

# Novel Metal Perhydrides for Hydrogen Storage

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Project ID: stp\_21\_hwang

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# Overview

## Timeline

- Start: April 1, 2004
- Finish: Phase 1, May 31, 2009;  
total project, May 31, 2011
- % Complete: Phase 1, 98%

## Budget

- Total Project funding
  - DOE – Phase 1: \$694,816; total project: \$1,719,806
  - Cost Share – Phase 1: \$195,677; total: \$451,428
- Funding received in FY08: \$364,816
- Funding received in FY09: none

## Barrier

- A. Cost
- B. Weight and Volume
- C. Efficiency

## Partners

- Interactions/ collaborations
  - Clemson University
  - University of Minnesota
  - NanoMas, Inc.
  - Boda Corporation
  - Oak Ridge National Lab
- Project lead
  - Michigan Technological University

# Objectives

- The overall focus of this project
  - Develop a new kind of materials capable of binding H<sub>2</sub> molecules into clusters
  - Enhance H<sub>2</sub> adsorption/desorption by means of the “hydrogen cluster” formation/decomposition so that the capacity of materials for H<sub>2</sub> storage and the kinetics for H<sub>2</sub> release have potential to meet the DOE 2010 and 2015 target
- The objective over the past year
  - Study the H<sub>2</sub> adsorption behavior of material systems having charged species in the material structure
  - Design & develop material systems capable of auto-charging under H<sub>2</sub> pressure
  - Study the H<sub>2</sub> adsorption behavior of materials systems capable of auto-charging under H<sub>2</sub> pressure
  - Design & develop devices for directly measuring H<sub>2</sub> sorption in electric field
  - Study the H<sub>2</sub> adsorption behavior of materials systems charged by applied electric potentials
- Relevance to Overall DOE Objectives
  - By the concept of charge-induced H<sub>2</sub> cluster formation, the H<sub>2</sub> storage capacity of the materials has potential to exceed 0.06kg H<sub>2</sub>/kg system, the DOE 2010 target

# Result Highlights

- Hypothesis of charge-induced hydrogen sorption enhancement has been experimentally demonstrated.
- Electrically charged system yields 200 to 550% hydrogen sorption enhancement for the spill over approach at room temperature under 1-5 bar pressure.

# Milestones

## 04-30-2008 :

- Materials and devices developed for direct H<sub>2</sub> sorption measurement in electric field
- The effect of charge-induced hydrogen sorption enhancement has been identified and verified using direct sorption measurement approach with five material systems:
  - Dehydrated vermiculite having interlayer cations
  - Activated carbon with charge generating materials
  - NiO with charge generating materials
  - Activated carbon charged by applied electric potentials
  - Pt/carbon-activated carbon (Spill Over approach) charged by applied electric potentials

## 04-30-2009

- Design and develop materials with high intrinsic H<sub>2</sub> sorption capacity
- Design and develop of storage systems hosting high charge population
- Combine and optimize the high intrinsic sorption system & high charge population system to meet the DOE target

## Go/No Go Milestone

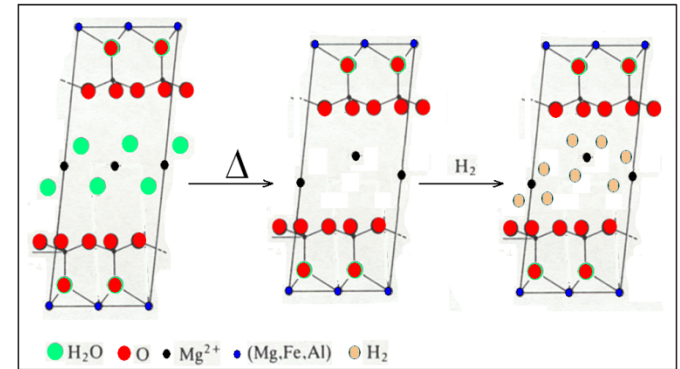
Whether the new system has the potential to achieve the technical target of exceeding 6wt% hydrogen storage capacity will be the criteria for the decision

