311,855

Barriers

- General
 - Weight & Volume
 - Rates (Refueling and discharge)
- Reversible Solid-State Material
 - Hydrogen Capacity & Reversibility
 - Lack of Understanding of H₂ Spillover

Partners

- Sample/adsorbed H Verification, Characterization & Mechanism **NREL, Rice U, APCI, NIST, UNC, SwRI®**
- Plan industrial collaboration after the initial phase of study and sorbent optimization

Project Objectives

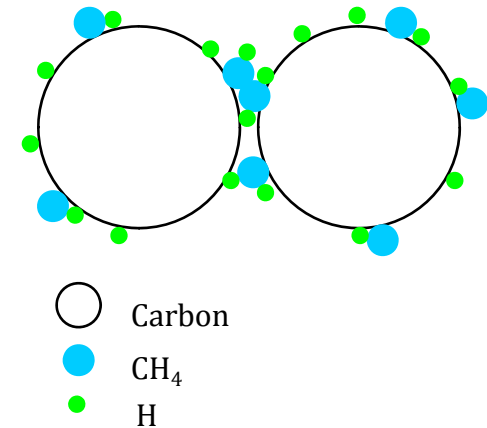
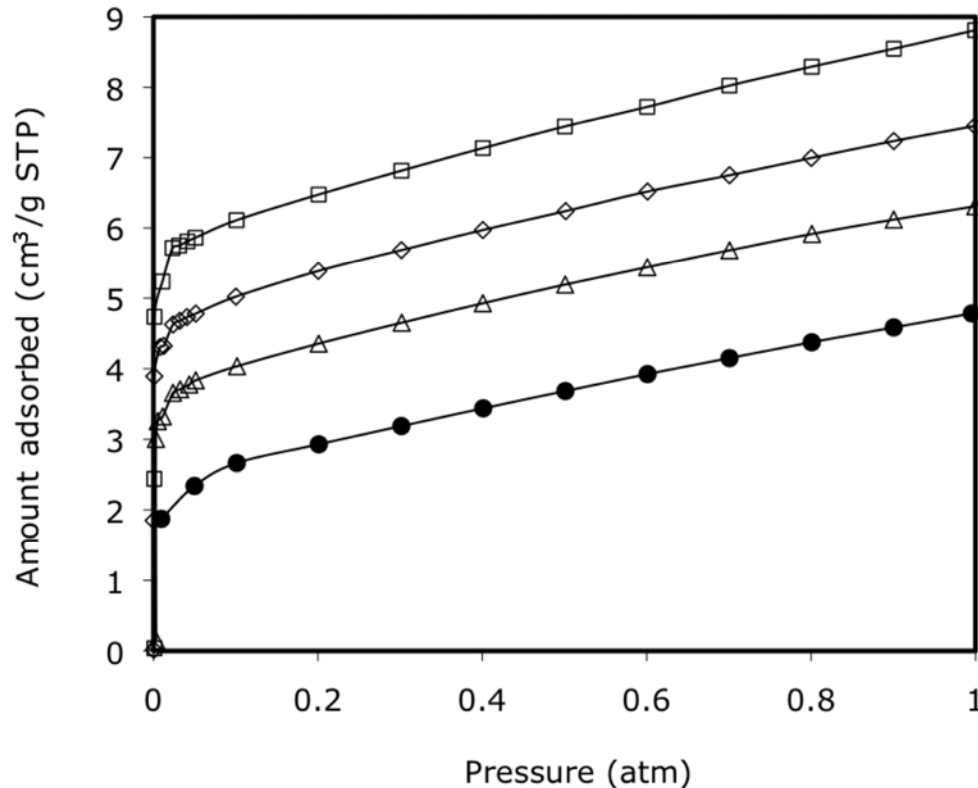
- To develop hydrogen storage sorbent materials with system capacities in excess of 6 wt% (and 45 g/L) at ***ambient temperature*** by using the spillover mechanism
- To develop spillover sorbents with high rates at ambient temperature for both charge and discharge

Technical Approach

- Use our bridge-building technique to significantly enhance spillover and storage at ambient temperature for MOFs (US & Foreign Patent applications filed, Yang et al., US20070082816A1 & WO2007046881A2, 2006)
- Synthesis of nanostructured carbons with ultra-high surface areas and develop effective direct metal-doping techniques for spillover-storage at ambient temperature
- Modify carbons to enhance spillover storage by adding heteroatoms (such as B and N) and surface functional groups (such as oxygen groups)
- Search for and develop “catalysts” for spillover to increase rates

