# 2010 DOE Hydrogen Program Review
# **Hydrogen Storage by Spillover**

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**Project ID: ST078**

# Overview

## Timeline

- Project start date: 2/1/05
- Project end date: 6/30/10
- Percent complete: 100%

## Budget

- Total project funding: $1,644,401
  - DOE share: $1,275,355
  - Contractor share: $369,046
- Funding received in FY09: $435,855
- Funding for FY10: $0

## Barriers

- General
  - Weight & Volume
  - Rates (Refueling and discharge)
- Reversible Solid-State Material
  - Hydrogen Capacity & Reversibility
  - Lack of Understanding of $H_2$ Spillover

## Partners

- Sample/adsorbed H
  Verification, Characterization & Mechanism
  **NREL, Rice U, APCI, NIST, UNC, SwRI®**
- Plan industrial collaboration after 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

- Modify carbons by plasma treatment to enhance spillover storage by adding surface functional groups (such as oxygen groups)

- Search for and develop "catalysts" for spillover to increase rates

- Develop metal-doped non-carbon sorbents (i.e., zeolites) for spillover storage to achieve DOE volumetric target (28g/L for 2010, at 298K)

- 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

# Technical Progress: Understanding Kinetics of Spillover
*Adsorption and Desorption of $H_2$ on Pt/Carbon in Steps at 298K (Results on bridged IRMOF-8 are similar)*
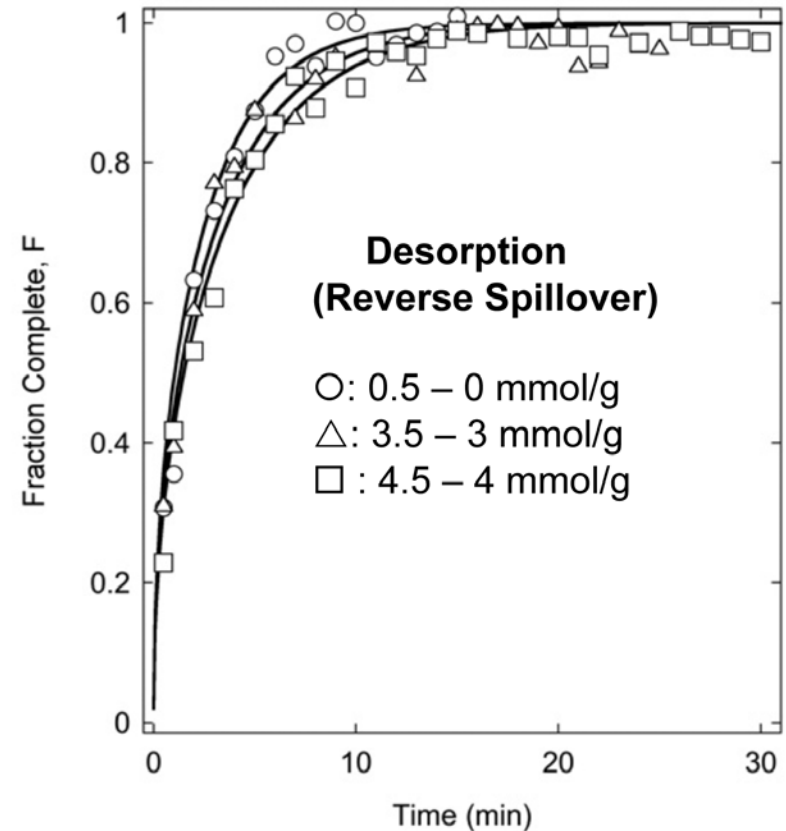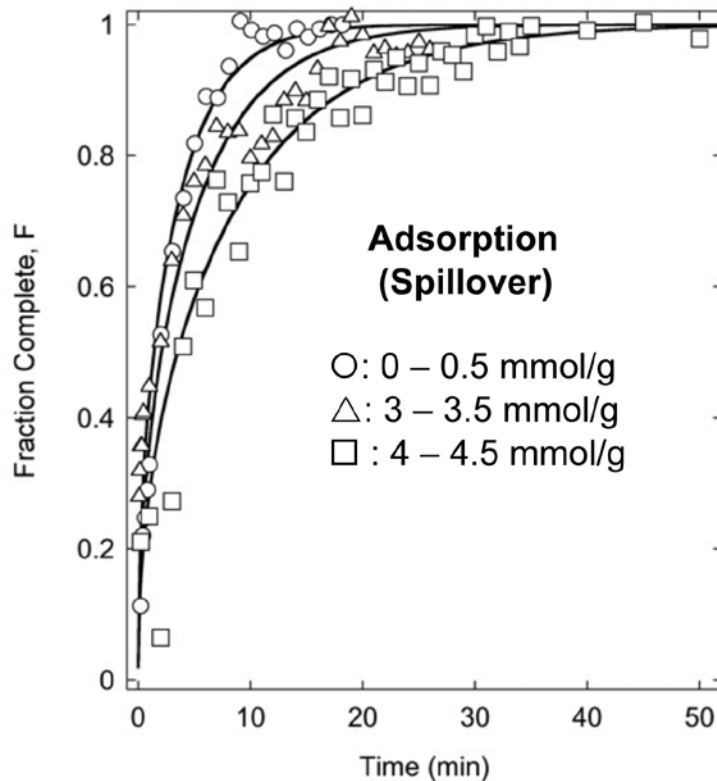


