Capacitive Hydrogen Storage Systems:

Molecular Design of Structured Dielectrics

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OVERVIEW

- **TIMELINE**
  - New-Start in FY09.
  - End-Date: October, FY11
  - 15% complete

- **BUDGET**

DOE Funding (Natl. Lab Call):

  - $451K received to date ($270k additional is anticipated).
  - Projected FY10 Budget: $740k

- **BARRIERS**
  - H_2 Physisorption/Chemisorption Fundamentals
  - Net Efficiency of Storage System
  - Charge/Discharge Rates

- **PARTNERS**
  - Selected as an "Independent Project"
  - Team has established collaborations in materials development (Tulane U., Hamilton College, UC Davis, Texas A&M, Rice U., UC Santa Barbara)

RELEVANCE

Objective: to develop storage materials that enable high H_2 loading under more economical ranges of T & P; that have controllable uptake/release dynamics; and that have moderate thermal management requirements.

These will be tailored porous materials giving controlled dielectric response.

An electric field is applied across the non-homogeneous porous substrate.

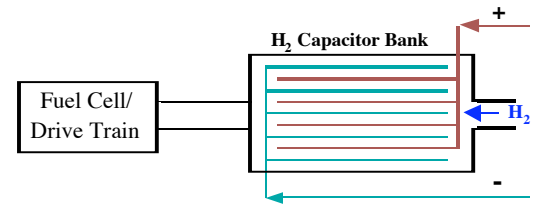
The field produces controlled, localized, dielectric response in the substrate.

Localized polarizability should enhance hydrogen binding at those sites.

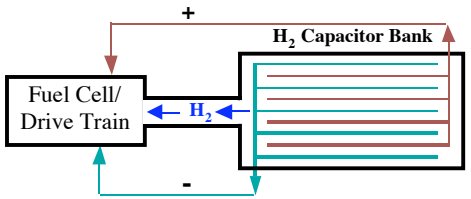
Upon discharge of the "capacitor" the displacement field is removed, and in turn, the energy binding the H_2 dissipates.

RELEVANCE

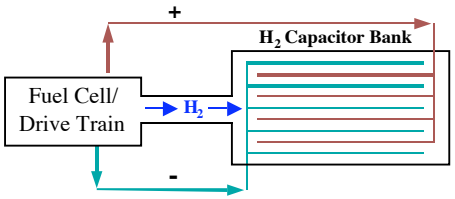
Hydrogen Loading



Acceleration



Deceleration



Operational Concept. Hydrogen loading involves simultaneous introduction of hydrogen and voltage. Expect voltages to be high (10-20 kV) while current is small (μA). As demand increases, capacitor is discharged releasing additional H_2.During deceleration, voltage from regenerative braking (and any hydrogen from the fuel cell) are used to recharge the capacitor. Re-establishing strong E-fields binds the available hydrogen. May also require drawing some charge from a high voltage capacitor.

PROGRAMMATIC IMPACT:

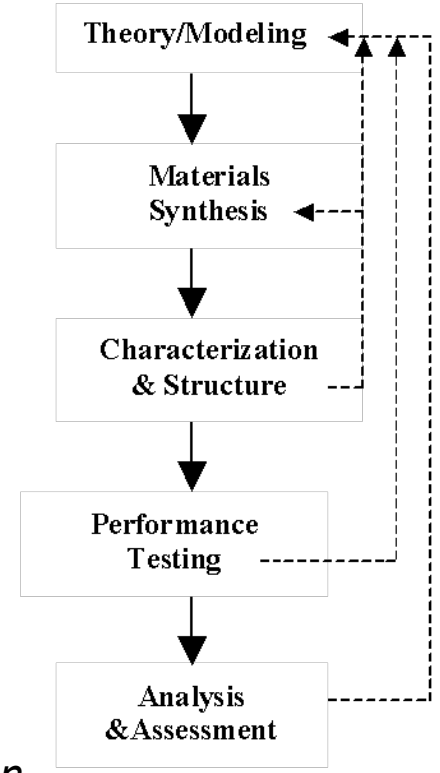
- **Thermal Management (10-15 kJ/mole E-field enhancements expected)**
- **Hydrogen Loading "Goals." (at more practical T&P combinations)**
- **Better Control over Charge/Discharge Dynamics**