Technical Progress: Bridges for Spillover

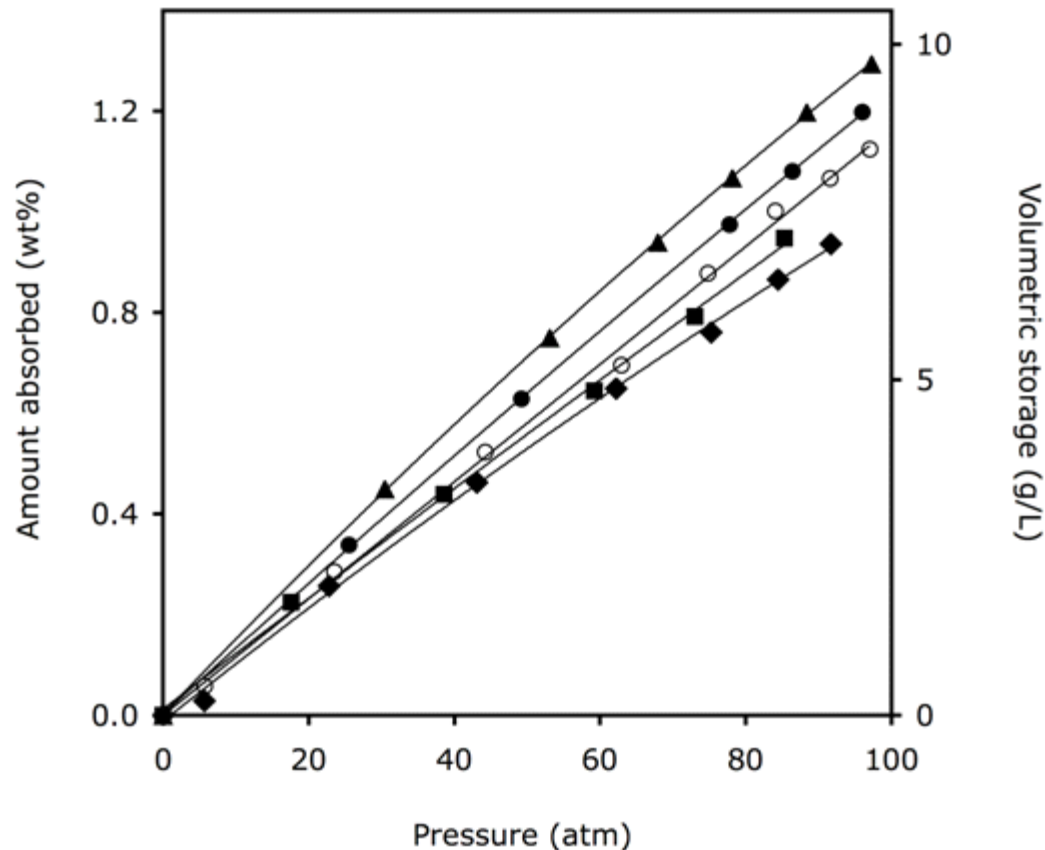
Adsorption isotherm of H₂ on Pt/AX-21 at 298K with presorbed CH₄ at P(CH₄) = 0 (●), 5.0×10⁻⁴ (◇), 1.2×10⁻³ (□) and 3.4×10⁻³ atm (△). The 3 presorbed CH₄ points (fractional coverages << 1) fall essentially on the origin due to the large Y-axis scale.



- Gas adsorbate molecules serving as bridges for spillover is observed for the first time.
- Use of the Benson-Boudart method for determining supported metal dispersion yields over-estimates.
- Notes: (a) CH₄ is presorbed also at 298K to simulate binary CH₄/H₂ adsorption, and adsorption of CH₄ is reversible at 298K. (b) CH₄ is mostly adsorbed on carbon, and at 3.4×10⁻³ atm, 1.3×10⁻⁴ molecule of CH₄ is adsorbed on per surface carbon atom.