*Desorption rates are always faster than adsorption rates !*

# Technical Progress: Kinetics of Spillover
# Recombination of H Atoms and Direct Desorption Rates



Spillover

Reverse Spillover

Metal
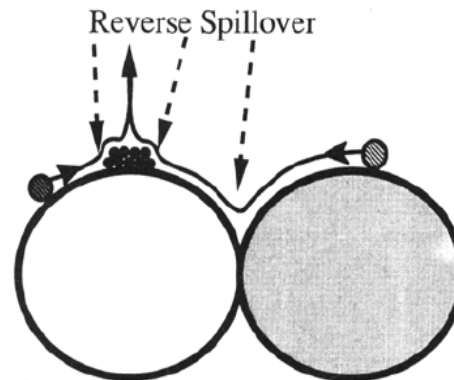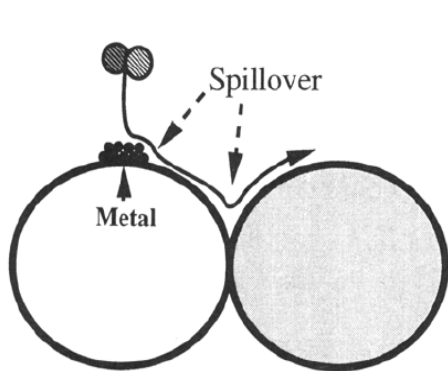
*Courtesy of Conner & Falconer, 1995*

Desorption Rate – Adsorption Rate
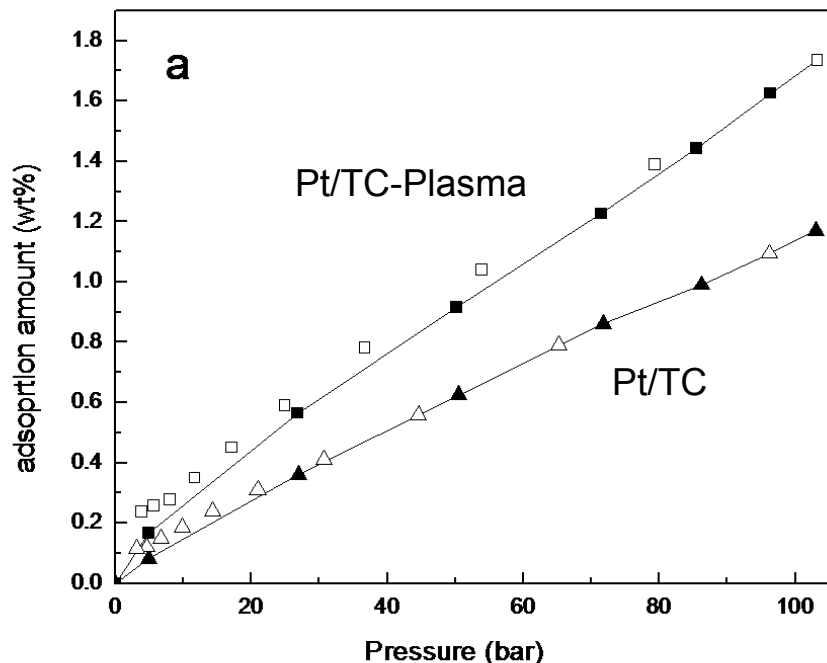  = Recombination Rate  ➔

Reason: Recombination of H atoms on carbon leads to direct desorption, which is included in desorption but not in adsorption rate measurement.

