Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

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Project ID: st026

OVERVIEW

- **TIMELINE**

  - New-Start in FY09 (delayed start due to Fed. Budget uncertainties)
  - End-Date: October, FY11
  - 30% complete (no available funds 10/09-2/10; restarted mid-Feb. 2010)

- **BUDGET**

  DOE Funding (Natl. Lab Call):

  - $711k received in FY09.
  - Projected FY10 Budget: $500k

- **BARRIERS**

  - H_2 Physisorption/Chemisorption Fundamentals
  - Net Efficiency of Storage System
  - Control over hydrogen 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)

OBJECTIVES/RELEVANCE

Motivation: Given the physical properties of hydrogen, the manipulation of temperature and pressure alone are not likely to achieve the target goals. Another physical variable is needed.

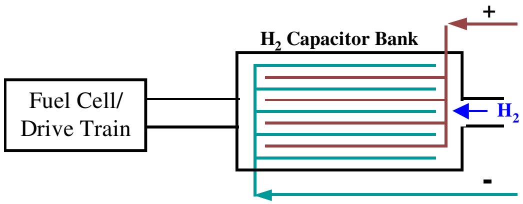
Objective: Use applied electric fields to facilitate high H_2 adsorption/loading under more economical ranges of T & P, with controllable uptake/release dynamics, and with moderate thermal management requirements.

Features:

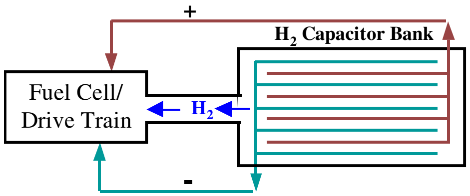
- Materials will be tailored porous substrates with controlled dielectric response.
- An electric field is applied across the porous substrate.
- The field produces controlled, localized, dielectric response in the substrate.
- Localized polarizability should enhance hydrogen binding at those sites.
- Upon discharge of what is effectively a "capacitor" the displacement field is removed, and in turn, the energy binding H_2 dissipates.

OBJECTIVES/RELEVANCE

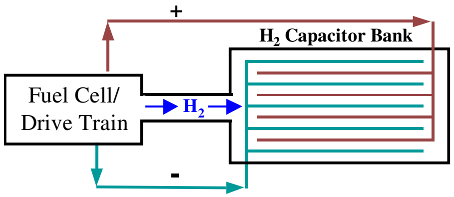
Hydrogen Loading



Acceleration



Deceleration



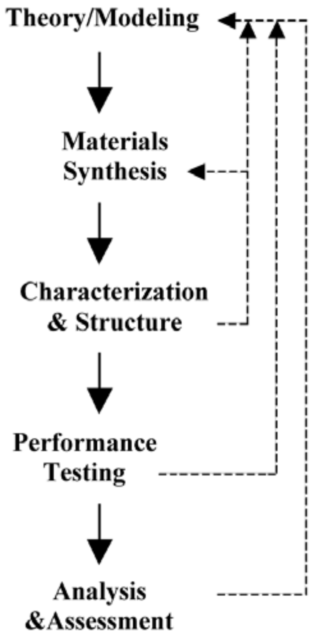
<u>Operational Concept</u>. Hydrogen loading involves simultaneous introduction of hydrogen and voltage. Expect voltages to be high (10-20 kV) while current is small (μA). As demand increases, capacitor is discharged releasing additional H_2. During deceleration, voltage from regenerative braking (and 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.

POTENTIAL 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**

APPROACH

- **Materials Synthesis, Characterization, and Structure**
    - *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**
    - *Binding Site Characterization for H_2 in Dielectrics*
    - *Effect of External Electric Field on Structure & Binding*


Theory/Modeling

Materials Synthesis

Characterization & Structure

Performance Testing

Analysis &Assessment

Impact on Technical Barriers:

- **Field-enhanced H_2 sorption at polarizable sites provides a avenue to reach loading goals (6 wt%) at practical combinations of T and P.**
- **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 ~ $(\varepsilon'' E^2 \omega)/8\pi$ 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 in binding

- 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

Major Milestones Associated with Proof-of-Concept:

- Test/classify/synthesize promising porous dielectric substrates. (initial round complete; additional iteration to follow).

- Demonstrate enhanced hydrogen loading in the presence of electric field (now underway).

- Develop performance criteria basis for subsequent down-selection relative to target loading (awaiting additional performance data).

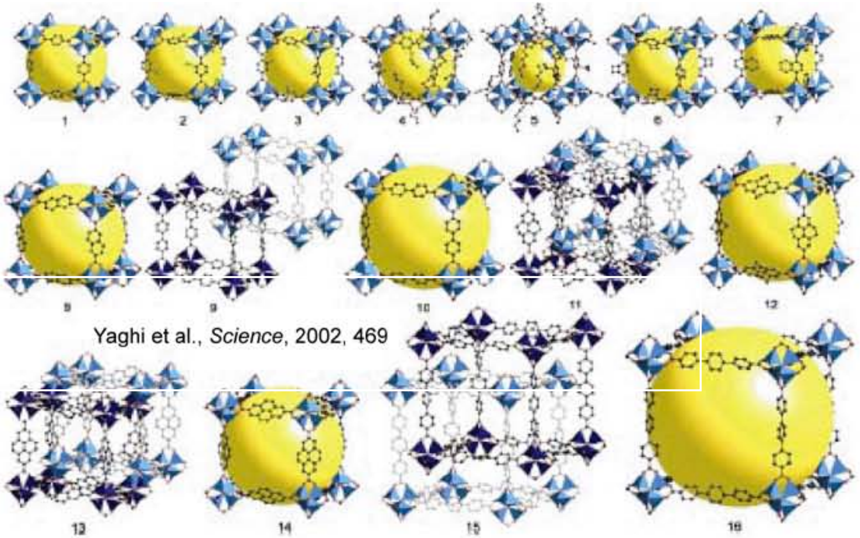
FY10 Go/No-Go Decisions Center on:

- 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 necessarily shift to the inorganic dielectrics. (initial results imply compatibility)

TECHNICAL PROGRESS: STARTING POINT

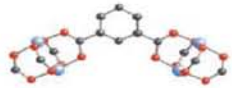
Select Baseline Materials that Allow for Adjustable Dielectric Properties