RELEVANCE

- New insights into H_2 Physisorption/Chemisorption at Sites of High Local Polarizability
- Net Efficiency: acceptable hydrogen wt% at more accessible T and P. Electric-field enhancement of binding (capacitive storage) integrates well with electric drive system.
- Better control over charge/discharge dynamics (field modulation vs. thermal diffusion alone)

APPROACH

- **Materials Synthesis, Characterization, and Structure**
  - *Known Dielectrics (baseline)*
  - *Design Dielectrics for Specific Purpose*
  - *Materials Characterization Structural Determination*
- **Performance Testing and System Analysis**
  - *Device Design and Fabrication*
  - *Electrochemical Characterization and Testing*
  - *Performance Measurements and Analysis*
- **Theory and Modeling as Guidance**
  - *Simulate Substrate Materials in the Absence of Hydrogen*
  - *Binding Site Characterization for H_2 in Dielectrics*
  - *Effect of External Electric Field on Structure & Binding*



APPROACH

Impact on Technical Barriers:

- H_2 sorption at polarizable organic sites (in addition to metal sites) provides a avenue to reach loading goals (6 wt%) at more practical combinations of T and P. Requires fundamental understanding of hydrogen sorption.

- In theory, much of the electric energy applied during hydrogen uptake can be recovered upon discharge affecting the Net Efficiency of Storage Systems

- Modulation of the electric field promises more control over the hydrogen Charge and Discharge Rates

APPROACH

Address the major challenges of Capacitive Hydrogen Storage:

- Over a charge/discharge cycle - how much energy is dissipated as heat?
  [Classic electrostatics: Loss ~ $(\varepsilon_2 E^2 \omega)/8\pi$ for a homogeneous dielectric]
- Does strong binding at specific sites near the outer edges of the dielectric limit H_2 flux
  (must H_2 desorb and migrate inward to the next available site?)
- Do significant stresses develop in the substrate during charging and discharging?
- To what degree can break-down potential be avoided as applied voltage is increased?

Relation to other aspects of DOE H_2 Program:

- Further elucidate role of metal centers versus polarizable organic sites

- May provide means of enhancing other high surface area sorbents under development: metal-carbon hydrides; metal perhydrides; activated carbons; carbides; metal organic frameworks.

- Use of static electric field compliments works using Electron Charging; Electromagnetic Radiation

APPROACH

Milestones (FY09) associated with establishing Proof-of-Concept:

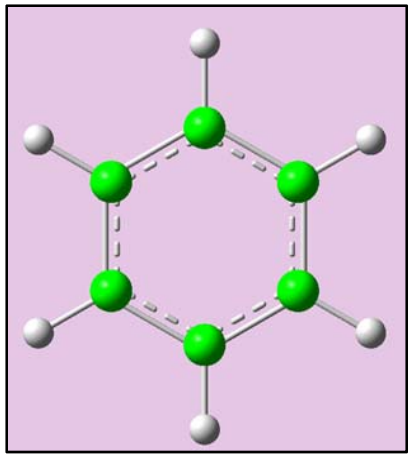
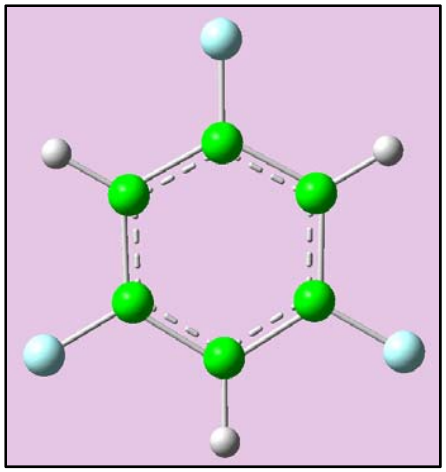
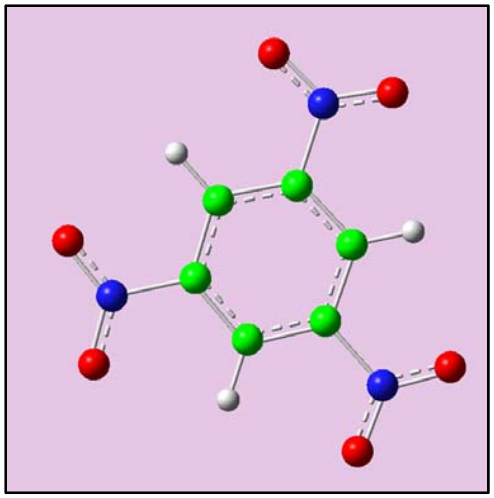
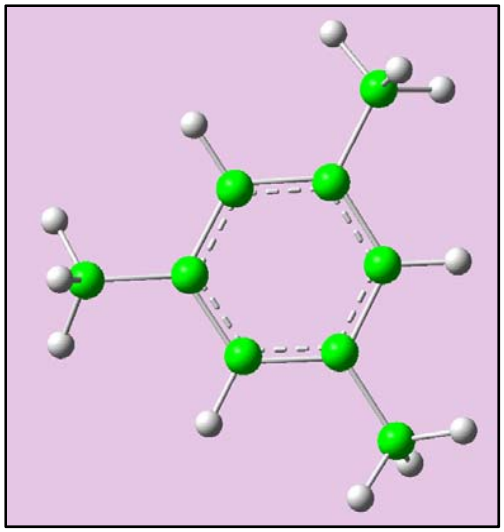
- Test/classify organic-containing dielectric substrates and develop fabrication methods for inorganic substrates.
- Demonstrate enhanced hydrogen loading in the presence of electric field.
- Develop performance criteria with subsequent down-selection of organic-based dielectric structures