*Lachawiec and Yang, J. Phys. Chem. C. 113, 13933 (2009)*



0 – 0.5 mmol/g

3 – 3.5 mmol/g

4 – 4.5 mmol/g

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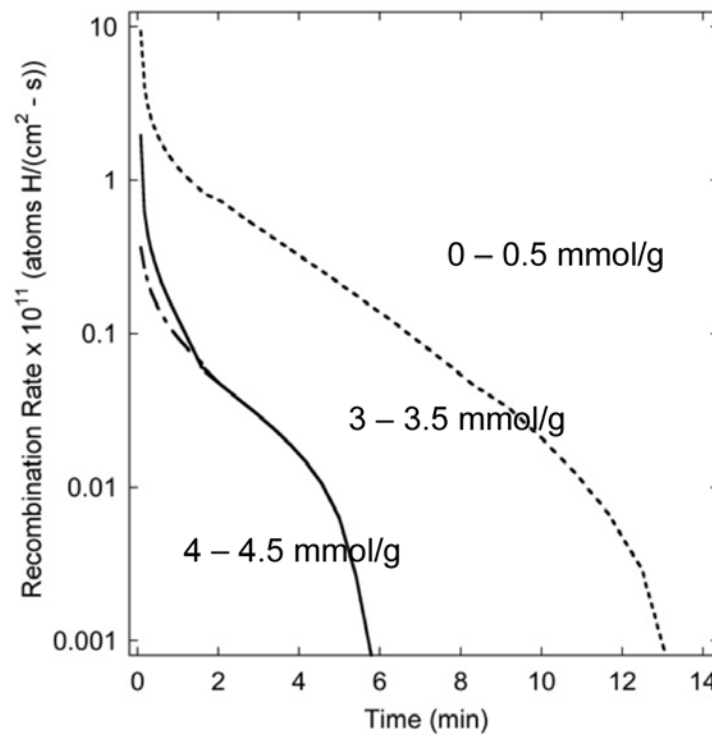
# Technical Progress
## Increased Spillover Storage (at 298K) on Carbon (i.e.,Templated Carbon, TC) by O$_2$ Plasma



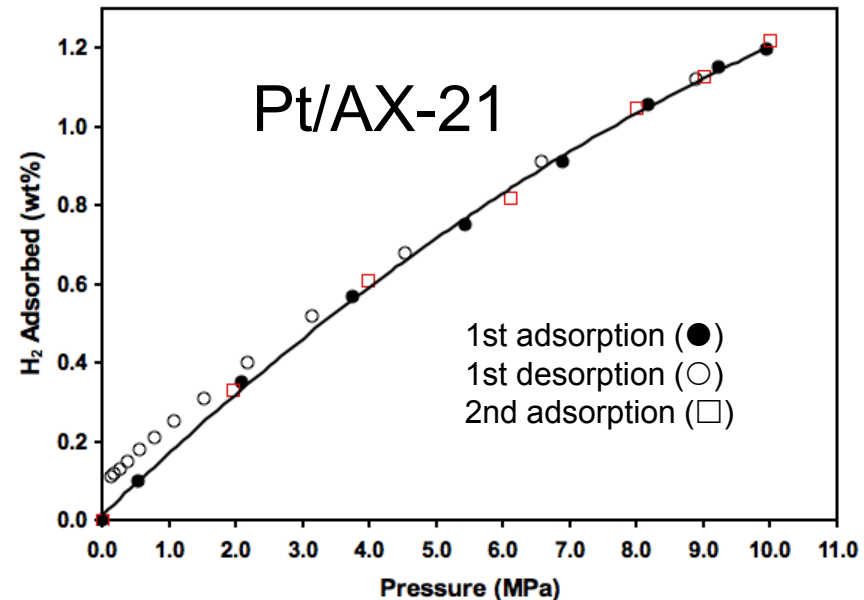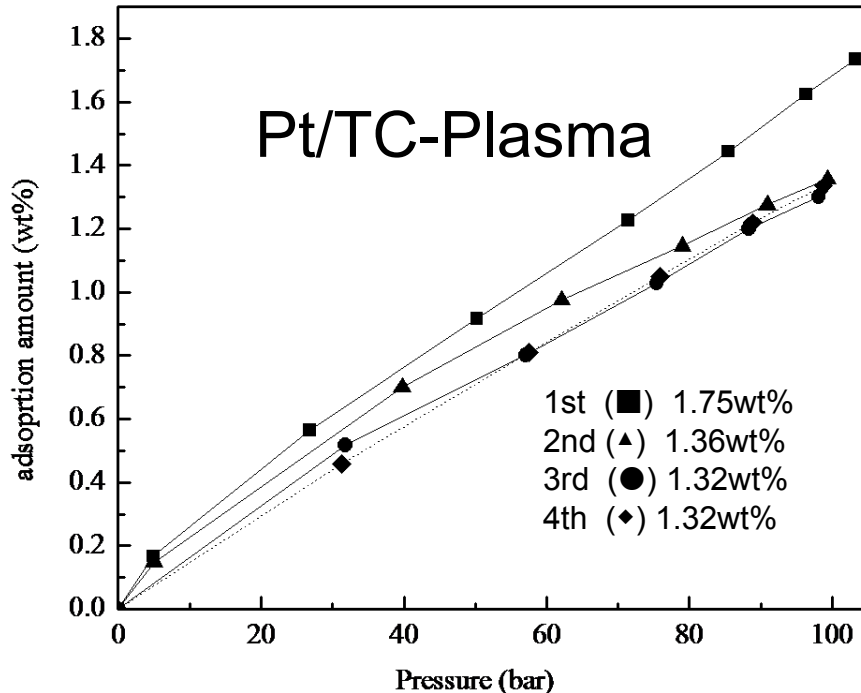| S.A. and XPS (C$_{1s}$ Rel. Area) | TC | TC-Plasma | Pt/TCPlasma 4$^{th}$ cycle |
|---|---|---|---|
| BET S.A., m$^2$/g | 3554 | 3110 | |
| C-C (284.6eV) | 89.4% | 65.08% | 67.53% |
| C-OH (286.1eV) Hydroxyl | 4.61% | 5.72% | 6.37% |
| C=O (287.6eV) Semiquinone | 3.77% | 25.76% | 25.13% |
| -O-C=O (289.6eV) Lactone | 2.19% | 3.44% | 0.97% |