# Approach

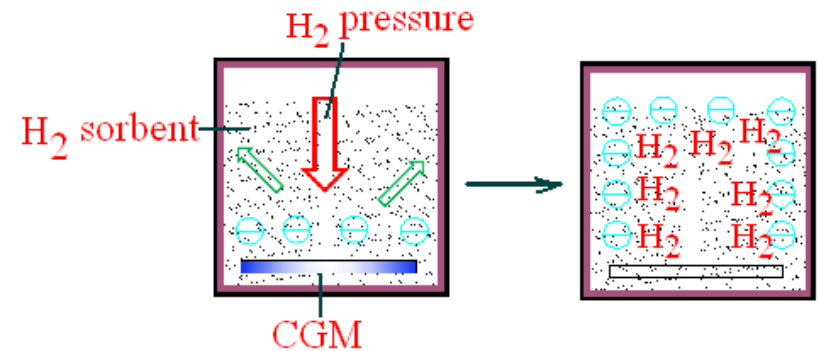
- The study is based on the concept that protons, metal and non-metal ions are capable of forming  $H_2$  clusters and thus to enhance the  $H_2$  storage capacity
  - Proton-Hydrogen clusters:  $H^+ + nH_2 \rightarrow [H(H_2)_n]^+$  (e.g.  $H_3^+$ ,  $H_5^+$ , etc.)
  - Cation-hydrogen clusters:  $M^{Z+} + nH_2 \rightarrow [M(H_2)_n]^{Z+}$  [e.g.  $Mg^{2+}(H_2)_4$ ,  $Ni^{2+}(H_2)_8$ , etc.]
  - Anion-hydrogen clusters:  $X^{Z-} + nH_2 \rightarrow [X(H_2)_n]^{Z-}$  [e.g.  $F^-(H_2)_4$ ,  $O^{2-}(H_2)_8$ , etc.]
- However, where to look for these charged species?
  - Gaseous phase? – Too dilute to be practical
  - Simple ionic compounds? – cations and anions are too close to accommodate  $H_2$  clusters
- In the 08' research, the following approaches were employed for studying the charge effect
  - Utilize minerals that could expose metal ions to  $H_2$  by proper treatment
  - Utilize materials that could generate charge under  $H_2$  pressure
  - Apply electric potential to  $H_2$  adsorbents

# Approach

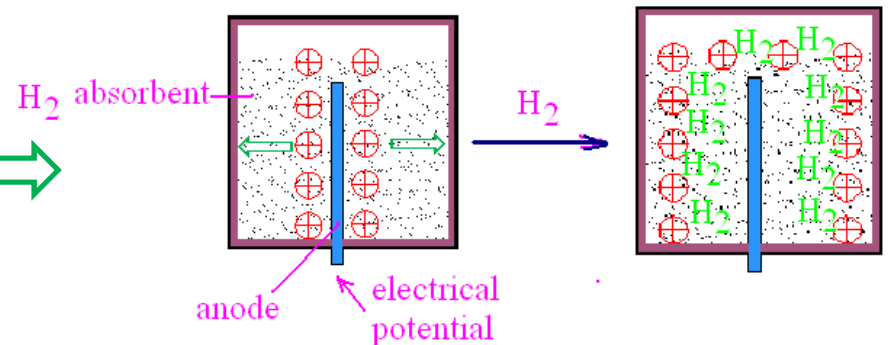
- Utilize minerals that could expose metal ions to  $H_2$  by proper treatment



- Utilize pressure-induced charge generating materials (CGM)



- Apply electric potential to  $H_2$  adsorbents



# Technical Progress/ Accomplishments Summary

- Advance the research focus from computer modeling to direct H<sub>2</sub> sorption
- H<sub>2</sub> sorption on five material systems has been investigated:
  - Dehydrated vermiculite
  - Activated carbon + charge-generating materials (CGM)
  - NiO +CGM
  - Activated carbon + 2000V potential
  - Pt/carbon + activated carbon + 2000 V potential
- All of the five systems demonstrated enhanced H<sub>2</sub> sorption in the presence of charges