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

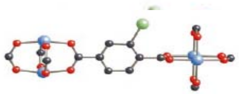
Metal-Organic Frameworks

- 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



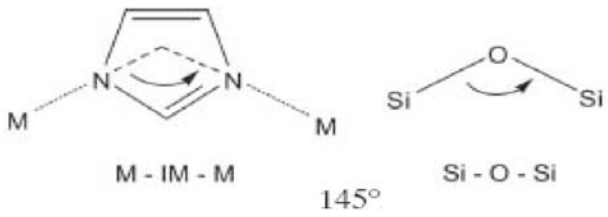
Cluster

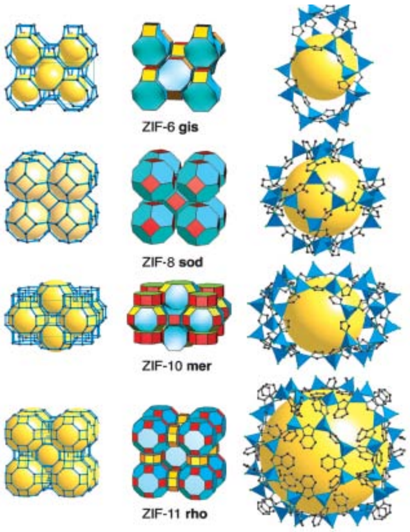
2D layers



3D framework

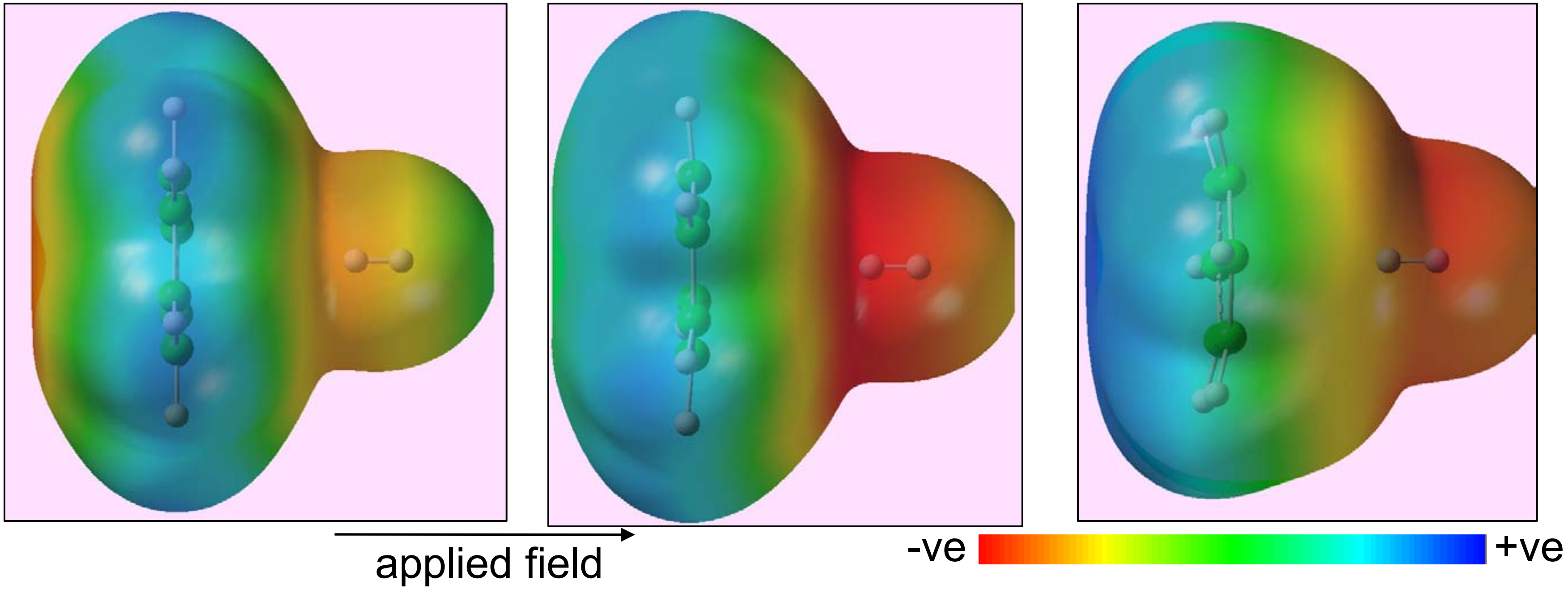
Zeolitic Imidazolate Frameworks (ZIFs)





TECHNICAL PROGRESS: MODELING

Applied Electric Field Shown to Enhance Hydrogen Binding (benzene example)



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

High field requirement suggests using ligands with a high density of "sloshy" electrons

TECHNICAL PROGRESS: MODELING

Calculated Hydrogen Bonding Site/Electron Density (CuBTC unit example)

Baseline Calculation:

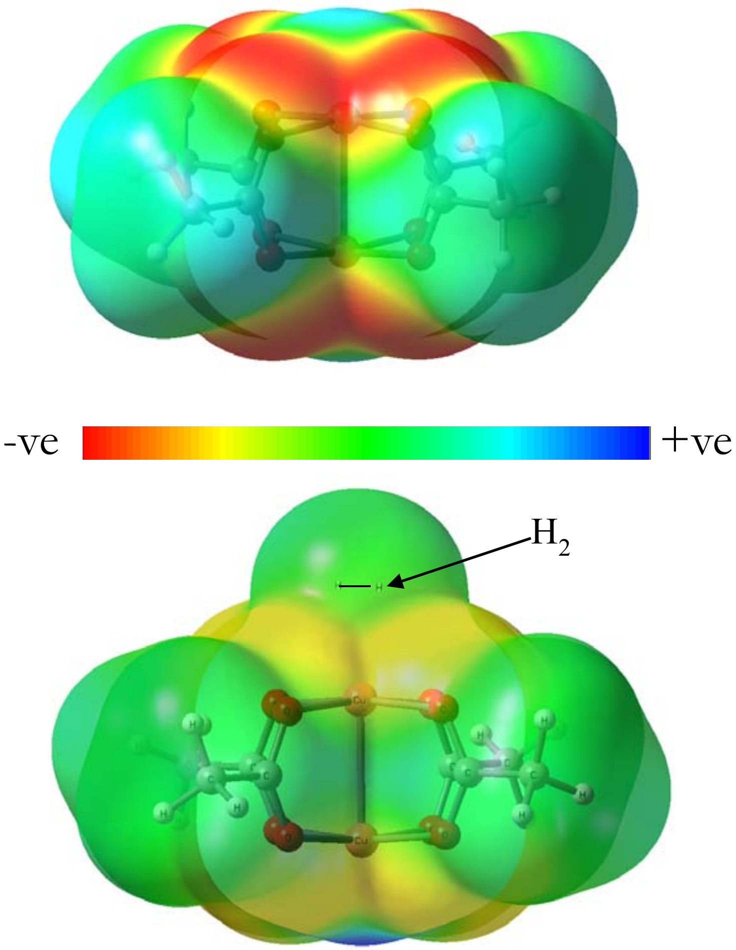
Singlet, B3LYP, geometry optimization, 6-31G** basis set (C,H,O), Cu (LANL2DZ basis set and ECP)

- Calculated electrostatic potential projected on calculated total density surface

Hartree Fock calculation with MP2 corrections (required for H_2)

Notable results:

- Little perturbation in electronic structure from presence of H_2
- Cu-(H_2) bond lengths - singlet : 2.08Å, triplet : 2.73Å
- H-H bond length slightly shorter for singlet
- Calculations with field applied along Cu-Cu vector in progress



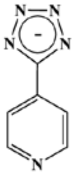
Directional E-Field will be added in next set of calculations

TECHNICAL PROGRESS: SYNTHESIS

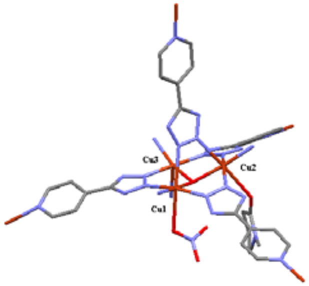
Synthesis of Lightweight Porous Dielectric Materials with More Polarizable Linkages

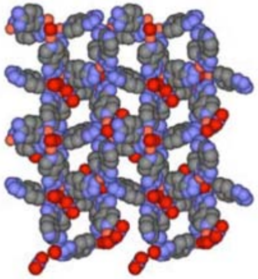
$Cu_2(OH)(TPy)_3$

Tpy =



Following modeling guidance, nitrogen-containing rings should provide additional polarizability (rel. to C-rings)