- Pretreatment of carbon by O$_2$ plasma before metal-doping increased surface oxygen groups, particularly semiquinone and lactone groups.
- The plasma pretreatment significantly increased the spillover storage to 1.75wt% at 100 bar.
- Heat of adsorption for Pt/TC-plasma was higher than that on Pt/TC (13 vs. 9.6 kJ/mol).



Lactone

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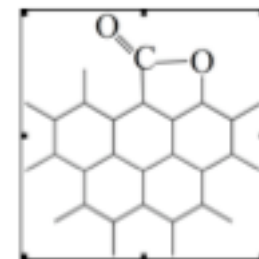
# Technical Progress

## Cyclic $H_2$ Adsorption/Desorption at 298K on 6wt% Pt/TC-Plasma

Pt/TC-Plasma

1st  (■)  1.75wt%
2nd (▲)  1.36wt%
3rd  (●)  1.32wt%
4th  (◆)  1.32wt%

*adsorption amount (wt%)* vs *Pressure (bar)*

Pt/AX-21

1st adsorption (●)
1st desorption (○)
2nd adsorption (□)

*$H_2$ Adsorbed (wt%)* vs *Pressure (MPa)*

• No further reaction occurred after 3 adsorption/desorption cycles.
• $O_2$ plasma treatment increased the reversible amount from 1.2wt% to 1.32wt%.
• XPS analysis showed that lactone groups reacted with the spiltover H.
• Molecular orbital calculations showed that among the oxygen groups, the strongest
  binding energy with H was with the lactone group.
(*Wang and Yang, J. Phys. Chem. C, 114, 1601 (2010)*)

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# Technical Progress
## Toward DOE Volumetric Target: Spillover on Zeolites at 298K



Ca-LSX($\bigcirc$)
Li-LSX ($\square$)
Mg-LSX ($\triangle$)
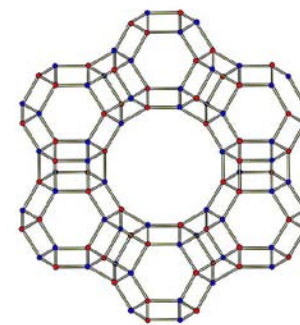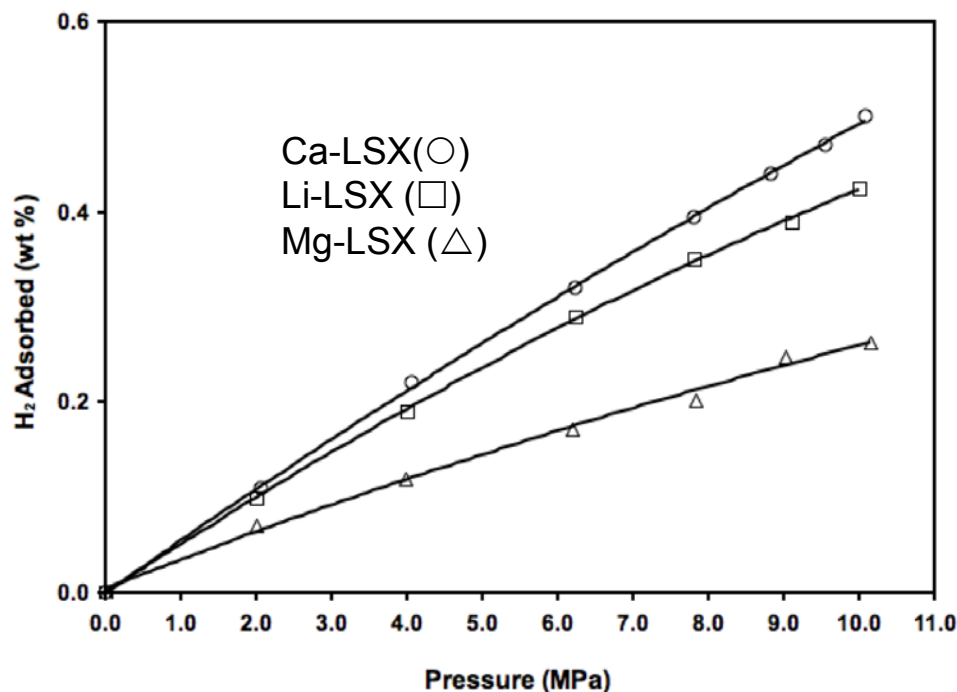
LSX: Low silica X zeolite
Faujasite with Si/Al = 1