Technical Progress: Bridges for Spillover

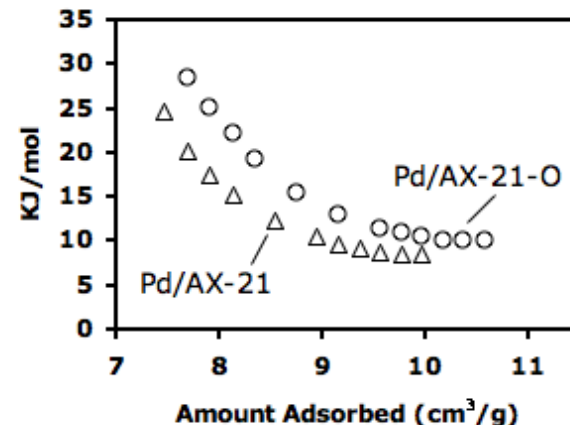
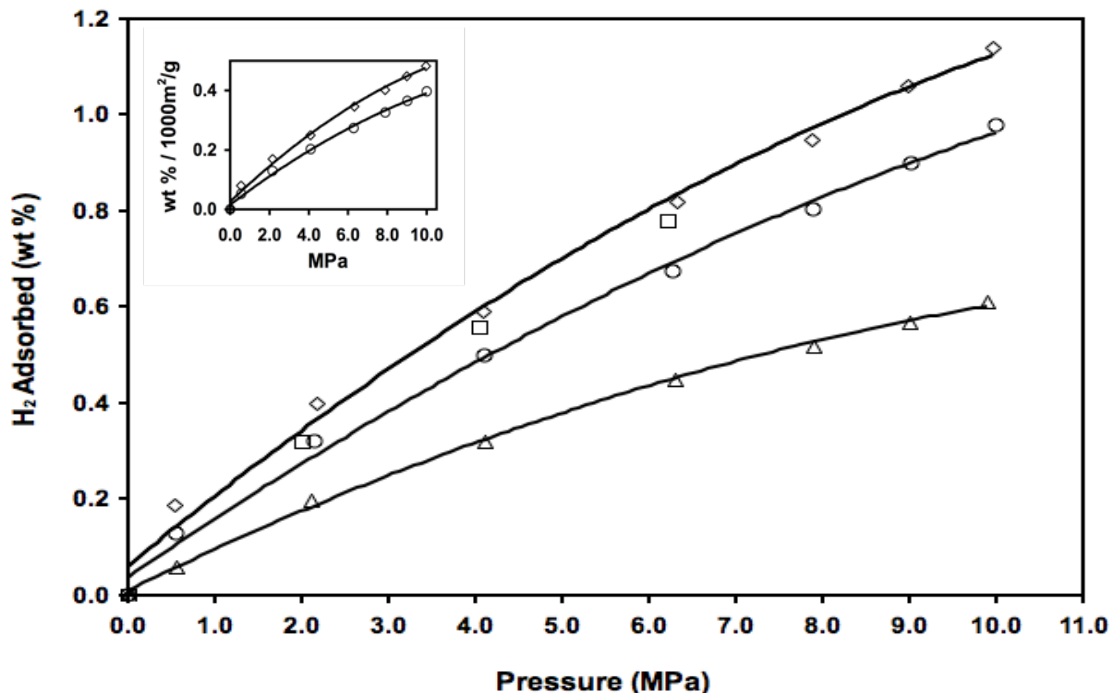
High pressure H₂ isotherm on Pt/AX-21 at 298K with presorbed CH₄ at P(CH₄) = 0 (○), 1.0×10⁻³ (●), 5.0×10⁻³ (▲), 1.0×10⁻² (■), and 0.1 atm (◆)



- By dosing 50 ppm CH₄ in H₂, the spillover-storage amount is increased by 15% or more. (Too much CH₄ would compete for ads. sites. The optimal concentration of CH₄ for max. spillover enhancement depends on the sorbent and is obtained empirically. All isotherms are reversible.)
- Enhancement effects by other hydrocarbons are being studied.
- Notes: (a) Theoretical spillover capacity for carbon > 2wt% per 1000 m²/g (assuming 1 H per surface C and 8.2 Å²/C site). (b) At 0.1 atm CH₄, CH₄ coverage ~ 0.01 monolayer.