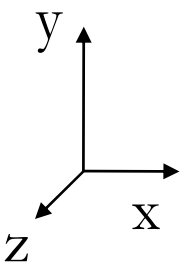
FY09 Go/No-Go Decisions Center on:

- Quantitative demonstration of electric field-enhanced hydrogen loading.
- Assessment of hydrogen compatibility with organic-containing substrates in the presence of dielectric breakdown. If incompatible, subsequent materials discovery will shift to the inorganic dielectrics.

TECHNICAL PROGRESS

Calculation of Static Polarizability

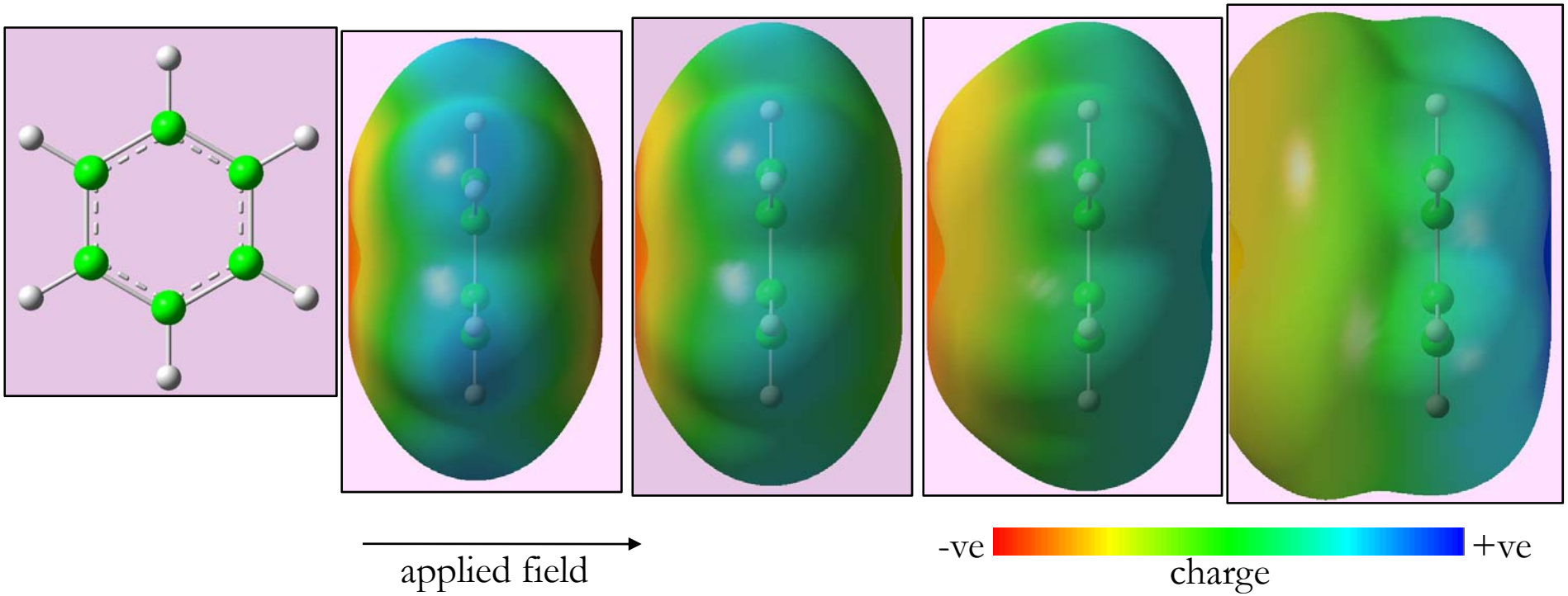