• The densities of zeolites are substantially higher (2-3 times higher) than that of carbons and MOFs, and have high densities of cations for interactions with hydrogen. Hence they are most promising for meeting DOE volumetric targets.

• Among zeolites, Ca-LSX and Li-LSX zeolites show the highest $H_2$ capacities (up to date) at 298K.
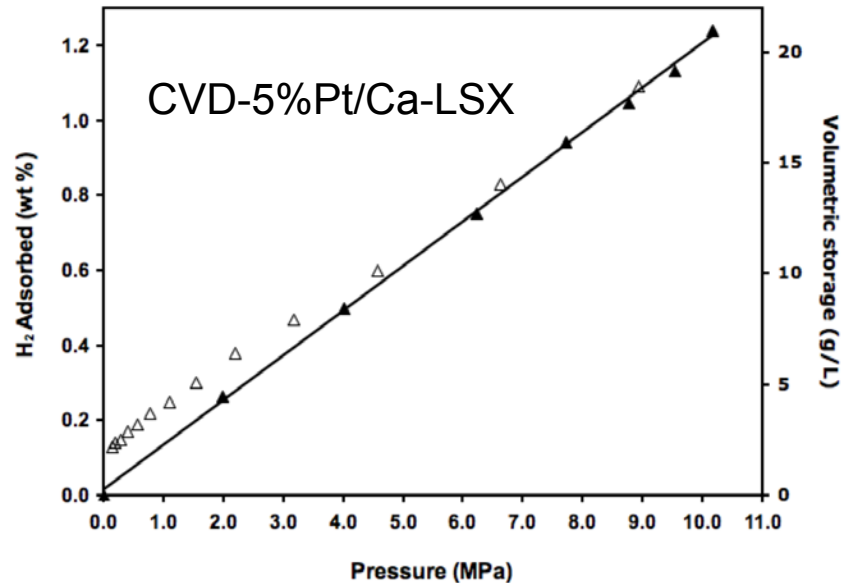
# Technical Progress
## Toward DOE Volumetric Target: Spillover on Zeolites at 298K

Pt (1-3 nm) doped by incipient wetness

Pt (1-3 nm) doped by CVD



5wt% Pt/Li-LSX

Li-LSX

CVD-5%Pt/Ca-LSX
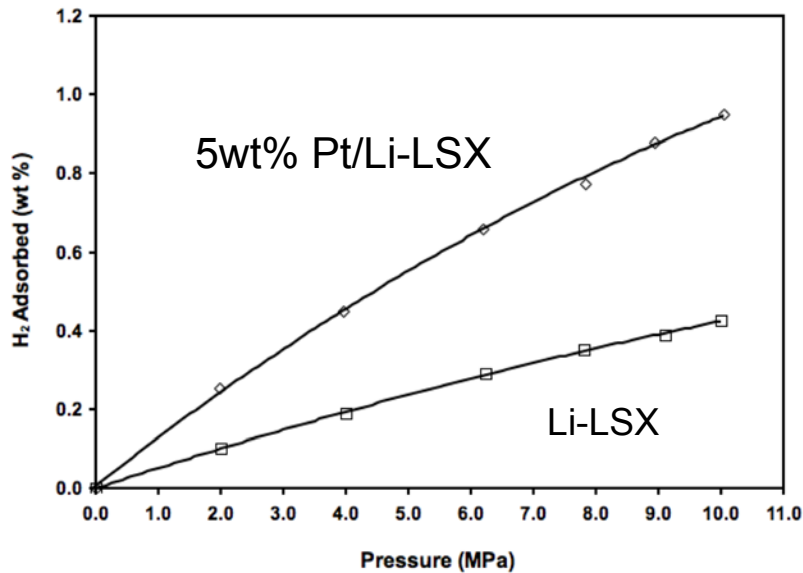
- The best spillover sample was Pt-doped by CVD using (Trimethyl) methylcyclopentadienyl platinum (IV) as Pt precursor.
- At 298K and 100 atm, the spillover capacity for Pt/Ca-LSX reached 1.27 wt% (enhancement = 2.4X), translated to a vol. capacity of 21 g/L, based on pelletized, dehydrated density of 1.65 g/cm$^3$.  (DOE Target = 28 g/L for 2010)