## ○ Dehydrated vermiculite

Dehydration temperature (°C)	150	500	700	900
Sorption enhancement (%)*	-	7	19	38

\* Relative to sorption on samples dehydrated at 150 °C , 80 bar

## ○ Activated carbon + CGM

Hydrogen pressure (bar)	50	60	70	80
Sorption enhancement (%)*	12	19	24	27

\* Comparison between sorption on samples with & w/o CGM

## ○ NiO+CGM

Hydrogen pressure (bar)	50	60	70	80
Sorption enhancement (%)*	57	72	83	87

\* Comparison between sorption on samples with & w/o CGM

## ○ Activated carbon + 2000V potential

Hydrogen pressure (bar)	1	5	20	40
Sorption enhancement (%)*	120	55	20	10

\* Comparison between sorption on samples with & w/o e-potential

## ○ Pt/carbon + activated carbon + 2000 V potential

Hydrogen pressure (bar)	1	5	20	40
Sorption enhancement (%)*	550	200	72	34

\* Comparison between sorption on samples with & w/o CGM



# Technical Progress/ Accomplishment: Treated Vermiculite

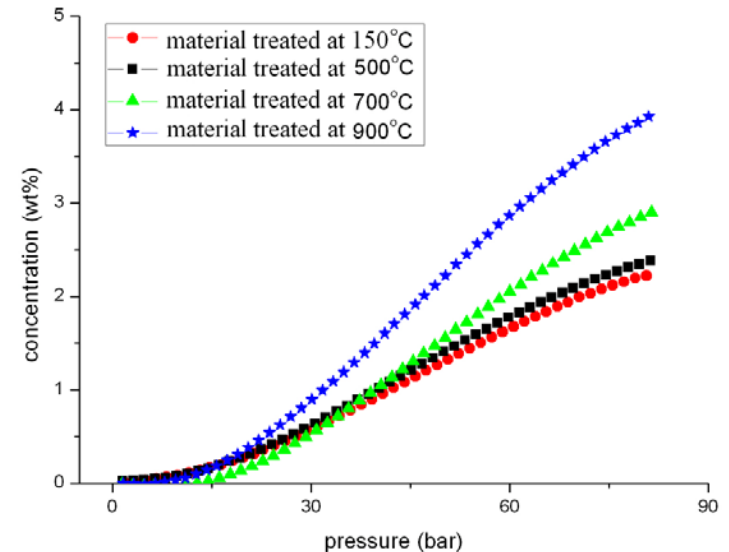
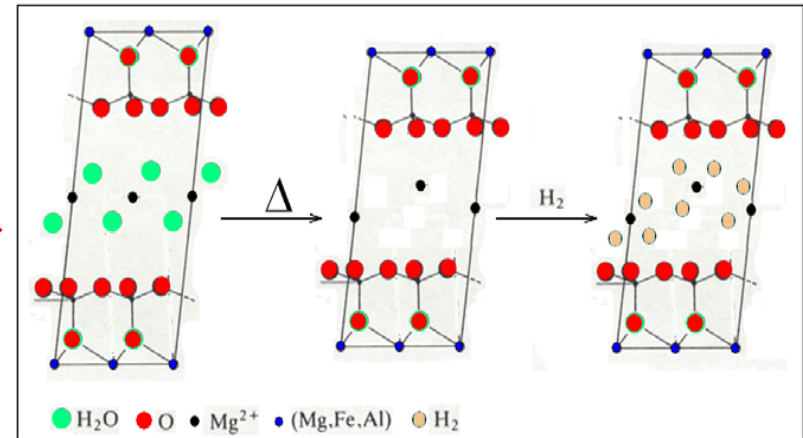
## • Concept

- Removal of H<sub>2</sub>O around Mg<sup>2+</sup> exposes the cations to H<sub>2</sub> atmosphere
- Clustering of H<sub>2</sub> around Mg<sup>2+</sup> could lead to enhanced H<sub>2</sub> sorption

## • Sorption behavior

- Increase of sorption was observed at 77K from samples with increased treatment temperature
- no noticeable differences of the surface properties between samples treated at different temperatures

- **The enhanced sorption is due to the increased Mg<sup>2+</sup> exposure**

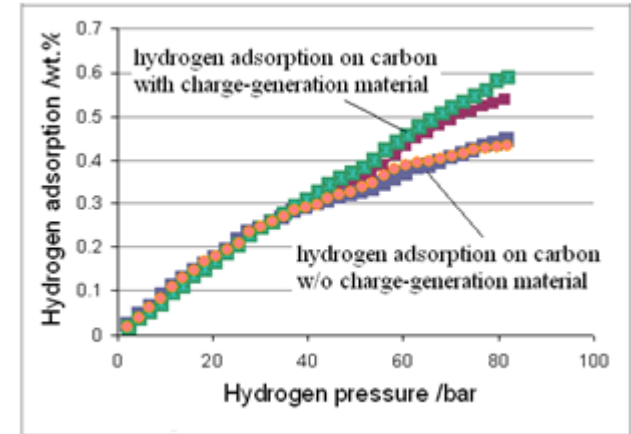


Treatment Temperature (°C)	BET surface (m <sup>2</sup> /g)	μ-pore area (m <sup>2</sup> /g)	Average pore diameter (Å)	Weight Loss (%)
150	13.23	3.68	120.5	–
500	–	–	–	4.47
700	11.33	3.76	98.90	7.05
900	13.26	1.90	113.9	–

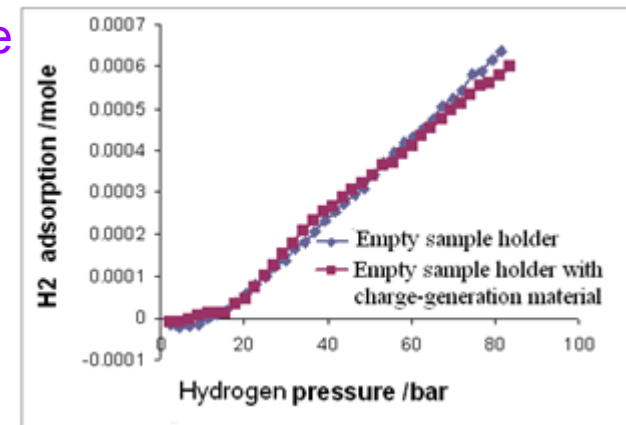
# Technical Progress/ accomplishments:

Material system containing charge generating materials (CGM)

- Concept
  - $\text{CGM} + \text{pressure} \rightarrow \text{CGM}^-$
  - $\text{CGM}^- + \text{Carbon} \rightarrow \text{CGM} + \text{Carbon}^-$
  - $\text{Carbon}^- + n\text{H}_2 \rightarrow [\text{CGM} \cdot n(\text{H}_2)]^-$
- Material
  - Commercial activated carbon
    - Surface properties
      - BET surface,  $1836 \text{ m}^2/\text{g}$ ;
      - Micropore,  $577 \text{ m}^2/\text{g}$
- Sorption behavior
  - Sorption difference observed from samples with and w/o CGM at  $\text{H}_2$  pressure over 55 bar
  - No sorption difference observed from blank sample holder with and w/o CGM
  - the excess hydrogen is directly adsorbed on carbon
- **The result supports the charge-induced sorption enhancement concept**



Room temperature sorption



Higher pressure generate more charges at CGM surface

# Technical Progress/ accomplishments:

## H<sub>2</sub> sorption on NiO enhanced by CGM

- Concept
  - Transition metal compounds as the charge-holding media
  - H<sub>2</sub> could cluster around the charges

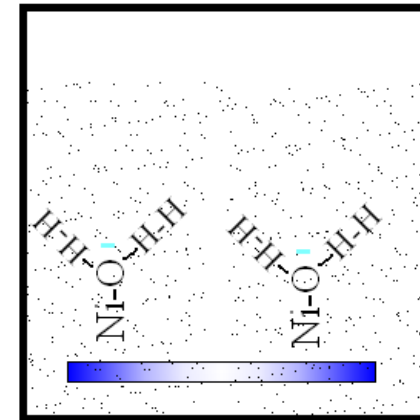


- $e + \text{Ni}=\text{O} \rightarrow \text{Ni}(d^{\cdot})=\text{O} \rightarrow \text{Ni}-\text{O}^{\cdot}$
- $\text{Ni}-\text{O}^{\cdot} + n(\text{H}-\text{H}) \rightarrow [\text{Ni}-\text{O}\cdots(\text{H}-\text{H})_n]^{\cdot}$

- Material

### Lab synthesized NiO

BET surface area	Micropore area	Average pore size
382 m <sup>2</sup> /g	1.71m <sup>2</sup> /g	70.8Å

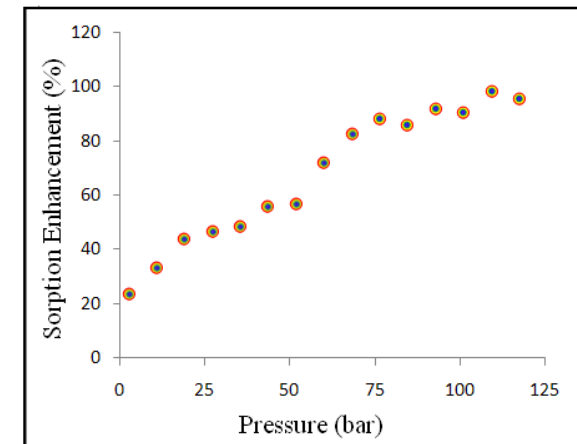
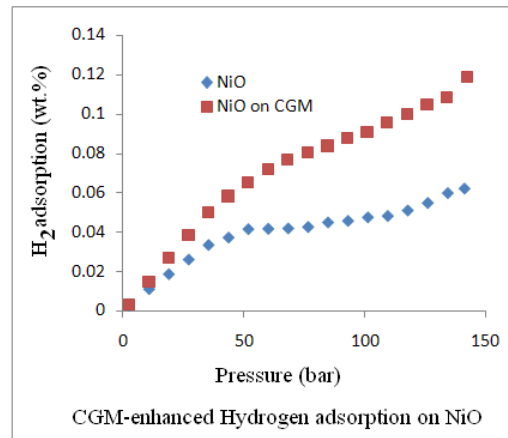


- Sorption behavior

Compared to the CGM-Carbon system

- Enhanced sorption occurred at much lower pressure
- The enhancement amplitude is much larger

