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# Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

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Los Alamos, NM 87545**

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Project ID: st026

# OVERVIEW

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- **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<sub>2</sub> 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

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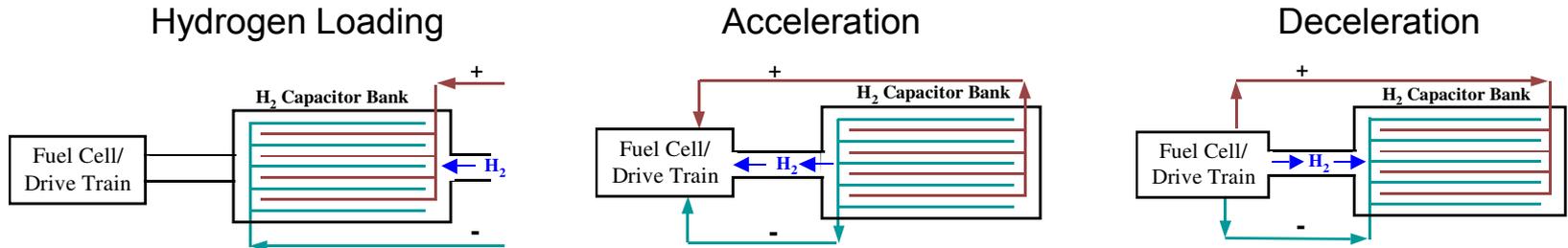
**Motivation:** Given the physical properties of hydrogen, the manipulation of temperature and pressure alone are not likely to achieve the target goals. Another physical variable is needed.

**Objective:** Use applied electric fields to facilitate high H<sub>2</sub> 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<sub>2</sub> dissipates.

# OBJECTIVES/RELEVANCE



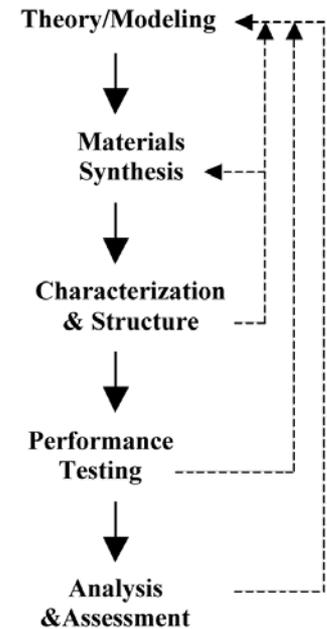
Operational Concept. Hydrogen loading involves simultaneous introduction of hydrogen and voltage. Expect voltages to be high (10-20 kV) while current is small ( $\mu\text{A}$ ). As demand increases, capacitor is discharged releasing additional H<sub>2</sub>. During deceleration, voltage from regenerative 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<sub>2</sub> in Dielectrics*
  - *Effect of External Electric Field on Structure & Binding*



## Impact on Technical Barriers:

- **Field-enhanced H<sub>2</sub> 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

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## Address the major challenges of Capacitive Hydrogen Storage:

- Over a charge/discharge cycle - how much energy is dissipated as heat?  
[Classic electrostatics: Loss  $\sim (\epsilon'' E^2 \omega)/8\pi$  for a homogeneous dielectric]
- Does strong binding at specific sites near the outer edges of the dielectric limit H<sub>2</sub> flux  
(must H<sub>2</sub> 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<sub>2</sub> 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

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## 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:

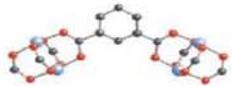
- Quantitative demonstration of electric field-enhanced hydrogen loading.
- Assessment of hydrogen compatibility with organic-containing substrates in the presence of dielectric breakdown. If incompatible, subsequent materials discovery will necessarily shift to the inorganic dielectrics. (initial results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

# TECHNICAL PROGRESS: STARTING POINT

Select Baseline Materials that Allow for Adjustable Dielectric Properties

## Metal-Organic Frameworks

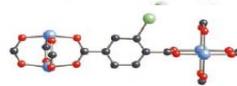
- Porous crystals with adjustable structure
- Ultra-high surface area
- Metal ions serve as vertices
- Organic groups act as "connectors" and as polarizable sites under E-Field