# Technical Progress
## Toward DOE Volumetric Target: Spillover on Zeolites at 298K

10wt% Ni doped by incipient wetness
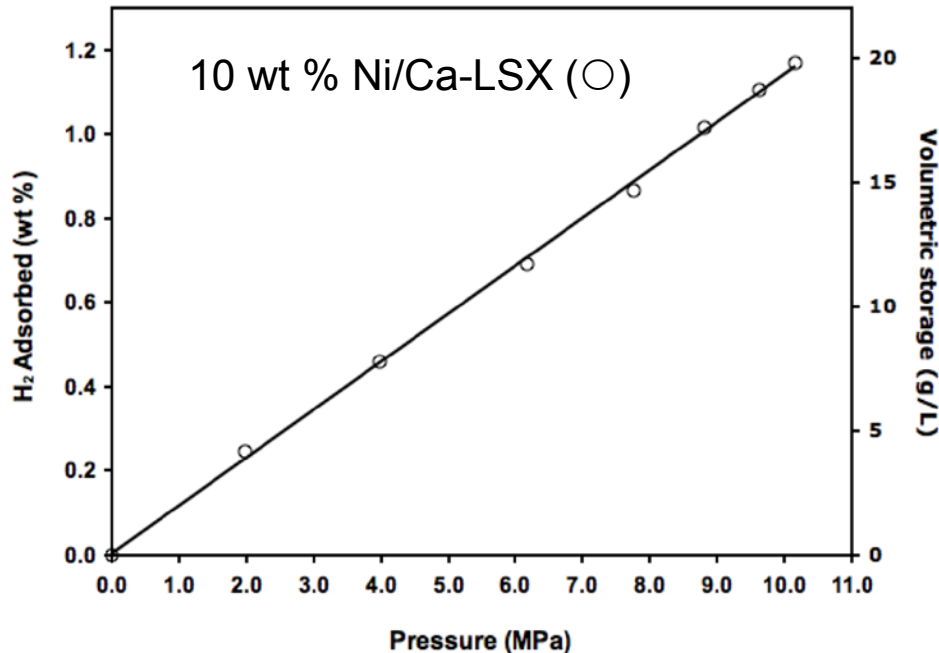


The volumetric capacity for Ni/Ca-LSX is estimated to be 20 g/L, based on the dry pellet density of 1.7 g/cm$^3$. (DOE volumetric target = 28 g/L for 2010)

(Wang & Yang, "Hydrogen Storage Properties of Low-Silica Type X Zeolites"
*Ind. Eng. Chem. Res., DOI:* 10.1021/ie1003152)

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# Technical Progress
## Improving Rates of Charge/Discharge by Added Catalyst (TiF$_3$)

Hydrogen on 6wt%Pt/Maxsorb at 298K
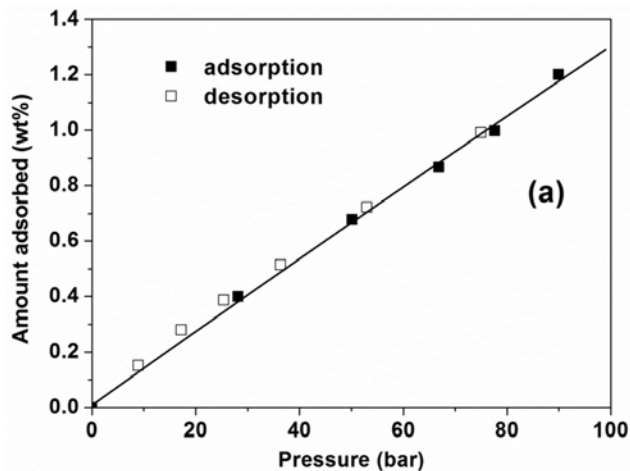
Pt/Maxsorb doped with 2wt% TiF$_3$
Heat-treated at 473K (A) & 673K (B)
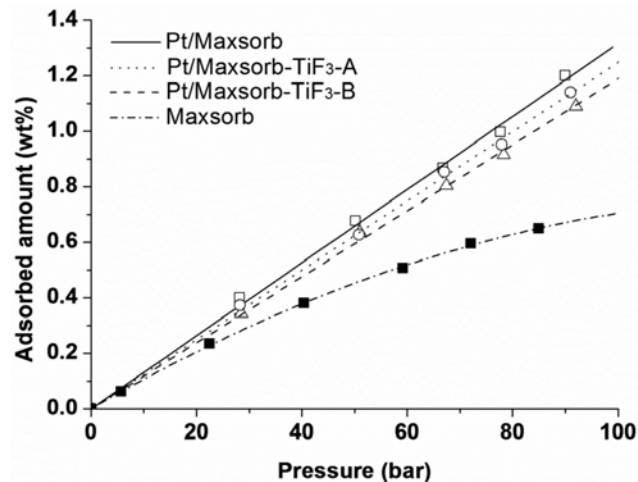
| Sample | BET SA (m$^2$/g) | Pore volume (cm$^3$/g) [a] | Median pore diameter (Å) [a] |
|---|---|---|---|
| Maxsorb | 3277 | 1.60 | 17.6 |
| Pt/Maxsorb | 2882 | 1.50 | 14.7 |
| Pt/Maxsorb-TiF$_3$-A | 2825 | 1.47 | 14.7 |
| Pt/Maxsorb-TiF$_3$-B | 2801 | 1.47 | 14.6 |