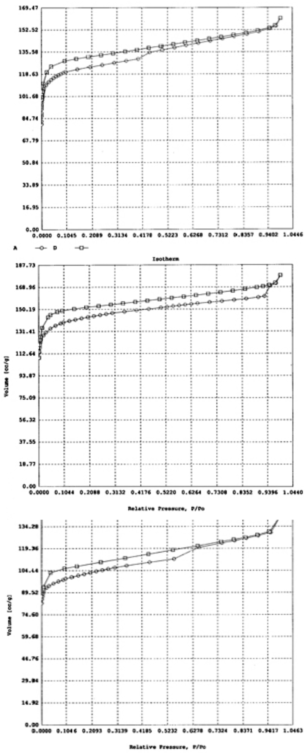


150°C

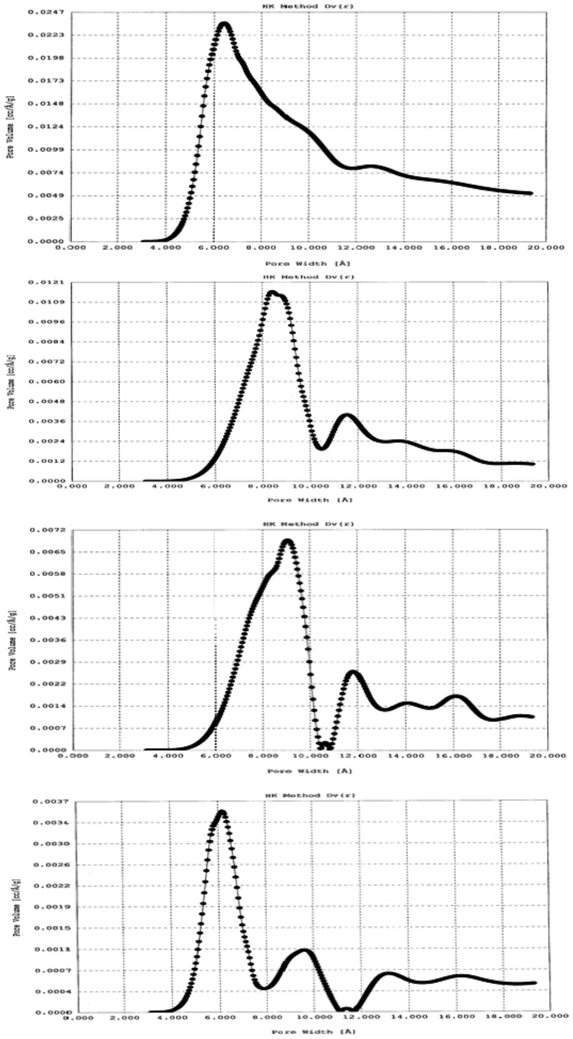
100°C
to
150°C

100°C

25°C



Comparable to 100°C



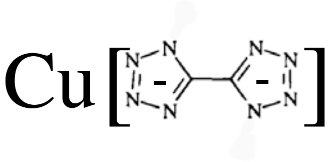
BET Adsorption

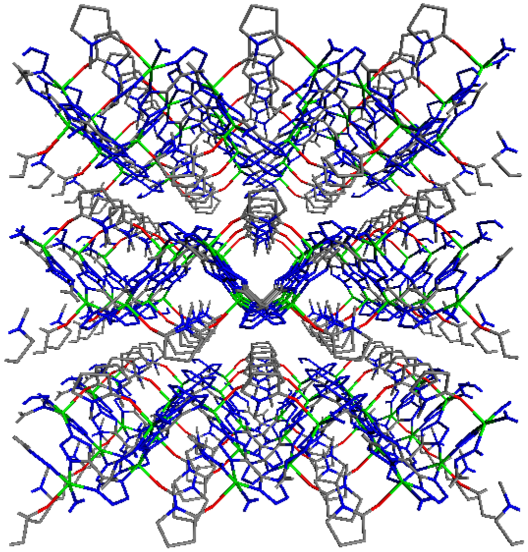
Pore size distribution

TECHNICAL PROGRESS: SYNTHESIS

Porous Dielectric Materials with Polarizable Linkages

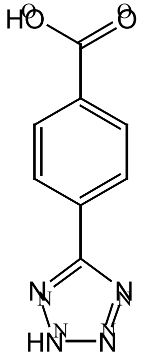
Highly polar copper-bitetrazole MOF

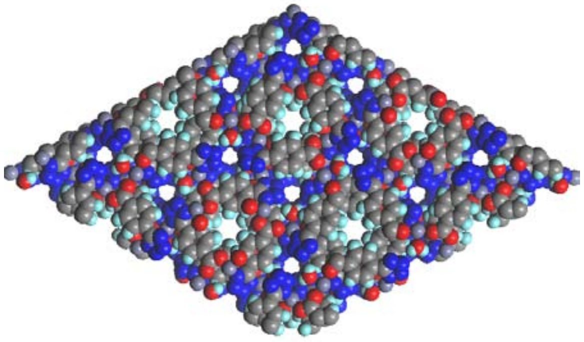




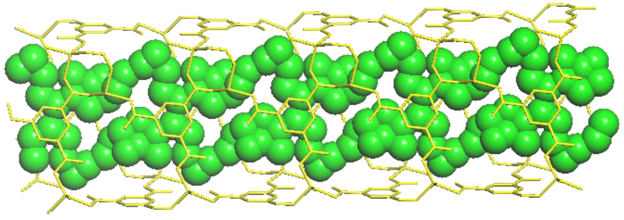
C-axis view of zig-zag layers.

Other Tetrazole and Imidazole Based MOFs as Polarizable Substrates





Hydrophilic /hydrophobic channels

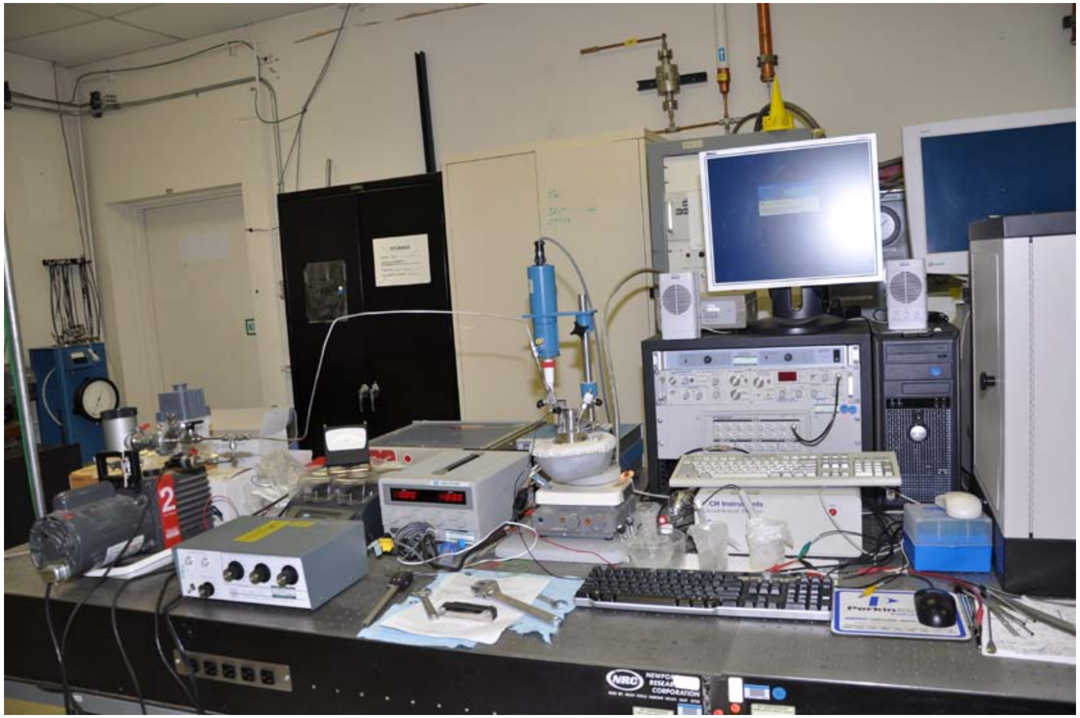


$[Me_2NH_2][Zn_2(BTC)(\mathbf{HBTC})]$.DMF

Although less porous than other MOFs, materials appear to be highly polarizable.