Cluster



2D layers



3D framework

## Zeolitic Imidazolate Frameworks (ZIFs)

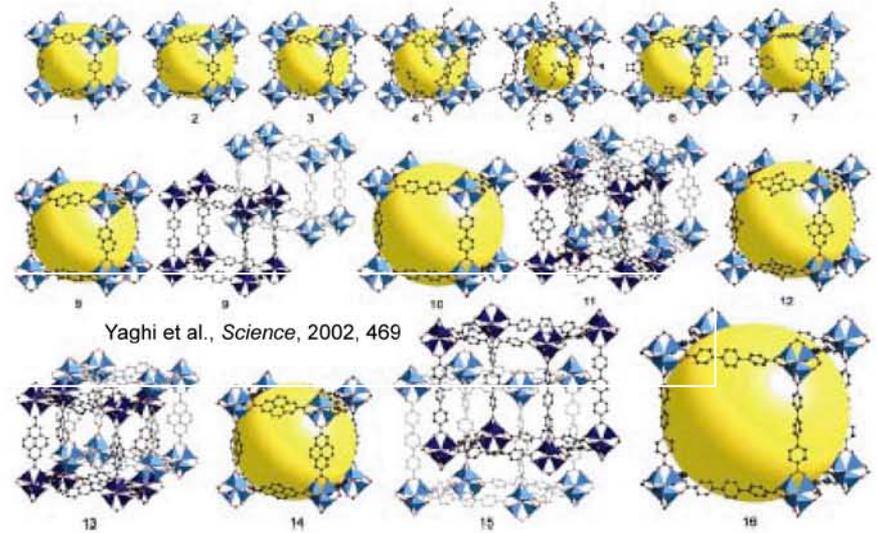


M - IM - M

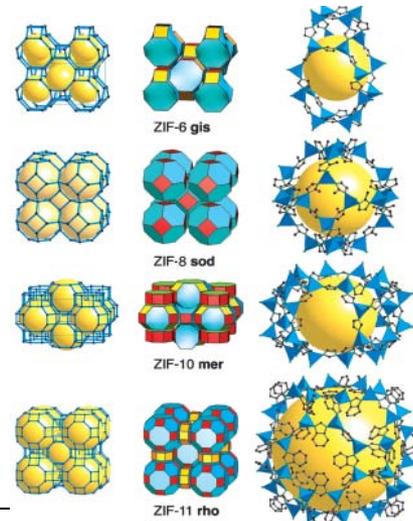


Si - O - Si

145°



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



ZIF-6 gis

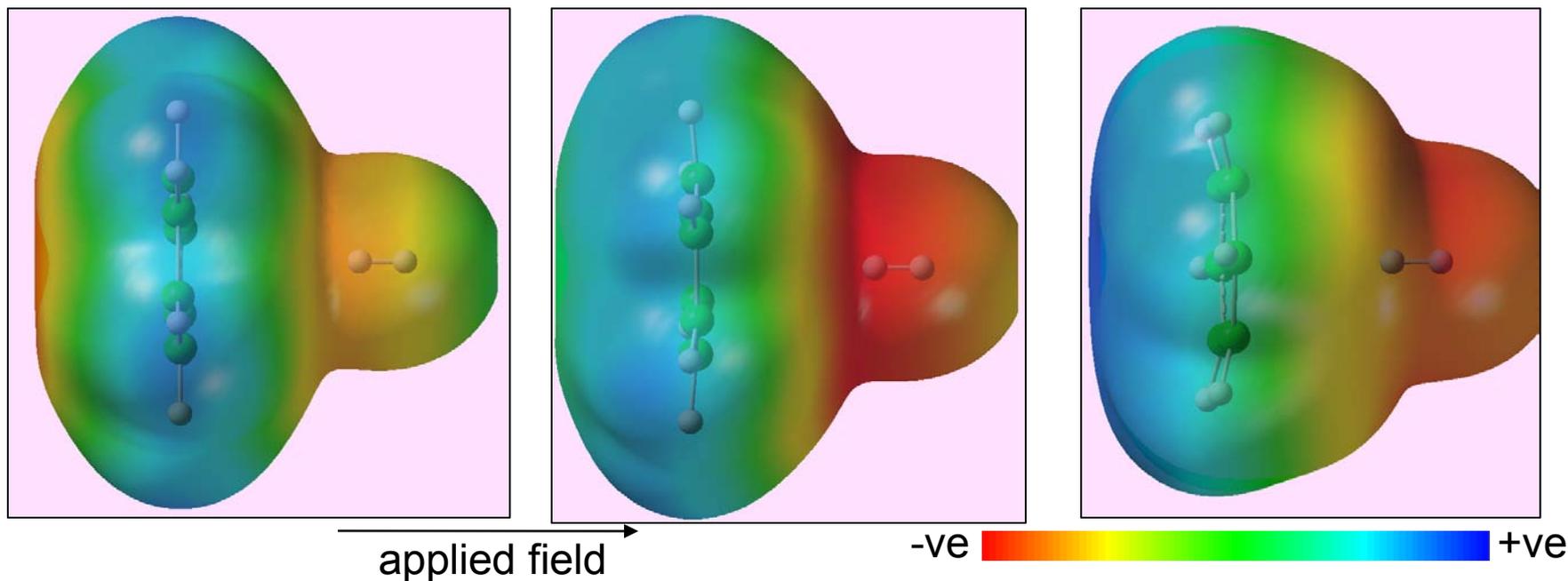
ZIF-8 sod

ZIF-10 mer

ZIF-11 rho

# TECHNICAL PROGRESS: MODELING

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



field (MVcm <sup>-1</sup> )	zero	102.8	257.1
RHF binding energy (kJmol <sup>-1</sup> )	+0.3	-2.7	-13.9
MP2 binding energy (kJmol <sup>-1</sup> )	-4.5	-6.0	-18.3
BSSE corrected (kJmol <sup>-1</sup> )	-2.6	-3.9	-15.0