- Doping 2wt% TiF$_3$ decreased the H$_2$ capacity slightly due to decreased surface area and pore vol.

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# Technical Progress
## Improving Rates of Charge/Discharge by Added Catalyst (TiF$_3$)

Adsorption Rates at 298K

Desorption Rates at 298K
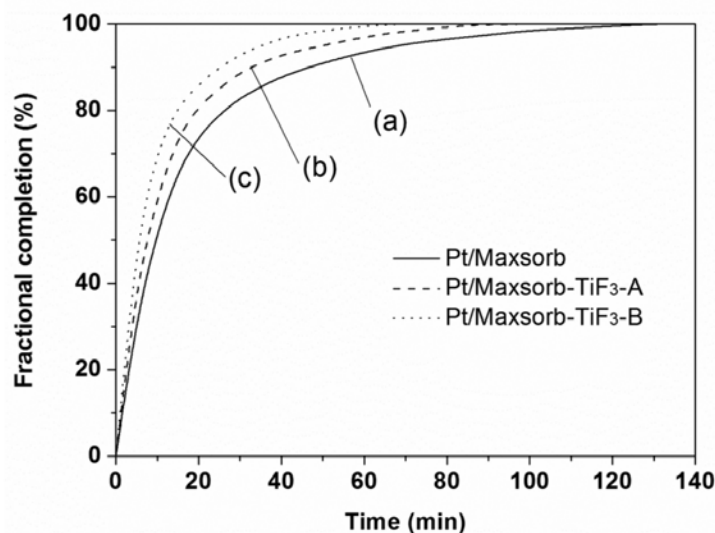


Pressure step: (a) 0-28.6 atm for Pt/Maxsorb;
(b): 0-28.7 atm for Pt/Maxsorb-TiF$_3$-A;
(c) 0-28.7 atm for Pt/Maxsorb-TiF$_3$-B.
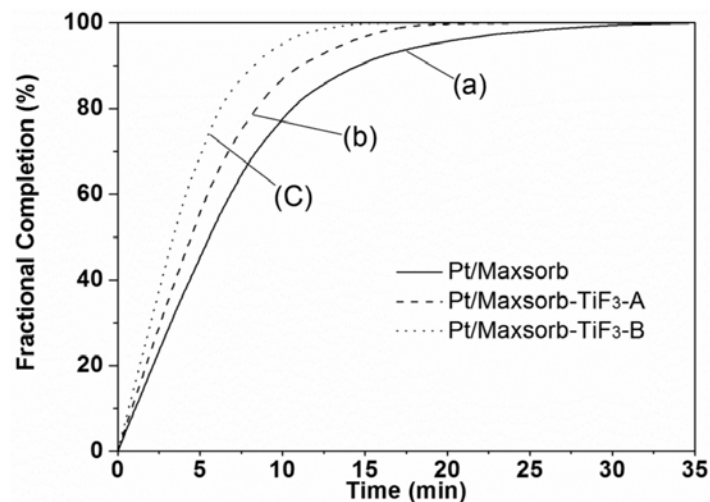
Pressure step: (a( 77.7-52.8 atm for Pt/Maxsorb;
(b): 78.1-53.1 atm for Pt/Maxsorb-TiF$_3$-A;
(c) 77.9-52.9 atm for Pt/Maxsorb-TiF$_3$-B.