## Room temperature sorption

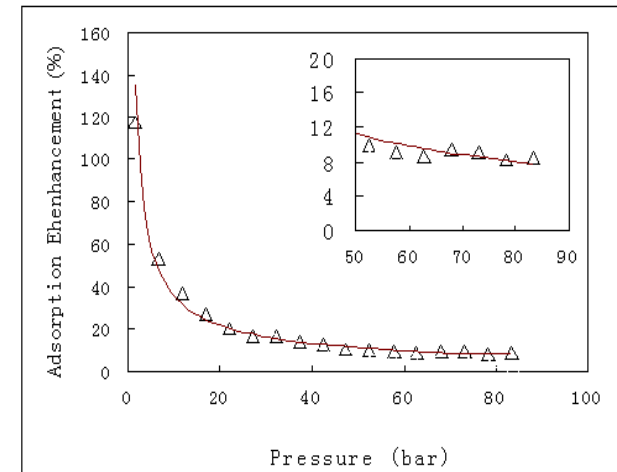
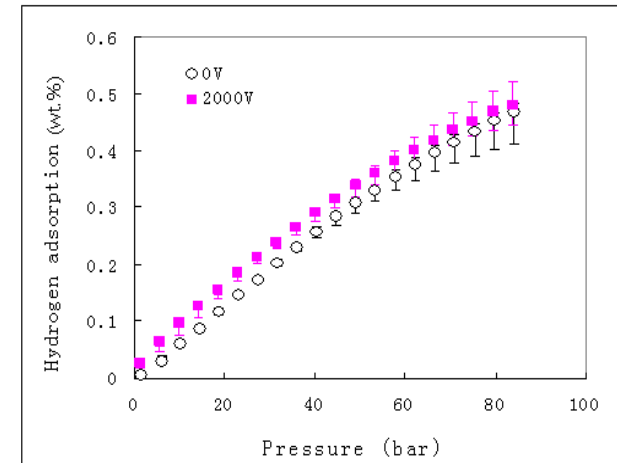


# Technical Progress/accomplishments:

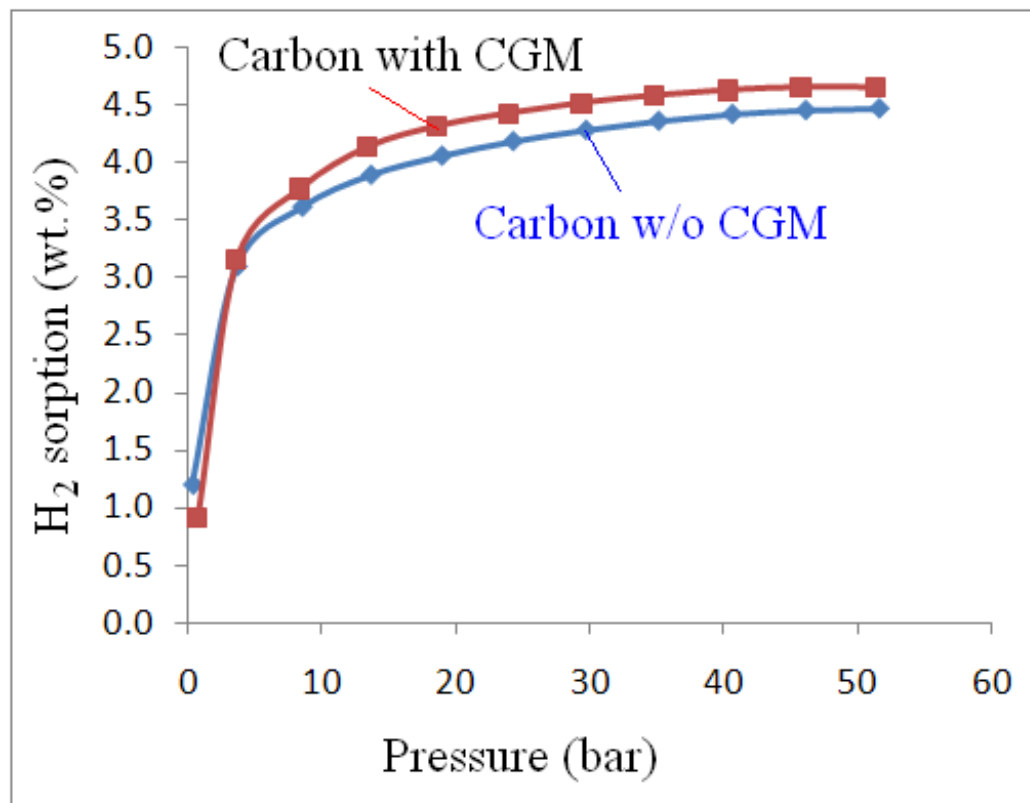
## Material system charged by applied electric potentials