Technical Progress: Spillover on Oxidized Carbon

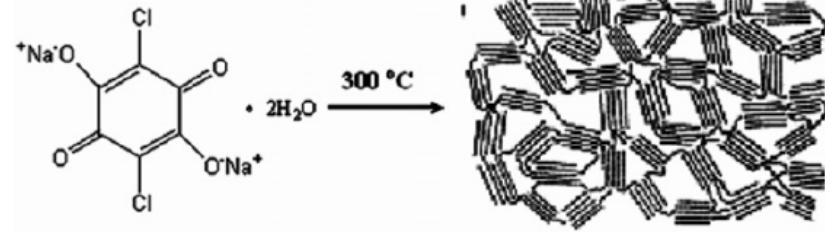
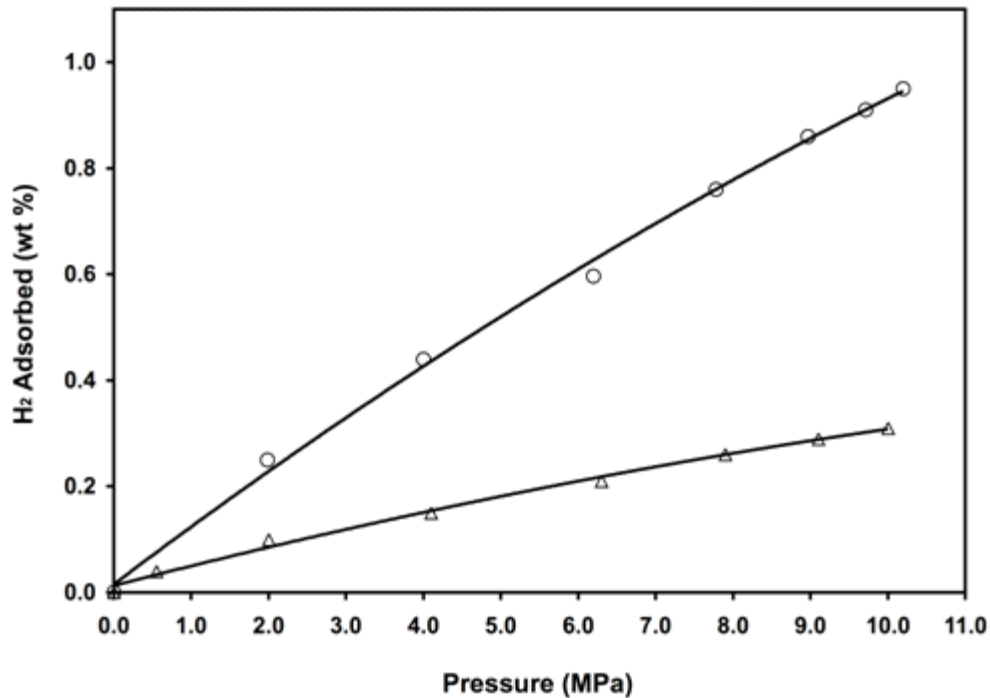
High-pressure hydrogen isotherms at 298 K for AX-21 (\triangle), Pd/AX-21 (\circ), Pd/AX-21-O (\diamond) and *2nd isotherm* on Pd/AX-21-O (\square); Inset: Hydrogen adsorbed on Pd/AX-21 (\circ) and Pd/AX-21-O (\diamond) normalized by BET surface area. 10wt% Pd doping for all samples
 AX-21-O: by oxidizing AX-21 in air at 200°C for 5 hr. O/C+O (w/w) = 13%
 BET S.A. : 2466 m²/g for Pd/AX-21 and 2362 m²/g for Pd/AX-21-O.



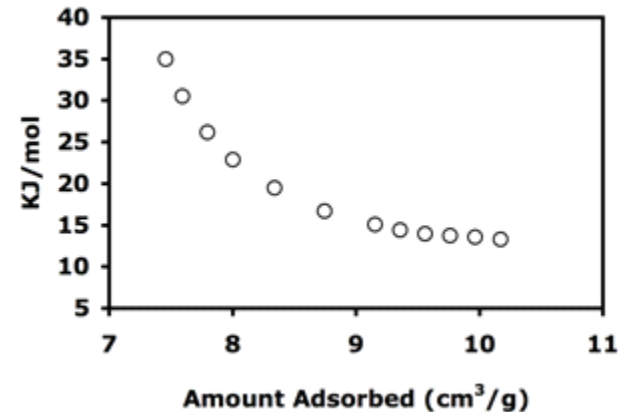
- Heats of adsorption: 9.0 kJ/mol for Pd/AX-21 and 10.1 kJ/mol for Pd/AX-21-O.
- Spillover amount was higher on oxidized carbon as a result of higher binding energy.
- Isotherms on Pd/AX-21 and Pt/AX-21 (after sample pre-treatment at 350°C *in vacuo*) are fully reversible. Three successive ads. Isotherms are identical. However, on oxidized AX-21, the 2nd ads. isotherm is slightly lower than the 1st, possibly due to reaction between H and weakly bound oxygen species. Further cyclic behavior is under study.

Technical Progress: Spillover on Graphite Oxide

High-pressure hydrogen isotherms at 298 K for 10% Pd/graphite oxide (○) and graphite oxide (△). BET S.A. : 788 m²/g for graphite oxide and 687 m²/g for Pd/graphite oxide. Heats of adsorption: 14.0 kJ/mol for Pd/graphite oxide.