• Rates for both charge and discharge at 298K are effectively increased by doping 2wt% TiF3.
• XPS results indicate that C-F bonds are formed in the doped samples
(Chen and Yang, Langmuir, DOI: 10.1021/la100172b)

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# Summary

- Metal doped zeolites are most promising in meeting DOE volumetric targets, e.g., the spillover storage capacities (at 298K and 100 atm) for Ni/Ca-LSX and CVD-5%Pt/Ca-LSX are 20 g/L and 21 g/L, respectively (DOE target = 28 g/L for 2010).

- Doping 2wt% $TiF_3$ on Pt/carbon nearly doubles the rates for both charge and discharge.

- $O_2$ plasma treatment, by forming lactone groups on carbon, increases the reversible amount of Pt/carbon from 1.2wt% to 1.32wt% (at 298K and 100 atm).

- For spillover storage, the desorption rate is always higher than that of adsorption, and the difference is the H-atom recombination rate.

- Spillover-storage is potentially capable of meeting DOE system targets.

- The results of this work can facilitate design for viable storage systems.

# Overview/Highlights (2005 – 2010)

- Achieved 1.2 wt% hydrogen storage on a Pt-doped superactivated carbon (AX-21) (and 1.3 wt% for Pt/Maxsorb) at 100 atm and 298K. Capacities of 1.6wt% was obtained on Ru/carbon, and 1.1wt% on Ni/carbon.

- Achieved volumetric capacities of 20 g/L and 21 g/L, respectively (DOE target = 28 g/L for 2010), for Ni/Ca-LSX and CVD-5%Pt/Ca-LSX zeolites at 298K and 100 atm.

- Developed a bridge-building technique for spillover storage, and obtained up to 4wt% storage with MOFs at 298K and 100 atm (US and foreign patents pending)

- The spillover storage process is reversible at 298K, i.e., full storage capacity is obtained after degassing at 298K.

- Developed a simple isotherm equation that is applicable to all spillover sorbents

- For all spillover sorbents, the rates of discharge at 298K exceeded the DOE target of 0.02 g/s/kW.

- Developed catalysts that could increase the rates of both charge and discharge for spillover storage

- Increased spillover storage capacities on carbon by 10-40% by each of the following techniques: introducing surface oxygen groups, doping nitrogen and/or boron, plasma treatments, and dosing $H_2$ with hydrocarbon impurities

- Using deuterium isotope tracer, direct evidence for dissociation/spillover and reverse spillover was obtained.

# Additional Slides

# Outline of Proper Metal Doping Procedure by Incipient Wetness for Pt/AX-21

- Measure 200mg dry AX-21 or Maxsorb (dried at 393K). Add acetone until all particles are completely dissolved in a very dilute slurry (~20-100mL) (*a more dilute solution increases metal dispersion and hence the spillover enhancement*).

- Dissolve 26 mg $H_2PtCl_6$ (Aldrich, 99.9%) in at least 20mg acetone and add at a consistent dropwise rate over at least 10 min while stirring vigorously (*using overly concentrated Pt precursor solution and/or faster mixing will lead to poor and UNEVEN metal dispersion and substantially less spillover[1-3]*). Stir vigorously for at least 10 min after the last drop is added.

- Sonicate (100 W, 42 kHz ) the solution for 1 hour and then evaporate the excess liquid in an oven at 333K (*allowing the solution to fully dry will lead to lowered enhancement*).

- Dry the sample further in a quartz tube under He flow at 393K for 2 h.  Change the flow to $H_2$ and raise the temperature to 573K at 1K/min and hold for at least 2 h (*holding for long times ensures complete reduction of Pt*)[4]. Switch the flow to He to purge (*purge for at least 4 h and cool at a rate no larger than 1K/min, otherwise Pt will react with air vigorous during sample transfer leading to poor metal dispersion*)[1].

- Sample is transferred to measurement system, using a degas procedure of 623K and a heating rate of no more than 5K/min under vacuum for 8 hours. (Degas at only 573K is not adequate since spiltover hydrogen during $H_2$ reduction will remain on the carbon surface.)[1]

- In $H_2$ measurement, the leak rate that is acceptable for physisorption[1] is not acceptable for spillover,[5] and allowing large dead spaces (in sample or reservoir cells) will lead to large errors.[1,5]

1. Stadie et al. *Langmuir*, DOI: 10.1021/la9046758
2. Chen and Yang, *Langmuir*, DOI: 10.1021/la100172b
3. Tsao et al., *J. Phys. Chem. Lett.* 1, 1060 (2010).
4. Li and Yang, *J. Phys. Chem*. C 2007, 111, 3405.
5. Lachawiec et al., *Rev. Sci. Instr.* 79, 063906 (2008).