TECH. PROGRESS: CHARACTERIZATION

Dielectric Properties Determined Using Electrochemical Impedance Spectroscopy



- Rig calibrated against vacuum and teflon.
- Pelletized samples prepared (verified structures survive pellet-forming process)
- Obtain real and imaginary parts of dielectric constant (imaginary relates to “losses”)
- Measures dielectric properties as a function of temperature and pressure
- Can gauge effect of adsorbed species on dielectric response.

TECH. PROGRESS: CHARACTERIZATION

Estimated Dielectric Constants (static) From Impedance Spectroscopy

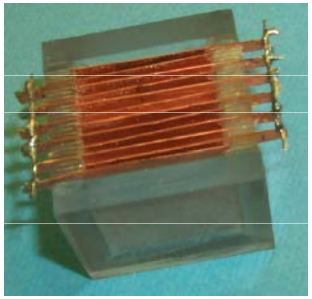
	Vacuum	Vacuum + heat	T = 90C
CuBTC	5.21 ± 0.05	2.74 ± 0.05	3.02 ± 0.05
MOF-2	5.58 ± 0.05		6.93 ± 0.05
MOF-5	8.61 ± 0.05	41.94 ± 0.05	22.67 ± 0.05
CuBTC + Ferrocene	40.61 ± 0.05		
MOF-5 + Ferrocene	8.29 ± 0.05		

- Analysis of frequency dependent data is underway to extract ε'' (imaginary part of dielectric constant), to estimate energy losses over a charge/discharge cycle. Classically:

$$\text{Loss} \sim (\varepsilon'' E^2 \omega)/8\pi$$

TECHNICAL PROGRESS: TESTING

Initial Measurement of Adsorption Affinity of a Gas Under Action of E-Field



Enclosure vessel (top) with electrical leads and Metal-Insulator-Metal capacitor bank (bottom) used in proof-of-concept experiments with carbon dioxide.

Initially test concept using gas with a strong quadrupole moment then move to hydrogen. H_2 has a non-zero, but small, quadrupole.

(Relative quadrupole moments: CO_2 - 4.3 esu ; H_2 - 0.662 esu)

Experiment	Applied Voltage	Final Ar Composition	Final CO_2 Composition
1	0 Volts	66.37%	33.63%
2	0 Volts	66.38%	33.62%
3	0 Volts	66.38%	33.62%
4	650 Volts	69.55%	30.45
5	650 Volts	70.61%	30.29%
6	650 Volts	70.14%	29.86%

Experiment	Applied Voltage	O_2 and N_2 Composition	Final CO_2 Composition
1	0 Volts	90.67%	9.33%
2	0 Volts	90.73%	9.27%
3	0 Volts	90.70%	9.30%
4	650 Volts	92.98%	7.02%
5	650 Volts	92.92%	7.08%
6	650 Volts	93.01%	6.99%

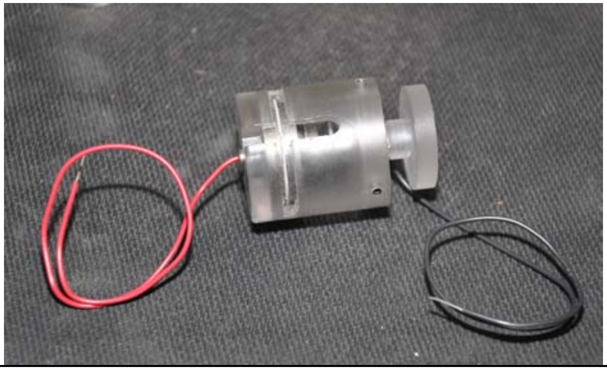
Powders used in these experiments proved difficult to pack into MIM capacitor, still effect of applying an E-field was apparent.

TECHNICAL PROGRESS: TESTING

Custom Apparatus for Quantifying Capacitive Storage Via Differential Pressure Measurements

- Measure adsorption over wide range of T and P (e.g. cells can be inserted into cryogen or pressurized)
- Measurements based on highly accurate "differential" pressure measurements (relative to a pressure known with high accuracy)
- H_2 adsorption expts. underway.

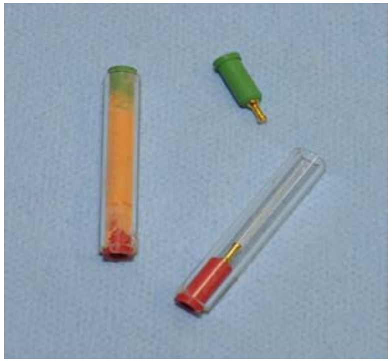
Spring-loaded parallel plate capacitor with electrical leads. Sample "wafers" are inserted between plates. Notches enable precise measurement of distance between the plates.



TECHNICAL PROGRESS: TESTING

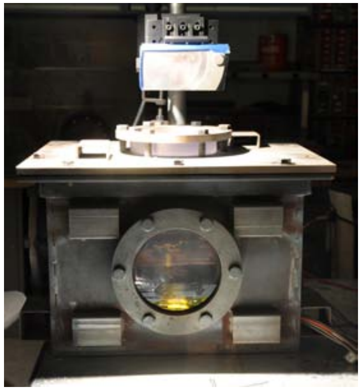
Reactivity of Hydrogen and Organic-Based Dielectrics in Presence of an Electrical Short

Intentionally "arc" across a MOF in the presence of H_2 gas to assess safety issues



Test Cell for arcing across adsorbents in the presence of hydrogen gas (variable path 1 to 10 mm)

Pressure vessel used for hydrogen arcing tests



"Boom-box" borrowed from LANL nano-energetic program.
Rated for 4.2 g TNT equivalent and the associated metal fragments

Testing is ongoing. Initial results (on common MOFs) suggest that arcing induces material degradation, but no violent "deflagration" is observed.

COLLABORATION

Project selected for funding 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

PROPOSED FUTURE WORK

FY10:

- Demonstrate quantitatively enhanced hydrogen loading in the presence of electric fields. (underway)
- Refine molecular models that reproduce bulk structural parameters (bond lengths, angles, relative orbital energies) to guide synthesis.
- Synthesize/Characterize/test next set of candidate dielectric substrates.
- Expand electrochemical characterization/correlate with sorption results.
- Further examine H_2/substrate compatibility under dielectric breakdown.

FY11:

- Demonstrate best computational method for system design, examining three : VASP, cp2k, and FreeON.
- Refine correlations between dielectric properties and performance.
- Probe the dynamics of molecular diffusion through pores. Assess heat transfer characteristics of promising substrates.
- Design, fabricate, and test scaled-up capacitive storage system.
- Summarize finding and outline most promising path forward for integrated system design.
- Quantitative comparisons of measured loadings with EERE storage targets.

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.

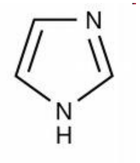
Technical Progress: Electronic structure calculations show induced polarizability in simple organic fragments and enhanced H_2 binding. Synthesis and dielectric characterization of candidate porous dielectrics underway. Capacitors and test rigs designed/fabricated to quantify hydrogen loading under application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

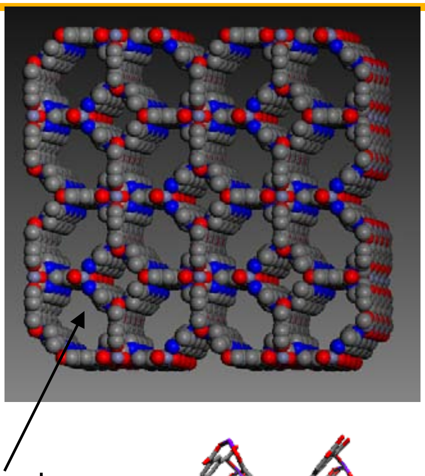
Proposed Future Research: Quantify enhancement of hydrogen adsorption under electric field; Explore T-P-voltage space, quantifying H_2 loading; Interrogate heterocyclic structures (e.g. tetrazole-based MOFs) and doped structures; Enhance modeling tools for guidance purposes; Explore charge/discharge dynamics.