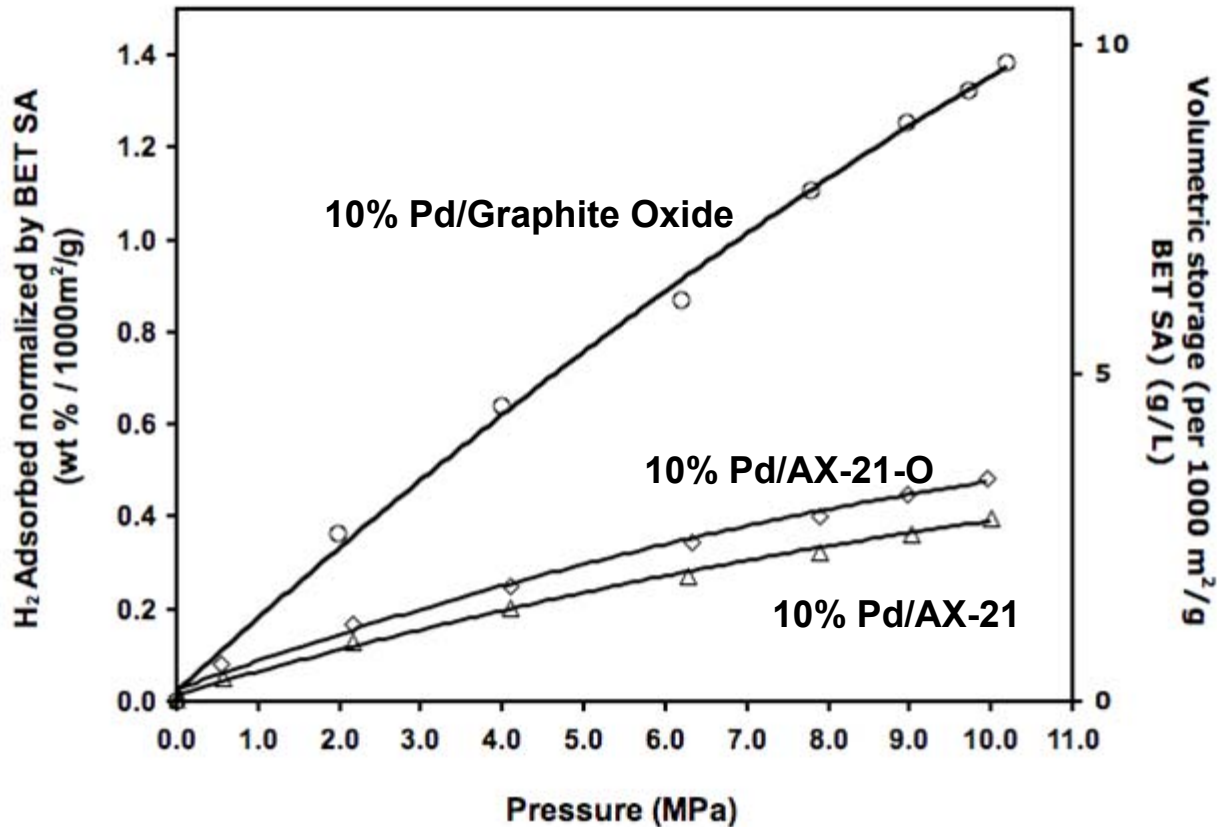
Graphite Oxide (~ C₂HO): From Bourlinos et al., *Carbon*, 45, 852 (2007)



- The spillover amounts were higher on graphite oxide and oxidized carbon, as a result of higher binding energies.
- Notes: (a) On $-\Delta H(\text{KJ/mol})$ vs. Amount Adsorbed: $10 \text{ cm}^3/\text{g} \cong 9\%$ of the amount adsorbed at 10 MPa. (b) The rates on oxidized carbon seem to be (very) slightly lower than on unoxidized C. (b) Cyclic behavior is under further study.

Technical Progress: Comparison of Spillover on Oxidized Carbons

High-pressure hydrogen isotherms at 298 K for 10% Pd/graphite oxide (○), Pd AX-21-O (◇) and 10% Pd/AX-21 (△), normalized by BET surface area .