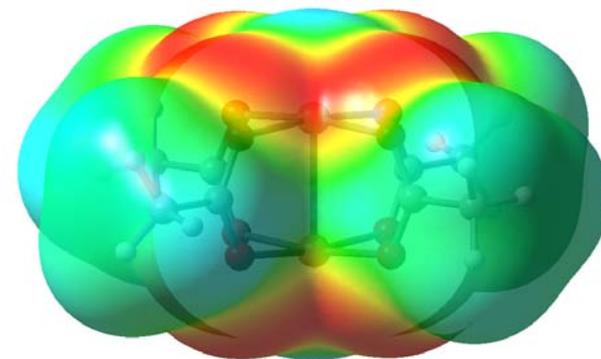
# TECHNICAL PROGRESS: MODELING

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

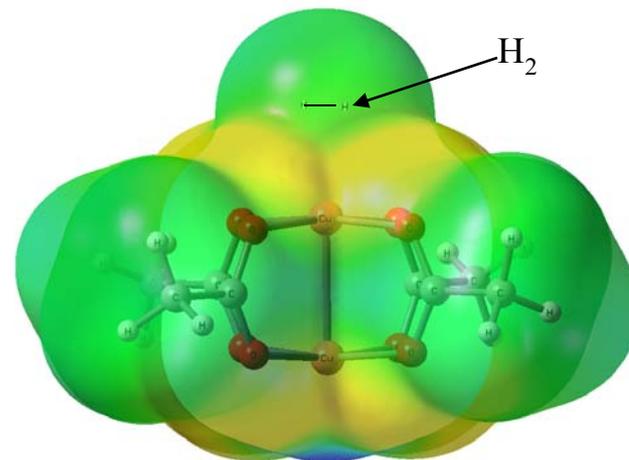


-ve  +ve

Hartree Fock calculation with MP2 corrections  
(required for H<sub>2</sub>)

## Notable results:

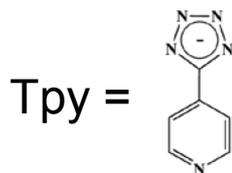
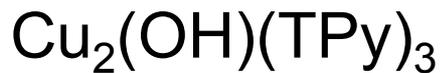
- Little perturbation in electronic structure from presence of H<sub>2</sub>
- Cu-(H<sub>2</sub>) bond lengths - singlet : 2.08Å, triplet : 2.73Å
- H-H bond length slightly shorter for singlet
- Calculations with field applied along Cu-Cu vector in progress