	isotropic polarizability ($Å^3$)	z-component (P_{33}) ($Å^3$)
benzene	**9.66**	**6.03**
trinitrobenzene	**16.98**	**14.63**
trimethylbenzene	**15.60**	**10.09**
trifluorobenzene	**9.68**	**5.63**

TECHNICAL PROGRESS

Effect of Applied Electric Field on Electron Density



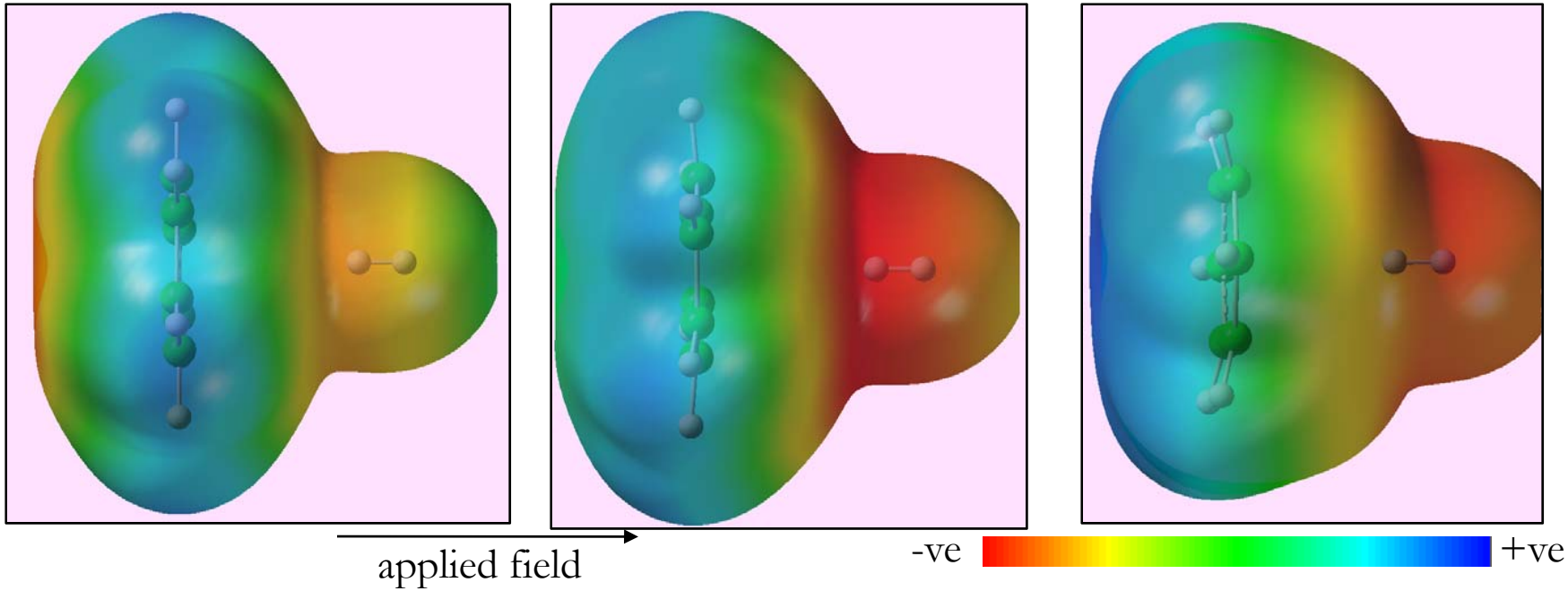
applied field

-ve charge +ve

field ($MVcm^{-1}$)	zero	51.4	257.1	514
molecular volume (cm^3mol^{-1})	70.03	70.03	78.84	92.88