SUPPLEMENTAL SLIDES

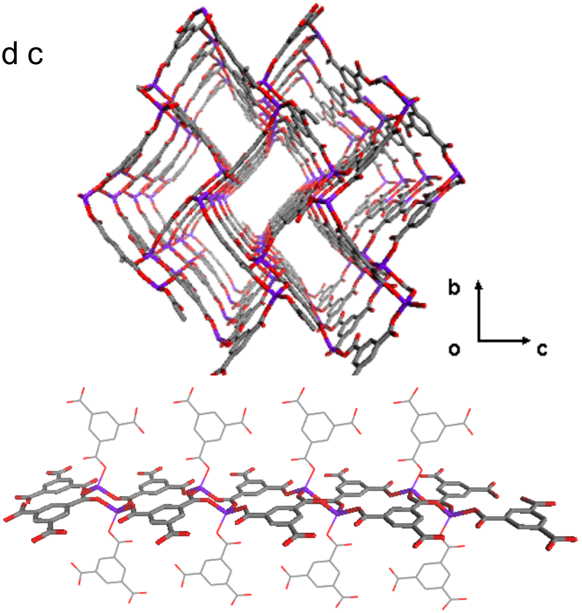
SYNTHESIS

Other Tetrazole and Imidazole Based MOFs and MOF Aerogels Developed as Polarizable Substrates

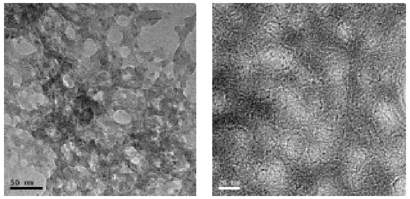




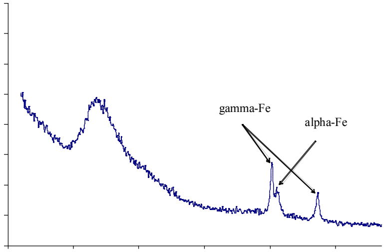
Imidazole formed c



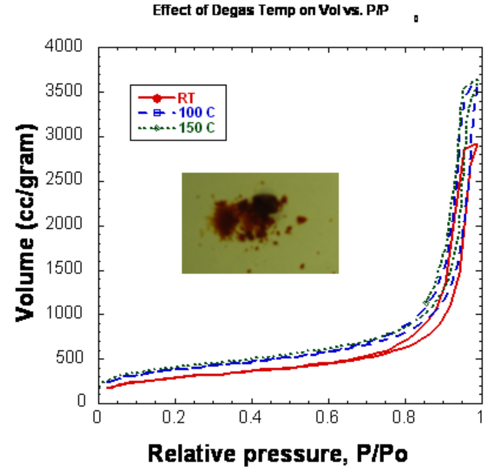
Anionic Zn-BTC frameworks



TEM analysis of Fe-BTC aerogel



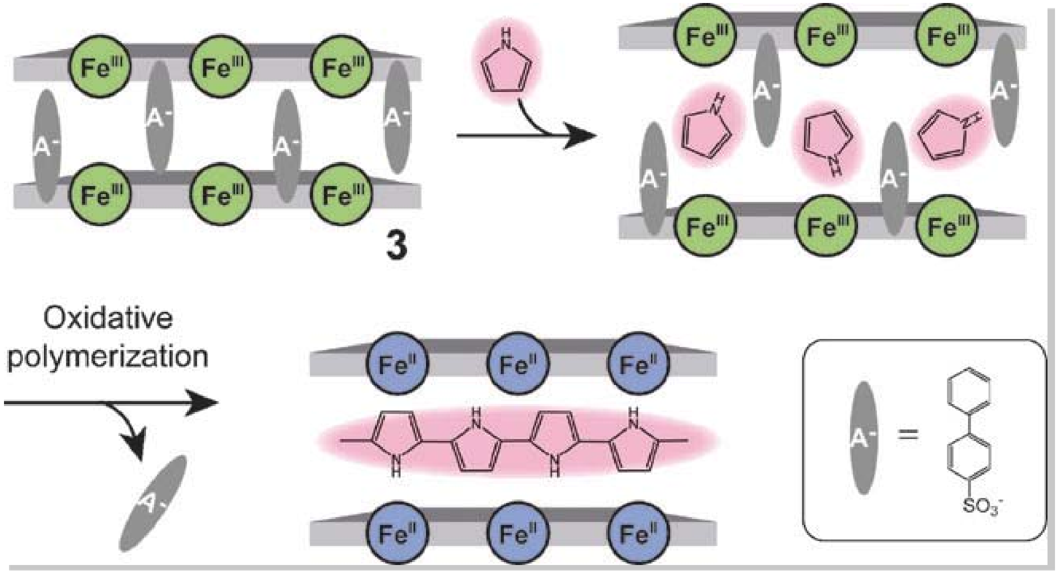
Powder XRD of reduced Fe-BTC aerogels

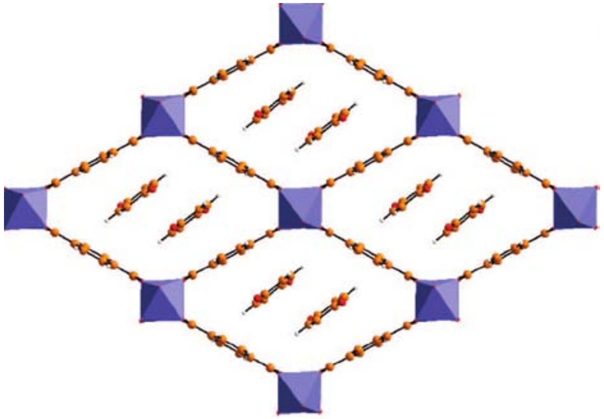


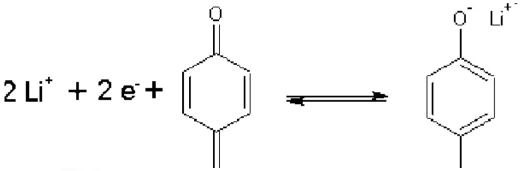
SYNTHESIS

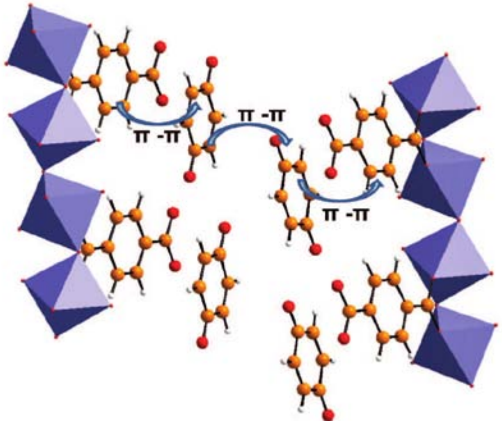
Exploring the Inclusion of Conducting Constituents into Frameworks

Introduction of conductive “islands” with thin provides another means of manipulating local polarizability (e.g. using Fe and Li based sub-structures)





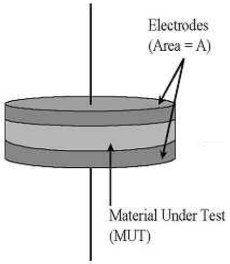




CHARACTERIZATION

Key Dielectric Properties Determined Experimentally: Correlate Binding with Dielectric Properties