- Concept
  - Anode<sup>+</sup> + Carbon → Anode + Carbon<sup>+</sup>
  - Carbon<sup>+</sup> + nH<sub>2</sub> → [Carbon·n(H<sub>2</sub>)]<sup>+</sup>
- Material
  - Commercial activated carbon
  - Surface properties
    - BET surface, 1836 m<sup>2</sup>/g; Micropore, 577 m<sup>2</sup>/g
- Sorption behavior
  - Applying an electric potential of 2000V induced an enhancement of hydrogen adsorption on activated carbon
  - The enhancement appears more noticeable when the hydrogen pressure is below 60 bar
  - Hydrogen pressure >60 bar, Adsorption enhancement <10%
  - Hydrogen pressure <60 bar; Up to over 100% adsorption enhancement observed
  - **Conclusion**
    - E-potential induced sorption enhancement is supported
    - Polarization or ionization of H<sub>2</sub> could be a responsible mechanism

## Room temperature sorption



# CGM enhanced H<sub>2</sub> Sorption at 77°K



Carbon: BET 3211 m<sup>2</sup>/g, micropore 3051 m<sup>2</sup>/g

# Technical Progress/accomplishments:

## Enhanced sorption by charging Pt/carbon

- Concept

- Spill-over of H<sup>+</sup>s



- Material

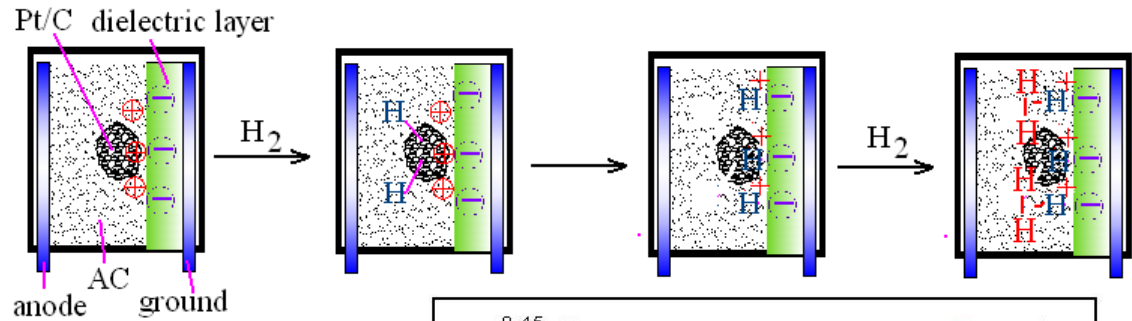
- Commercial activated carbon mixed with Pt/carbon
- BET surface: 1613 m<sup>2</sup>/g
- Micropore: 481 m<sup>2</sup>/g

- Sorption behavior

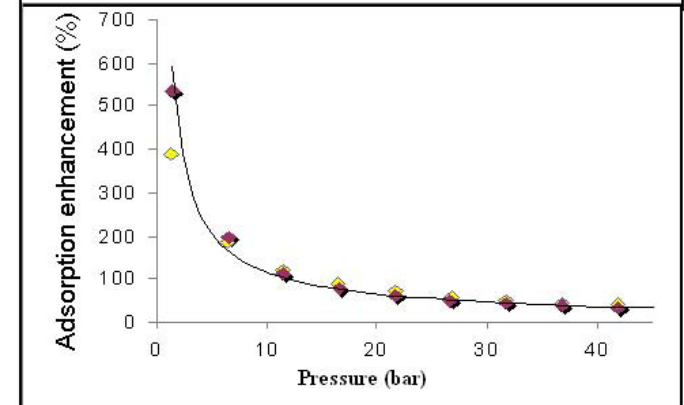
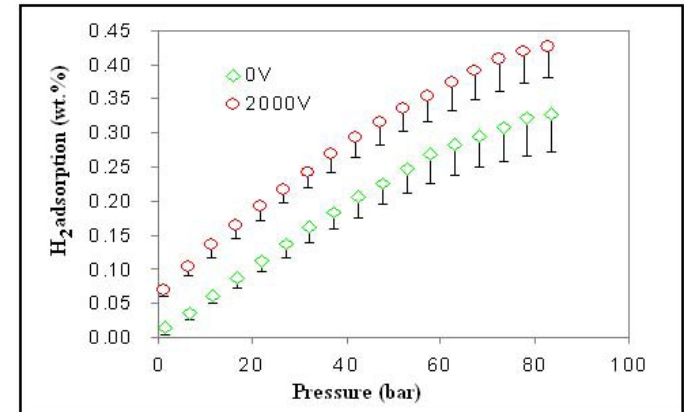
- Sorption difference between samples with & w/o electric potential observed
- Sorption enhancement is much more higher than samples without Pt