TECHNICAL PROGRESS

Applied Electric Field Shown to Enhance Hydrogen Binding



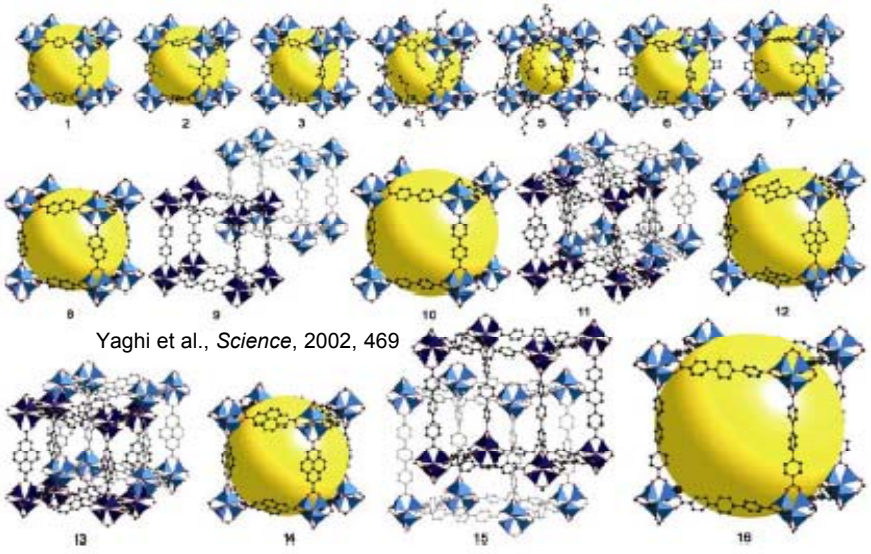
field ($MVcm^{-1}$)	zero	102.8	257.1
RHF binding energy ($kJmol^{-1}$)	+0.3	-2.7	-13.9
MP2 binding energy ($kJmol^{-1}$)	-4.5	-6.0	-18.3
BSSE corrected ($kJmol^{-1}$)	-2.6	-3.9	-15.0

TECHNICAL PROGRESS

Synthesis of Materials with Adjustable Dielectric Properties

Metal-Organic Frameworks

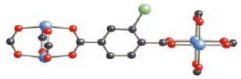
- Porous crystals with adjustable structure
- Ultra-high surface area
- Metal ions serve as vertices
- Organic groups act as "connectors" and as polarizable sites under E-Field



Yaghi et al., *Science*, 2002, 469

Cluster

2D layers



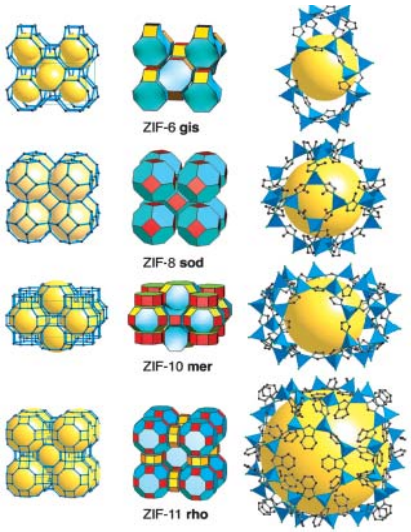
3D framework

Zeolitic Imidazolate Frameworks (ZIFs)