(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

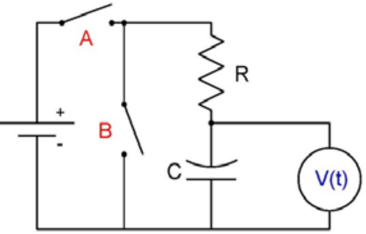
ε : Dielectric constant of the material

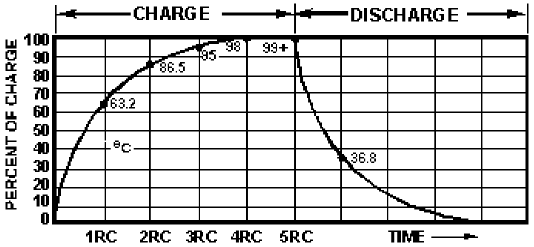
ε_r : Relative dielectric constant of the material: $\varepsilon_r = \varepsilon/\varepsilon_0$

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

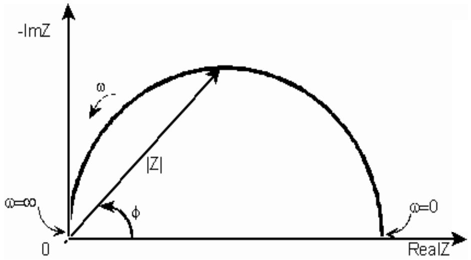
c) Switch-A open and Switch-B closed to discharge the capacitor through the known resistor R

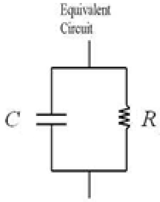
d) Voltage across the capacitor while discharging is:

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

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:

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

CHARACTERIZATION

EXPERIMENTAL VALIDATION OF TECHNIQUE:

Static Relative Dielectric Constant Measurements

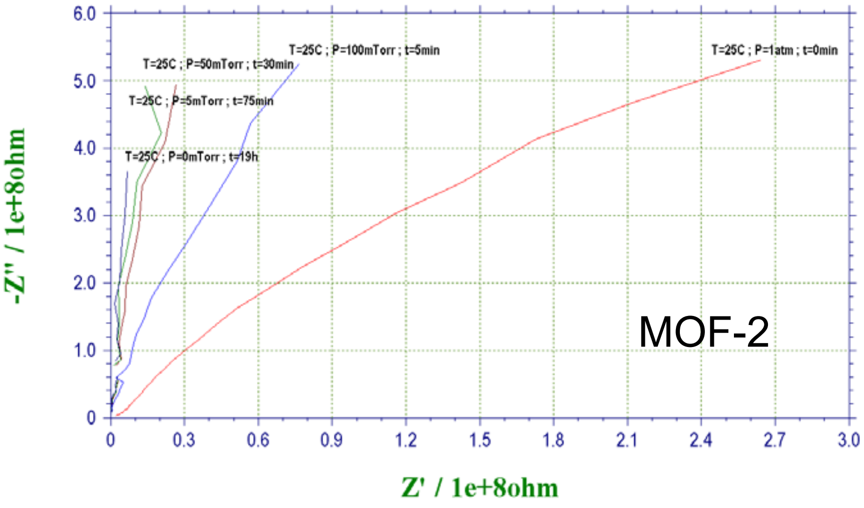
Condition	Measured	Literature Reference
Vacuum	0.96 ± 0.05	1
Teflon	2.29 ± 0.05	2.1

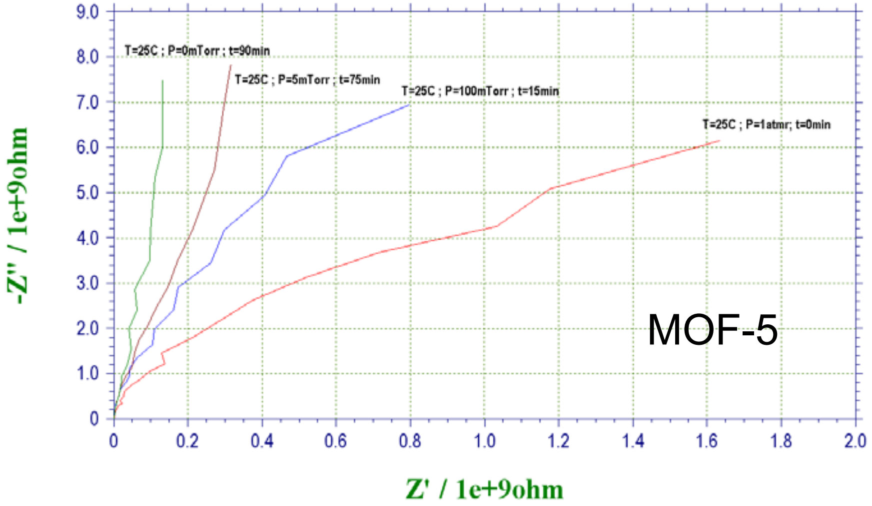
Effects of pelletizing (pressure) on Relative dielectric Constant

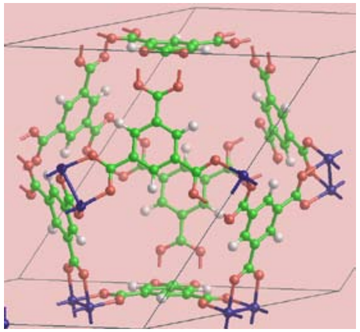
Sample	Pelletized @5000 Lbs	Pelletized @15000 Lbs
Alumina	5.65 ± 0.05	5.66 ± 0.05
CuBTC	4.91 ± 0.05	4.90 ± 0.05

CHARACTERIZATION

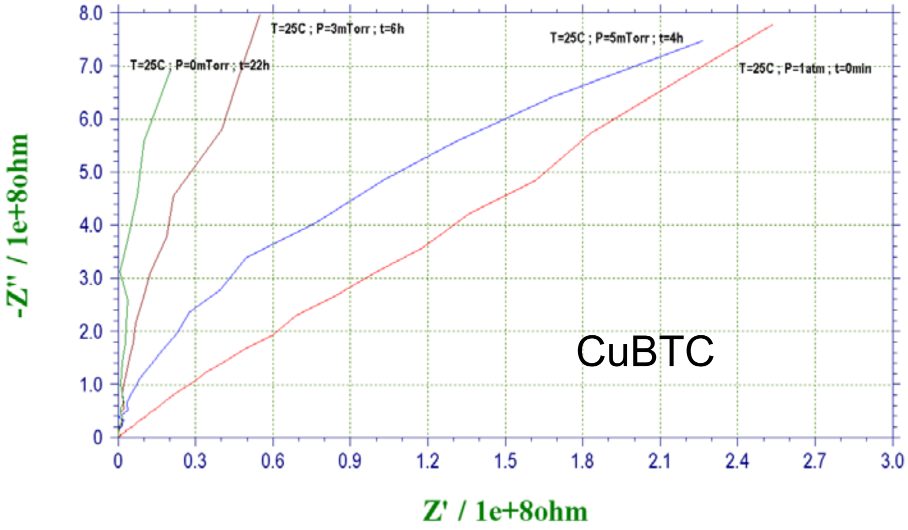
Dielectric Response Can Change Significantly Upon Application of Vacuum (evacuation)