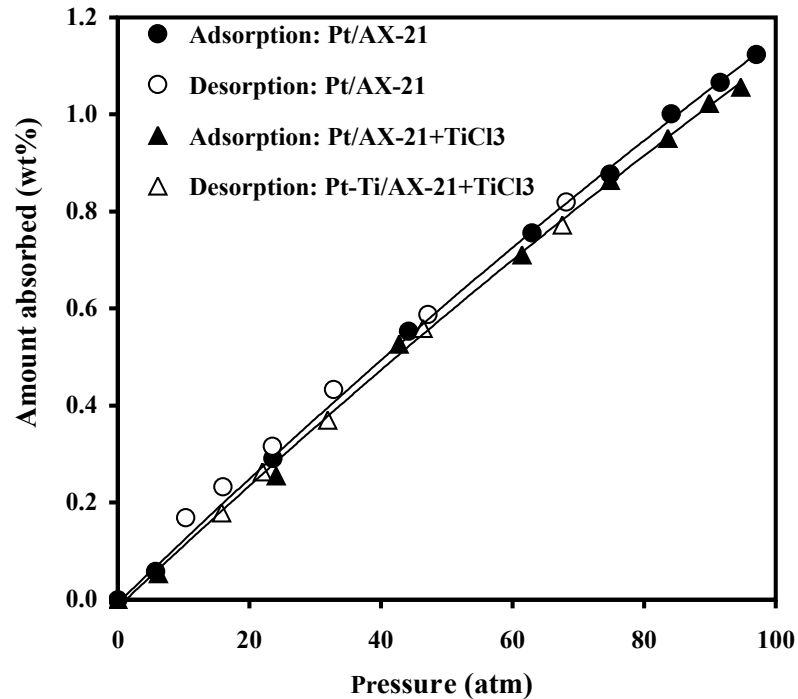


- The spillover amount on oxidized carbon depends on oxygen content (40% for GO, 13% for AX-21-O) and oxygen functional groups.
- Spillover on graphite oxide and oxidized carbons merits further research.

Technical Progress (con't)

Search for Catalysts: Spillover at 298K is slow. Although discharge rates exceed 0.02 g/s/kW, charge rates are slower than discharge.

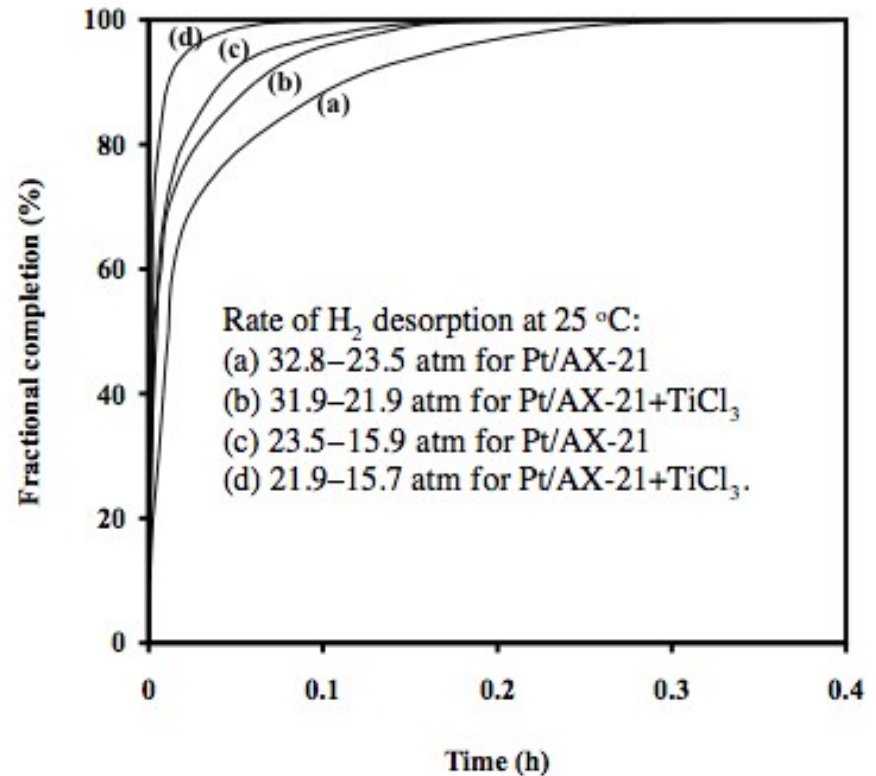
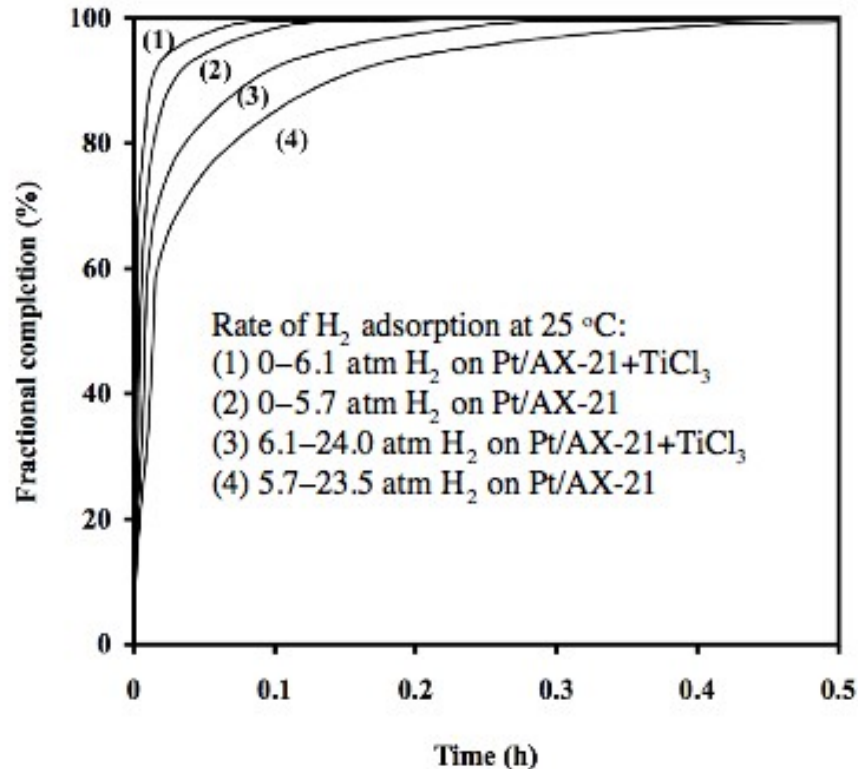
H₂ isotherms on Pt/AX-21 and Pt/AX-21+2%TiCl₃ at 298K