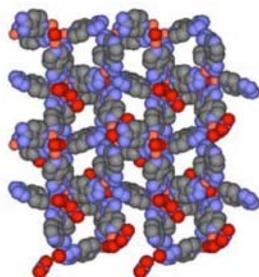
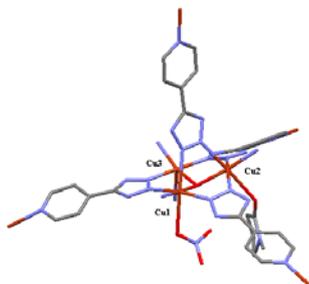
Directional E-Field will be added in next set of calculations

# TECHNICAL PROGRESS: SYNTHESIS

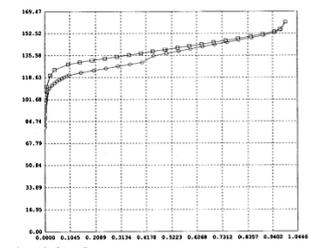
Synthesis of Lightweight Porous Dielectric Materials with More Polarizable Linkages



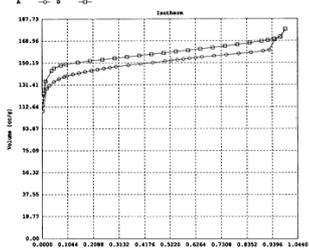
Following modeling guidance, nitrogen-containing rings should provide additional polarizability (rel. to C-rings)



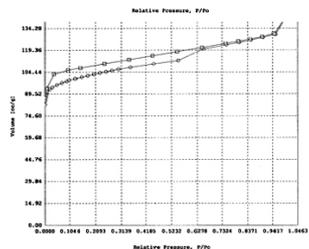
150°C



100°C  
to  
150°C

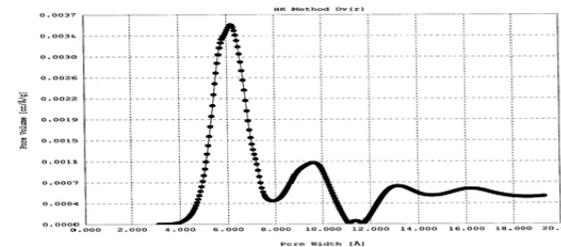
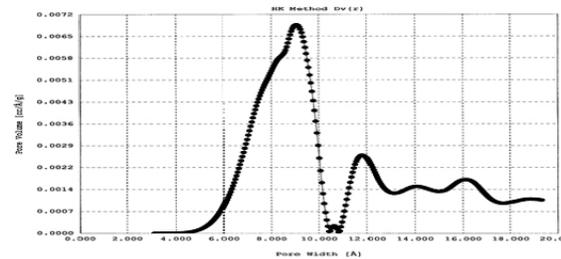
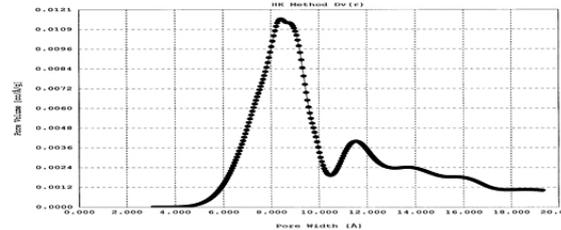
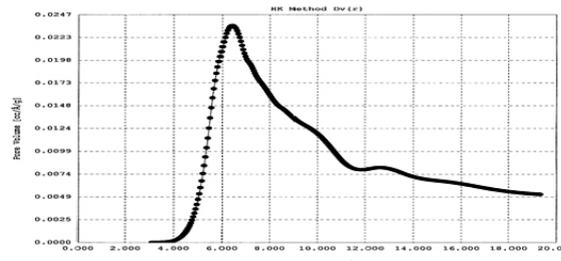