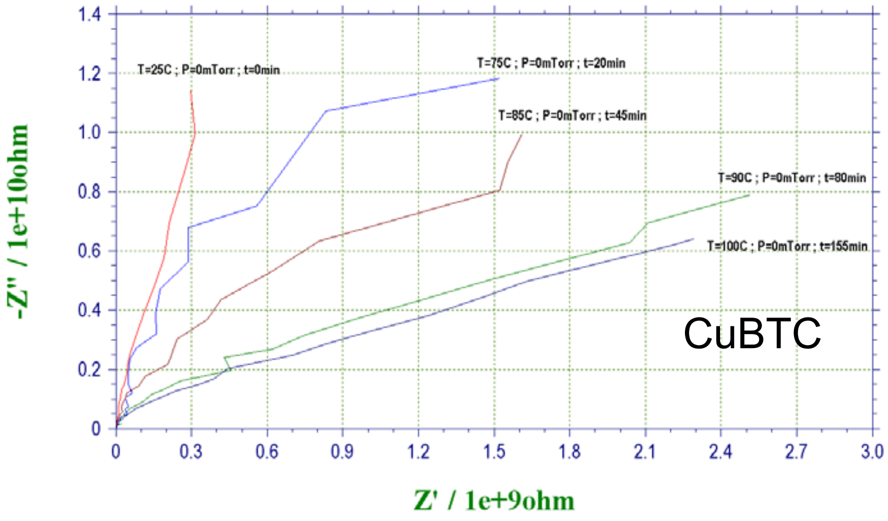
Cu(II)-BTC MOF

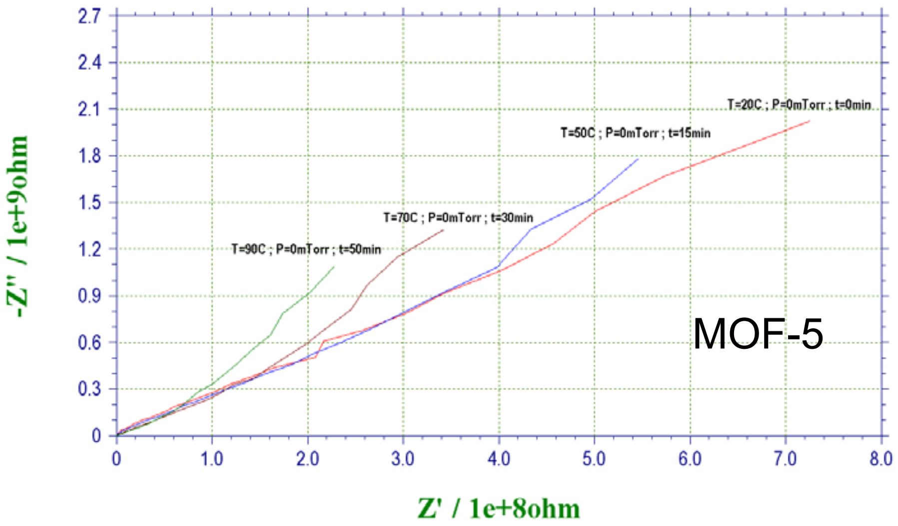


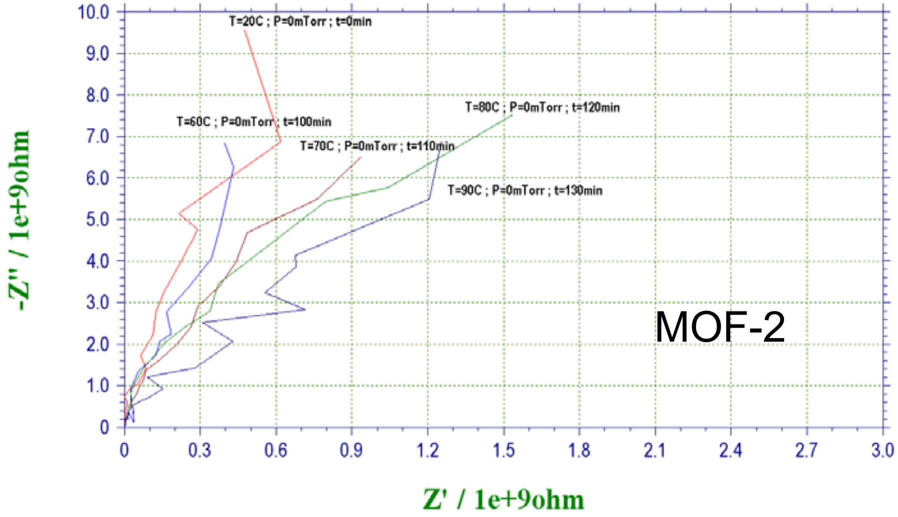
- Z', Z" are real and imaginary parts of the complex impedance
- A larger Z" at endpoint corresponds to a smaller dielectric constant
- The more vertical the response, the less leakage through the "capacitor"

CHARACTERIZATION

Application of Heat Following Evacuation (i.e. vacuum at ambient T)







- Higher temperatures lead to more leakage in MOF-2 and CuBTC (more vib/rotational loss?)

- In MOF-5 a higher dielectric constant and less leakage is seen (removal of water?)

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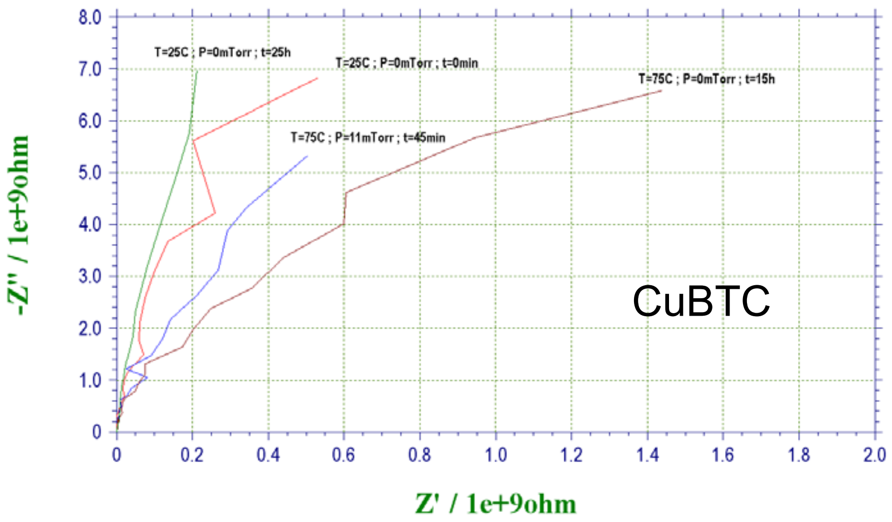
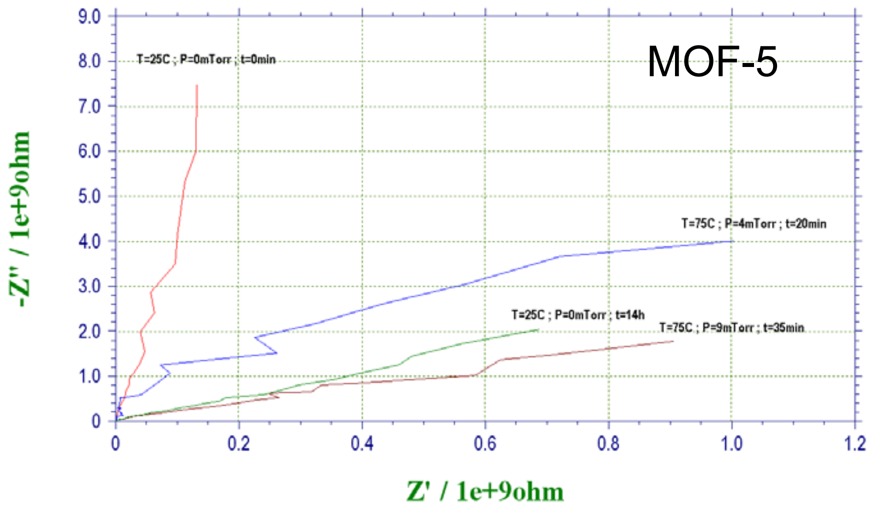
CHARACTERIZATION