M - IM - M

Si - O - Si

145°



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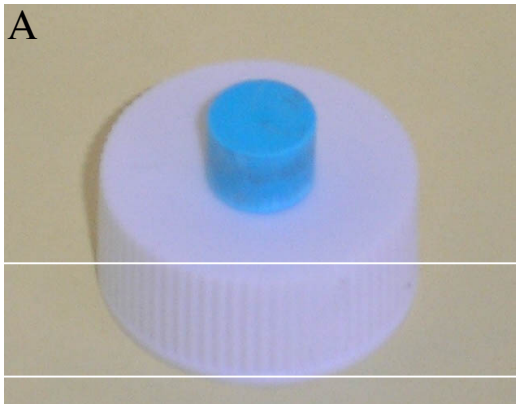
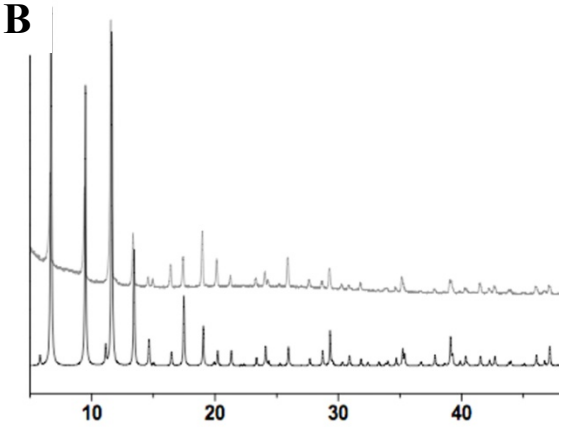
TECHNICAL PROGRESS

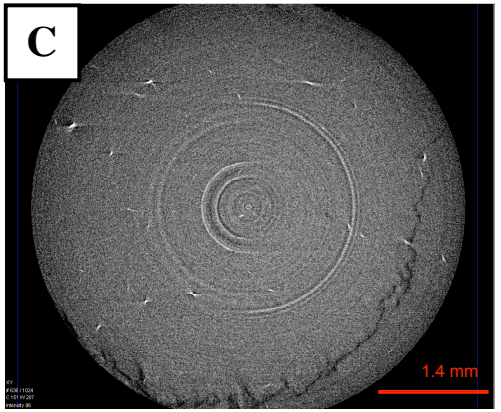
Preparing Test Samples of Materials with Adjustable Dielectric Properties

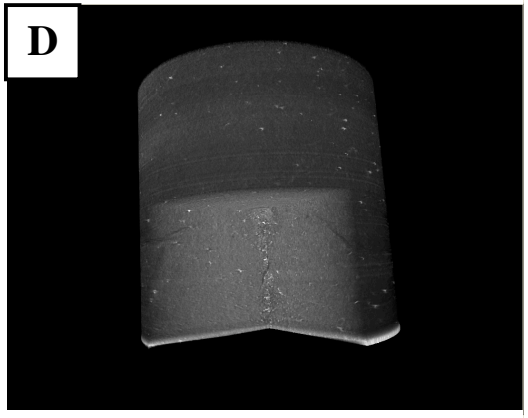
Issue: Are candidate materials mechanically robust enough to withstand pelletizing as part of testing?

Initial tests suggest that MOF structures maintain crystallinity following pressing into pellets.







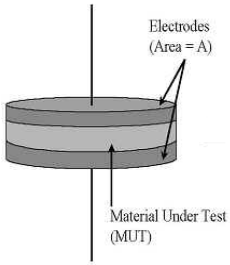


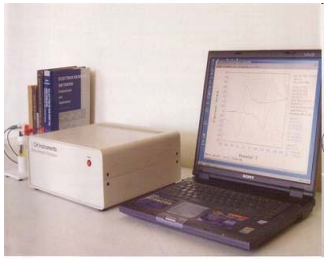
(A) Optical photograph of a pellet of HKUST-1 MOF compressed at 1000 psi. Image (B) is a powder XRD of HKUST-1 pressed MOF showing crystallinity is maintained through processing. Images (C) and (D) are 3-D Tomography, showing pressed pellet uniformity. Small bright spots in pellet may represent copper and copper oxide particles (which may provide a conduit for dielectric break-down).

TECHNICAL PROGRESS

Key Dielectric Properties Being Determined Experimentally: Correlate Binding with Dielectric Response

(1) Dielectric sample is sandwiched between two electrodes to form a capacitor.