- Conclusion

- The concept of proton spill-over on polarized surface is supported



Room temperature sorption



# Collaborations

- Partners

- Clemson University (Academic): collaboration on development of charge-holding materials for the system
- Boda Corporation (industry): collaboration on development of instrument components for study of H<sub>2</sub> in electric field
- NanoMas, Inc. (industry): collaboration on development of carbon-based materials for charge-induced H<sub>2</sub> sorption
- Oak Ridge National Lab (Federal): collaboration to study the charge-induced H<sub>2</sub> clustering using neutron diffraction

- Technology transfer

- Collaboration with ORNL to utilize neutron facility to get insight into the mechanisms of charge-enhanced H<sub>2</sub> sorption
- Collaboration with Boda corporation to utilize its expertise on instrument prototype fabrication
- Collaboration with Clemson University and NanoMas, Inc. to utilize their expertises on electric materials and nanomaterials synthesis and processing

# Future work: FY-09-10

1. Materials Improvement

2. System improvement

3. Combination of the improved system and materials and optimization



# Future Work: FY09-FY10

## 1. Materials improvement

Develop the charge-induced H<sub>2</sub> storage system with materials having high intrinsic sorption capacity (sorption without charge effects) for H<sub>2</sub> storage

- 08' research has just used conventional, commercially available materials
- In the 09'-10' research, the composition, the surface and the pore properties of the sorbent materials will be tuned so that materials with high intrinsic sorption capacity for H<sub>2</sub> storage will be produced
- High intrinsic sorption materials in-consideration

Materials	Intrinsic H <sub>2</sub> sorption capacity (wt.%)	reference
High-surface area activated carbon	8.0 (77k, 40bar); 3.0 (298K, 160 bar)	<i>Carbon</i> 45 (2007) 293–303
Pt/SWNT	3.4 (125k, 80 bar)	<i>INT. J. OF H<sub>2</sub> ENERGY</i> 33 ( 2008 ) 1028 – 1034
Pt/Carbon bridged with IR-MOF8	4.0 (298k, 100bar)	<i>J. Am. Chem. Soc.</i> 2006, 128, 8136-8137

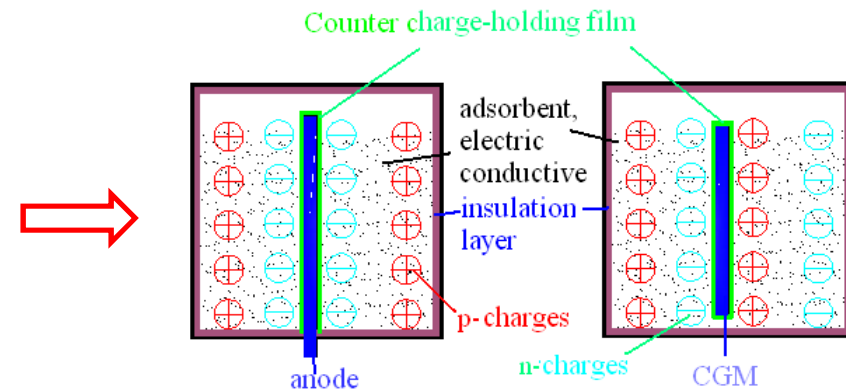
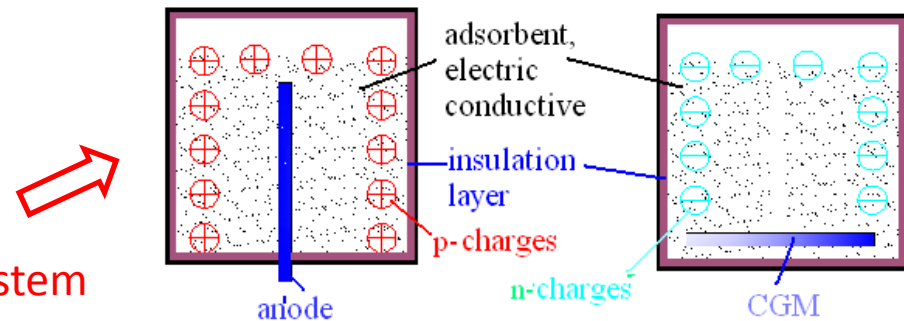
# Future Work: FY09-FY10

## 2. System improvement

Develop a system that will amplify the effect of charge-induced  $H_2$  adsorption enhancement