- Doping 2wt% TiCl₃ on Pt/AX-21 decreased spillover uptake slightly due to a decrease in BET surface area.
- The small hysteresis loop disappeared upon doping.

Technical Progress (con't)

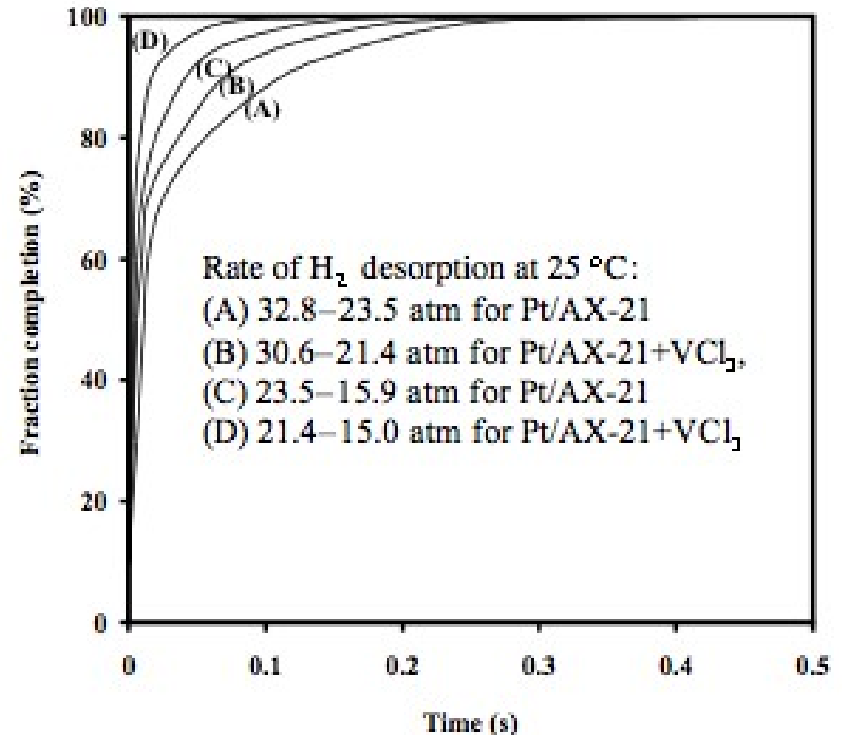
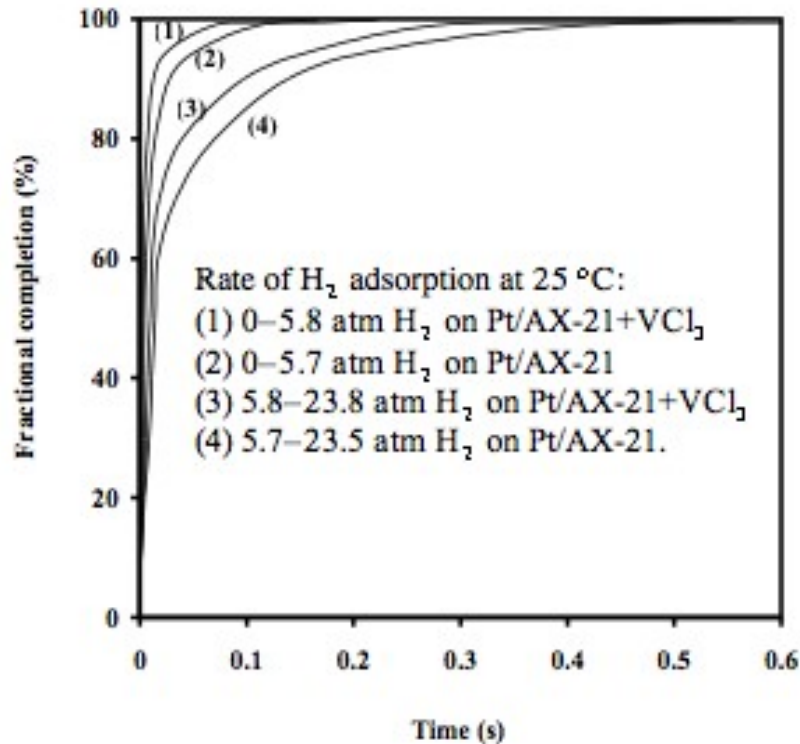
Charge/Discharge Rates on Pt/AX-21 and Pt/AX-21+2wt%TiCl₃ at 298K