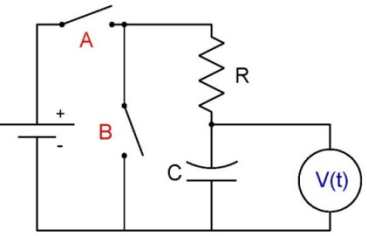


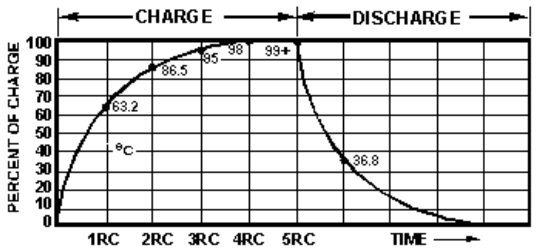


Capacitance: $C = Q/V = \varepsilon_0 \varepsilon_r A / d$

ε_0 : Dielectric constant of the free space
ε : Dielectric constant of the material
ε_r : Relative dielectric constant of the material: $\varepsilon_r = \varepsilon/\varepsilon_0$
A : Area of electrodes
d : Distance between electrodes

(2) DC Charge/Discharge method to calculate capacitance C



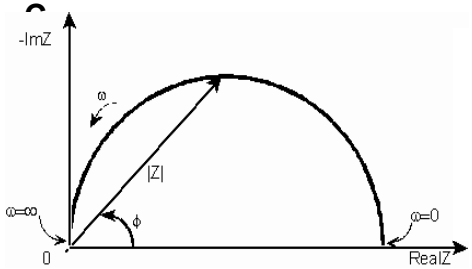


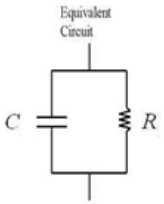
a) Testing capacitor C connected in series with a known resistor R as shown in figure above
b) Switch-A closed and Switch-B open to charge capacitor
c) Switch-A open and Switch-B closed to discharge the capacitor through the known resistor R
d) Voltage across the capacitor while discharging is:

$$V_{C(t)} = V_{C(t=0)}\, e^{-t/RC} \quad \text{(RC = time constant)}$$

e) Capacitance C is measured from the discharging curve and ε_r is calculated from: $C = \varepsilon_0 \varepsilon_r A / d$

(3) AC Impedance method to calculate capacitance C





$$\varepsilon'_r = \frac{d * C}{A * \varepsilon_0}$$

$$\varepsilon''_r = \frac{d}{\omega * R * A * \varepsilon_0}$$

a) Capacitor is modeled as equivalent circuit consisting of capacitor C and parallel resistance R (shown above)
b) C and R are calculated by fitting the experimental data to the equivalent circuit
c) Real (ε'_r) and Imaginary (ε''_r) components of the dielectric constant are calculated from C and R respectively using the equations shown in figure above
d) The Loss Tangent, which is related to the inherent dissipation of electrical energy, is calculated as:

$$\tan d = \varepsilon''_r / \varepsilon'_r$$

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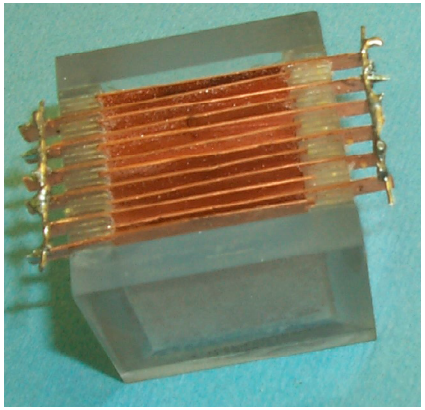
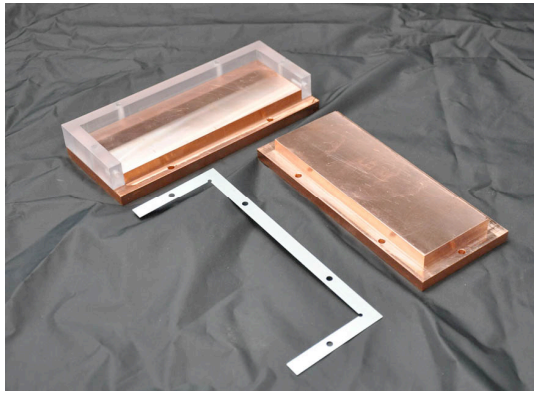
TECHNICAL PROGRESS

Rigs for Screening Materials with Adjustable Dielectric Properties

Capacitor Test Rigs under Construction and Initial Testing



Metal-Insulator-Metal capacitor bank (left) and enclosure vessel with electrical leads (right) used in proof-of-concept experiments.