### 2A. Introduce counter charges

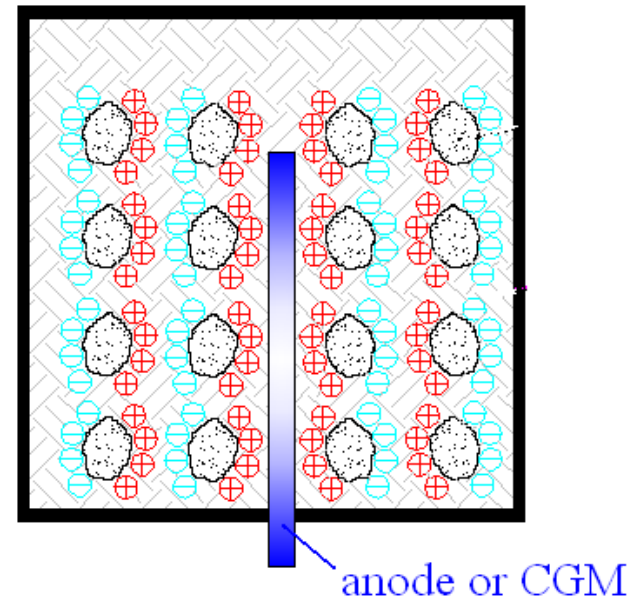
- Limited charge population in current system  
Due to mono-signed charge that can be held
- New system will be developed capable of including counter charges
- The plus and minus signed charges will be mutually balanced
- Charge population in the system will increase
- Charge-induced  $H_2$  sorption enhancement will be amplified



# Future Work: FY09-FY10

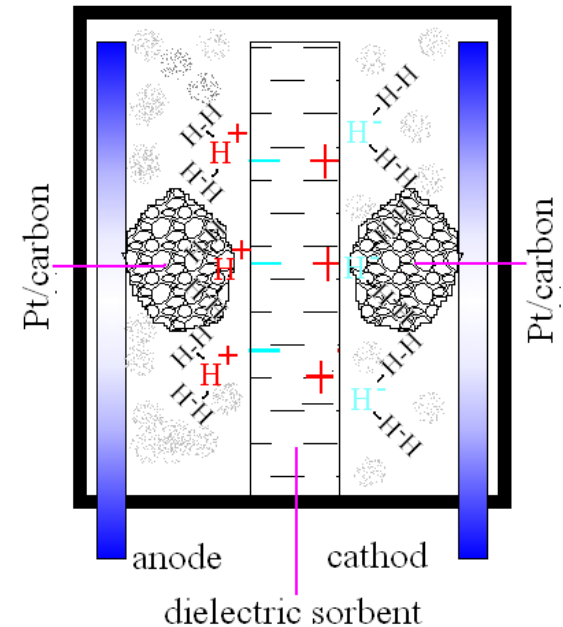
## 2B. Introduce charge-holding domains into the system

- The 09'-10' research will further introduce charge-holding domains into the system
- Each domain will hold a certain number of charges and the corresponding counter charges
- The domain sizes will be tuned and optimized
- The system is of long-range neutral
- Sufficient charges could be populated in the system
- Charge-induced H<sub>2</sub> sorption enhancement could be substantially increased



# Future Work: FY09-FY10

- 2C. Spill over H's concurrently with H<sup>+</sup>s
- The 08' research introduced H<sup>+</sup> spill-over mechanism (Slide 13)
  - The charge dipoles in the dielectric material was not fully utilized
  - The work in 09'-10' research will introduce H<sup>-</sup> spill-over mechanism into the system
  - These two mechanisms may double the spill-over effect



*3. Finally, combine the improved materials and systems, and develop an optimized H<sub>2</sub> storage system*

# Project Summary

- Relevance:

By the concept of **charge-induced hydrogen cluster formation**, the hydrogen storage capacity of the materials has potential to exceed 0.06kg H<sub>2</sub>/kg system, the DOE 2010 target

- Approach

Create **H<sub>2</sub> sorption system with charged species** by depriving H<sub>2</sub>O<sub>s</sub> around Mg<sup>2+</sup> in vermiculite structure, by introducing charge generating materials in the sorption system, and by applying electric potentials to sorbents in the system

- Technical accomplishments and progress:

- H<sub>2</sub> sorption on five material systems has been investigated
- Substantial sorption enhancements induced by charges were observed

Sorption systems	Charge-induced sorption enhancement (%)
Interlayer cations in vermiculite	38
Activated carbon + CGM	27
NiO + CGM	87
Activated carbon+ 2000V	27
Pt/Carbon-carbon + 2000V	550

- Proposed future research:

1. **Materials improvement: develop high intrinsic H<sub>2</sub> sorption materials**
2. **System improvement: develop charge-carrying systems capable of hosting large population of charges**
3. **Combine the improved materials and systems and develop an optimized H<sub>2</sub> storage system**