Results of a Initial Heating Cycle Under Vacuum





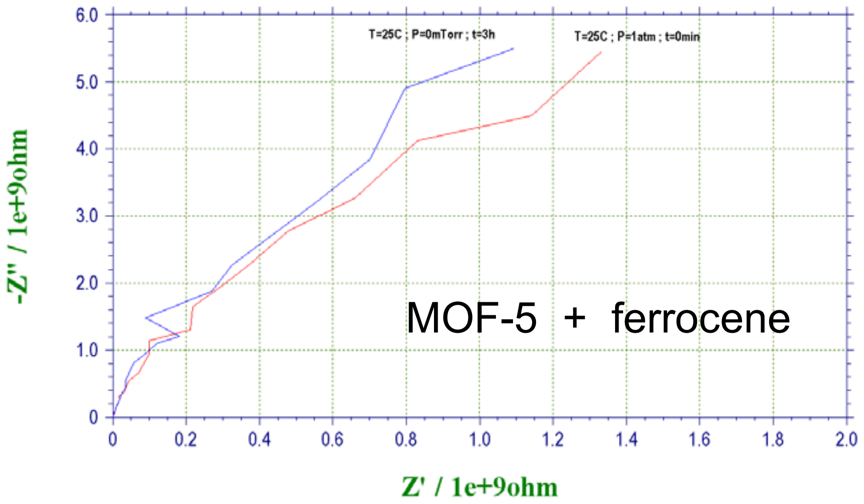
- Measured response at 25 C not effected much in CuBTC, whereas significant changes seen in MOF-5.

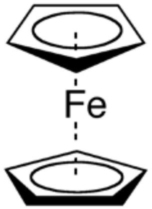
- Application vacuum likely removed the guest water while heat resulted in removal of coordinated (bound) water as well.

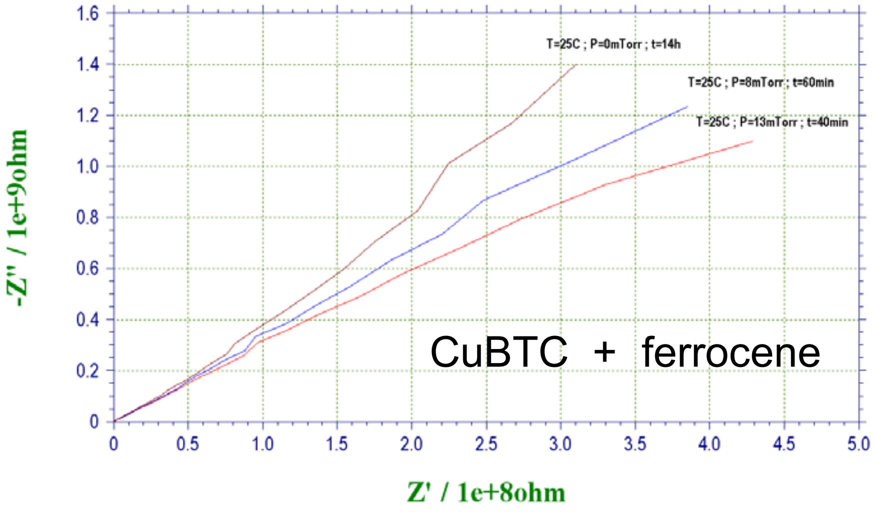
- Virtually no change seen in MOF-2.

SYNTHESIS/CHARACTERIZATION

Modified MOFs - Doped with Ferrocene to Alter Polarizability







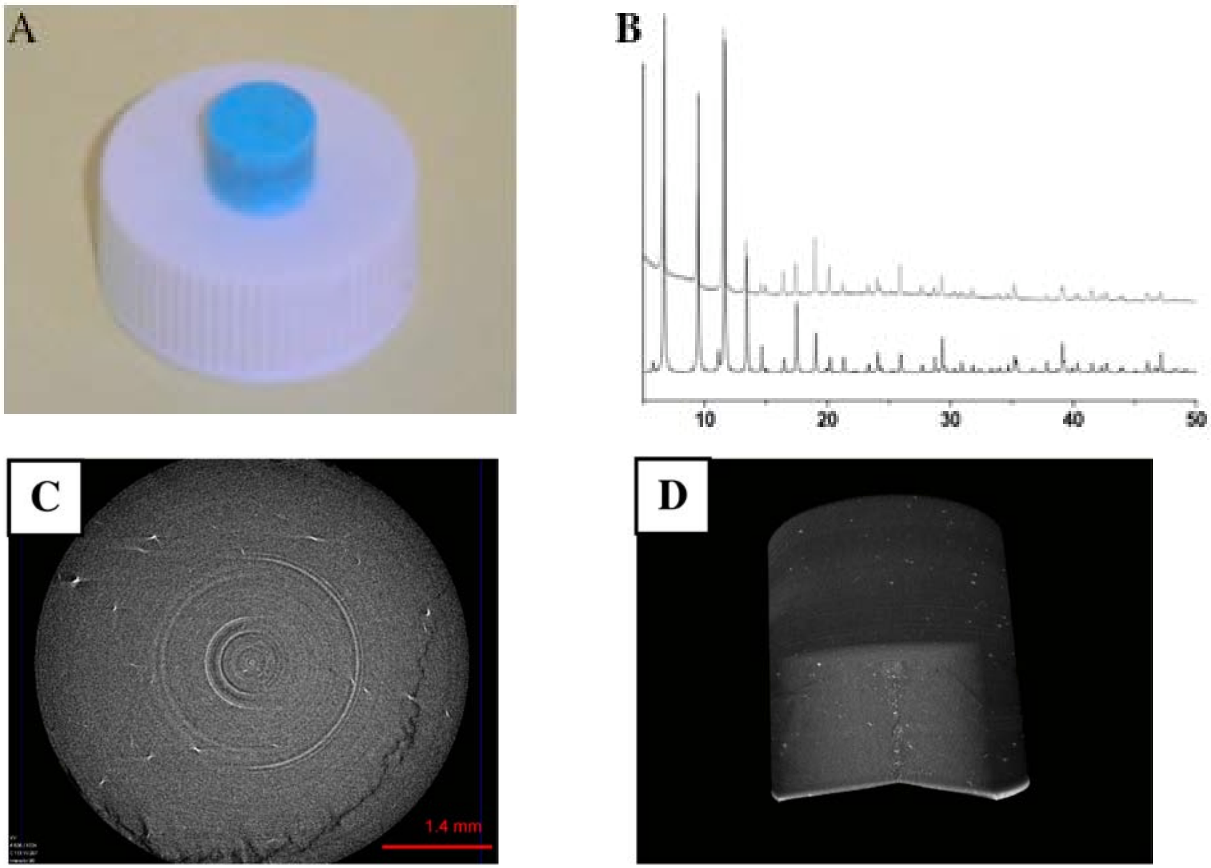
- Must be careful in interpretation - while ferrocene provides additional polarizable electron density,it is also volatile

PERFORMANCE TESTING

Pressed-Pellet 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 (blue) compressed at 1000 psi. Image (B) is a powder XRD of HKUST-1 pressed MOF showing crystallinity is maintained through processing. 3-D Tomography, (C, D) verified pressed pellet uniformity. Small bright spots were detected in pressed pellet tomography images that may represent copper oxide particles (which could provide a conduit for dielectric break-down).

THE PROJECT TEAM

Chosen to bring together the necessary expertise:

R.P. Currier	- Physical Chemistry/Chemical Eng.
D.J. Devlin	- Materials Science/Adsorption Measurements
S.J. Obrey	- Synthesis/Characterization
J.-M. Sansinena	- Electroactive Materials; Dielectric Measurements
Y. Zhao	- Crystallography/Characterization
N. Henson	- Theory/Computational Chemistry
R.J. Martinez	- Mechanical Design/Fabrication
Q. Wei	- Synthesis/Characterization (Post-Doc)