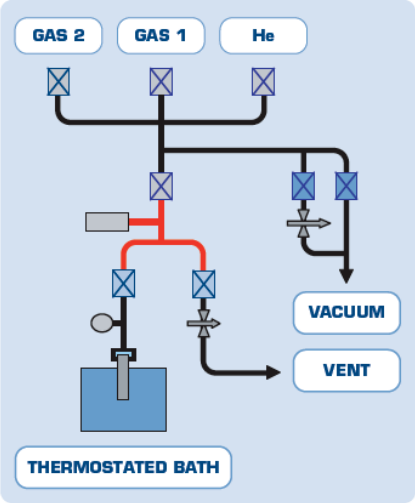
Parallel Plate Capacitor. (Left) test apparatus is shown disassembled showing copper plates, acrylic body and conductive shims. (Right) Assembled test apparatus with top removed. Close inspection shows thin test aperture where porous absorbent is placed for testing.

Expect both open metal sites and framework's hydrogen bonding ability to both influence binding affinity upon application of the Electric Field

TECHNICAL PROGRESS

Modification of BET Apparatus for Quantifying Capacitive Storage

Experimental Demonstration (Quantitative) of Enhanced Hydrogen Binding is now Underway



Conventional test rig being modified to accommodate the introduction of an E-field across the substrate.

Custom vacuum cell equipped with glass (left) or aluminum (right) body. A small parallel plate capacitor (housing dielectric sample) is contained in the cell. Hermetic epoxy seals allow the introduction of leads providing current for testing the influence of E-field on absorption.

While large polarizability is expected in the substrate, H_2 has a non-zero, but small, quadrupole. (Quadrupole moments: CO_2 - 4.3 esu ; H_2 - 0.662 esu)

COLLABORATION

Selected as an "Materials Discovery" Independent Project under the last National Laboratory Request for Proposals (New Materials/Processes for On-Board Storage)

Project Team has direct ties to/working relationship with the LANL-based chemical hydrogen storage "Center of Excellence"

Project Team has established collaborations on Materials Development with:

- Tulane University
- Hamilton College
- UC Davis
- Rice University
- UC Santa Barbara
- Texas A&M

FUTURE WORK

FY09:

- Develop stable molecular models that reproduce bulk structural parameters (bond lengths, angles). Determine relative orbital energies.
- Estimate magnitude of applied electric field required to significantly change binding properties
- Complete screening/classification of candidate dielectric substrates.
- Demonstrate quantitatively enhanced hydrogen loading in the presence of an electric field.
- Assess H_2/substrate compatibility under dielectric breakdown.

FY10:

- Determine effect of functionalization (e.g. of aromatic rings) on binding energies. Diffraction studies on dielectrics with hydrogen load to precisely identify the hydrogen sorption sites.
- Identification of best porous frameworks - e.g. metal-organic; ZIF; semiconductor composites.
- Quantitative comparison of measured loadings with EERE storage targets. Down-select materials for subsequent performance testing.

SUMMARY

Relevance: Electric field-enhanced (capacitive) hydrogen storage provides another variable in addition to T & P and potentially better control over charge/discharge dynamics.

Approach: Using theory/simulation as a guide, materials synthesis/characterization/testing is used to develop dielectrics with localized polarizability. These become H_2 binding sites upon application of an electric field.

Technical Progress: Electronic structure calculations show induced polarizability in simple organic fragments and enhanced H_2 binding. Synthesis and dielectric characterization of candidate porous dielectrics (MOF; ZIF) underway. Capacitors designed/fabricated to quantify hydrogen loading under application of E-field.

Collaborations: Tulane University, Hamilton College, UC Davis, Texas A&M, Rice University, UC Santa Barbara

Proposed Future Research: Examine heterocyclic organic groups (e.g. tetrazole); 2D layered graphitic structures (covalent-organic frameworks with intercalation between layers (e.g. pyrene). Enhance modeling tools for guidance. Explore T-P-voltage space, quantifying H_2 loading. Probe charge/discharge dynamics.

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