100°C



25°C

Comparable to 100°C



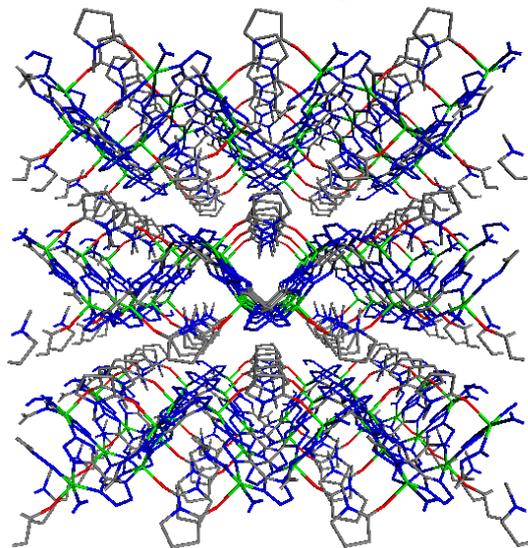
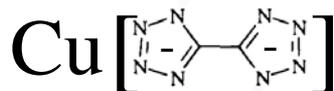
BET Adsorption

Pore size distribution

# TECHNICAL PROGRESS: SYNTHESIS

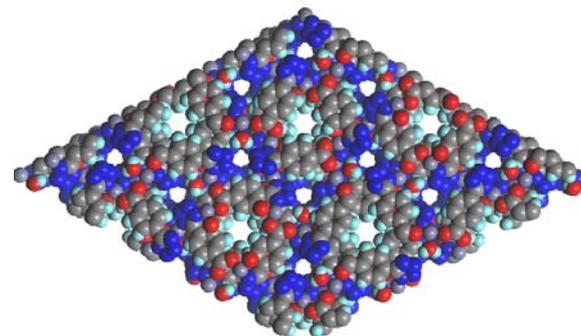
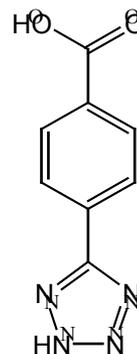
Porous Dielectric Materials with Polarizable Linkages

## Highly polar copper-bitetrazole MOF

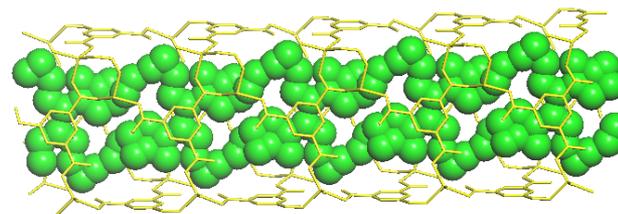


C-axis view of zig-zag layers.

## Other Tetrazole and Imidazole Based MOFs as Polarizable Substrates



Hydrophilic /hydrophobic channels



$[\text{Me}_2\text{NH}_2][\text{Zn}_2(\text{BTC})(\text{HBTC})]\cdot\text{DMF}$

*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

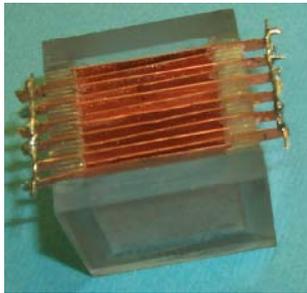
	Vacuum	Vacuum + heat	T = 90C
CuBTC	<b>5.21 ± 0.05</b>	<b>2.74 ± 0.05</b>	<b>3.02 ± 0.05</b>
MOF-2	<b>5.58 ± 0.05</b>		<b>6.93 ± 0.05</b>
MOF-5	<b>8.61 ± 0.05</b>	<b>41.94 ± 0.05</b>	<b>22.67 ± 0.05</b>
CuBTC + Ferrocene	<b>40.61 ± 0.05</b>		
MOF-5 + Ferrocene	<b>8.29 ± 0.05</b>		

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

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

# 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<sub>2</sub> 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<sub>2</sub> 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

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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

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- 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<sub>2</sub>/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

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**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<sub>2</sub> binding sites upon application of an electric field.

**Technical Progress:** Electronic structure calculations show induced polarizability in simple organic fragments and enhanced H<sub>2</sub> 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.