- By sequential doping of 2wt% TiCl₃ on Pt/AX-21, rates of both charge and discharge at 298K increased.
- Co-doping 2wt% TiCl₃ showed similar catalytic effects.

Technical Progress (con't)

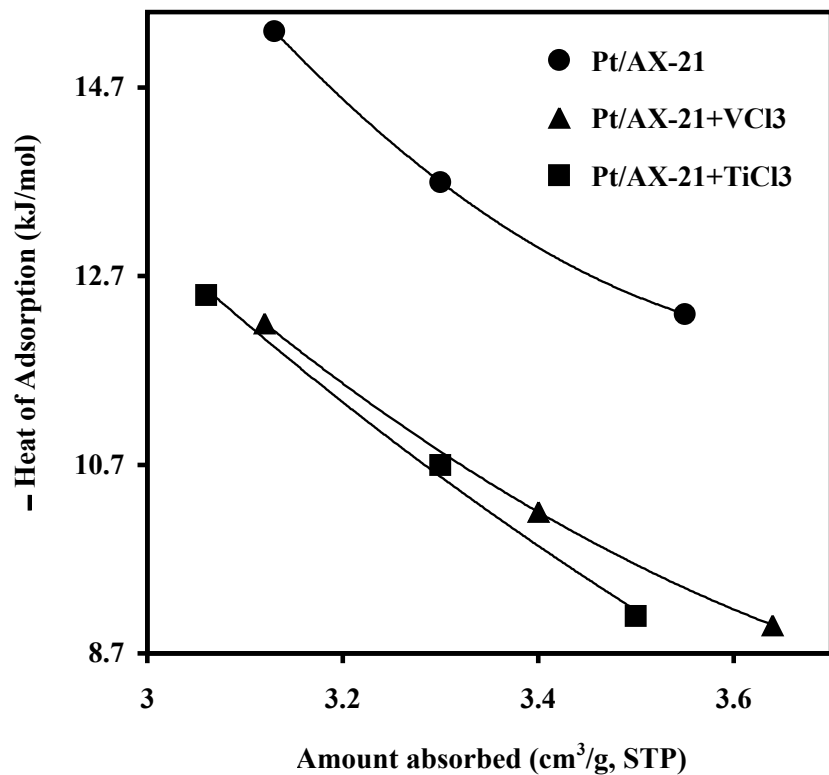
Spillover Rates on Pt/AX-21 and Pt/AX-21+2wt%VCl₃ at 298K



- By sequential doping of 2wt% VCl₃ on Pt/AX-21, rates of both charge and discharge at 298K increased.
- Co-doping 2wt% VCl₃ showed similar catalytic effects.

Technical Progress (con't)

Heats of Adsorption and Activation Energies for Surface Diffusion (ΔE) for Pt/AX-21 and Catalyst-Doped Pt/AX-21



Sample	Pressure step (mmHg)	ΔE (kJ/mol)
Pt/AX-21	65.0–74.0	7.5
Pt/AX-21+TiCl ₃	65.0–71.0	6.5
Pt/AX-21+VCl ₃	67.0–74.0	6.8

- The catalytic effects seemed to be related to the lowering in heats of adsorption.
- The activation energy for spillover was also reduced by catalysts (which led to faster surface diffusion). Further work is in progress.

Summary

- There are many ways to increase spillover-storage; two are shown here.
- Adsorbed gas molecules, from gaseous impurities in H_2 , can increase spillover-storage.
- Oxygen surface functionalities on carbon can increase spillover.
- A class of catalysts has been found for spillover rates - in both directions.
- Spillover-storage is potentially capable of meeting DOE system targets.
- The results of this work can facilitate design for viable storage systems.

Work in progress and future work plan

- Storage on oxidized carbons by spillover
- Storage by spillover with bridge-building on MOFs
- Quantitative understanding of kinetics of spillover-storage
- Developing catalysts for increasing spillover rates for both charge and discharge, and an understanding of catalytic mechanism
- New direct metal-doping techniques (including plasma treatments) on AX-21 and other ultra-high-surface-area carbons (i.e., templated carbons)