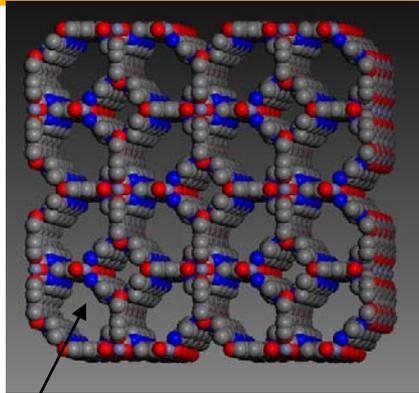
**Proposed Future Research:** Quantify enhancement of hydrogen adsorption under electric field; Explore T-P-voltage space, quantifying H<sub>2</sub> loading; Interrogate heterocyclic structures (e.g. tetrazole-based MOFs) and doped structures; Enhance modeling tools for guidance purposes; Explore charge/discharge dynamics.

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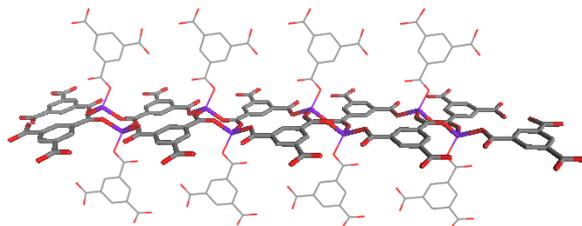
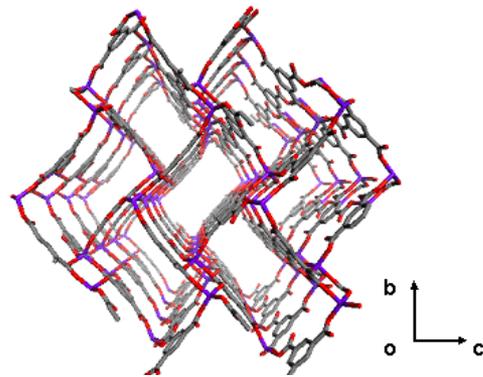
# SUPPLEMENTAL SLIDES

# SYNTHESIS

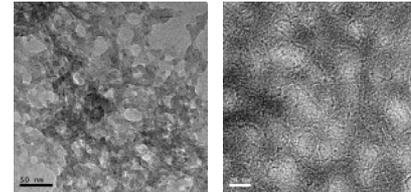
Other Tetrazole and Imidazole Based MOFs and MOF Aerogels Developed as Polarizable Substrates



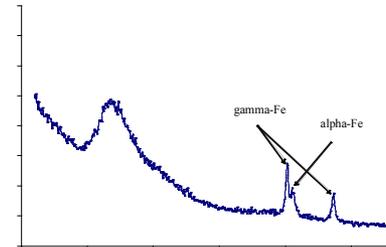
Imidazole formed c



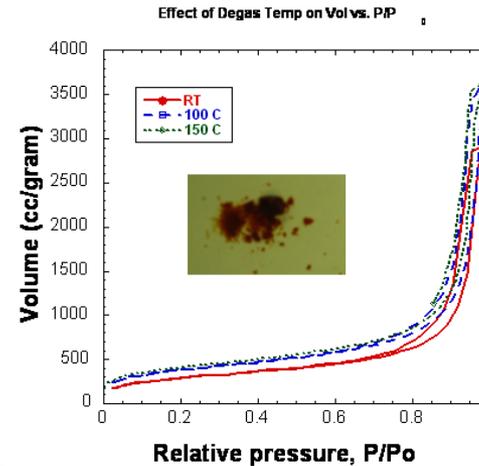
Anionic Zn-BTC frameworks



TEM analysis of Fe-BTC aerogel



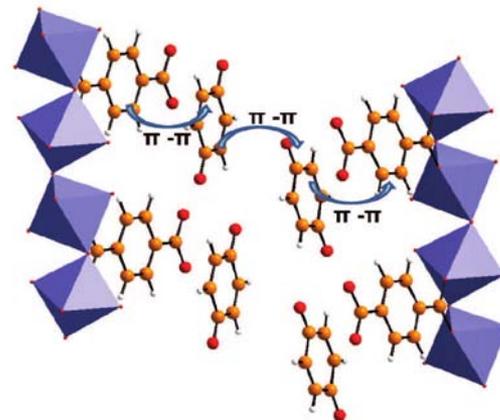
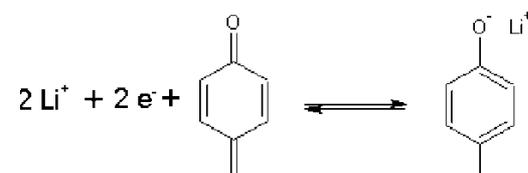
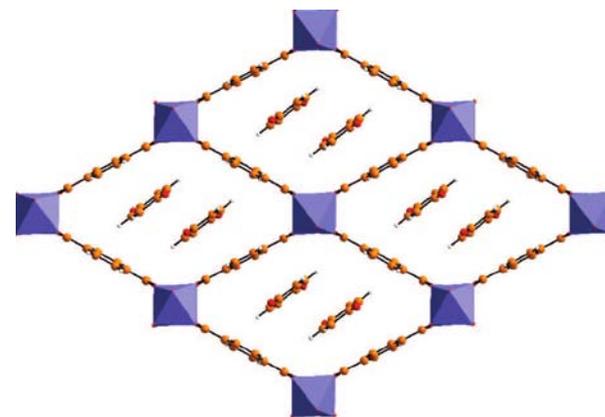
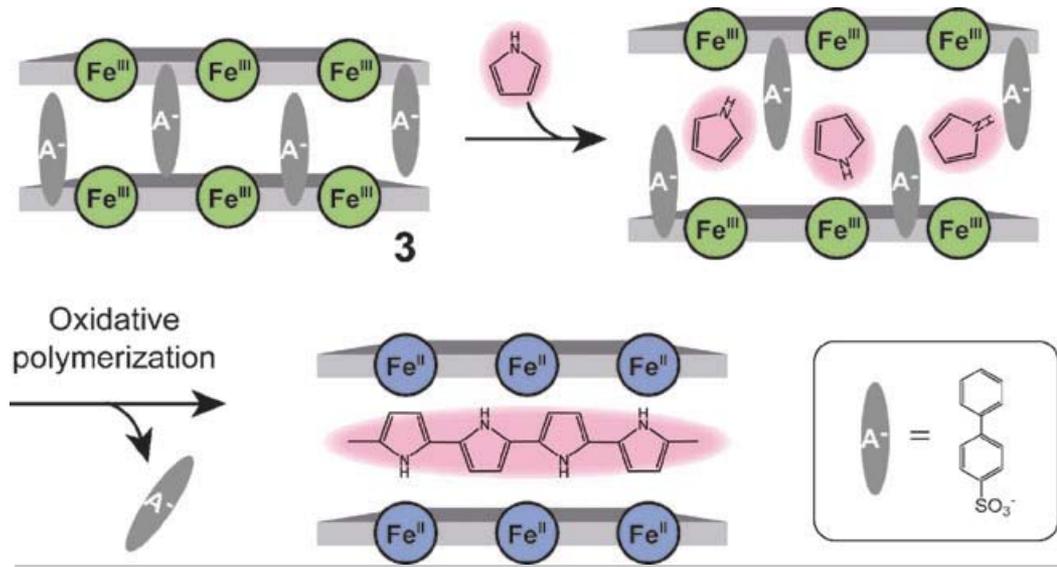
Powder XRD of reduced Fe-BTC aerogels



# SYNTHESIS

## Exploring the Inclusion of Conducting Constituents into Frameworks

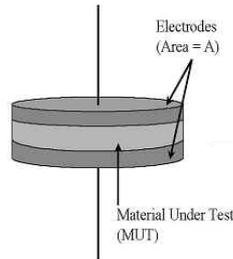
Introduction of conductive “islands” with thin provides another means of manipulating local polarizability (e.g. using Fe and Li based sub-structures)



# CHARACTERIZATION

Key Dielectric Properties Determined Experimentally: Correlate Binding with Dielectric Properties

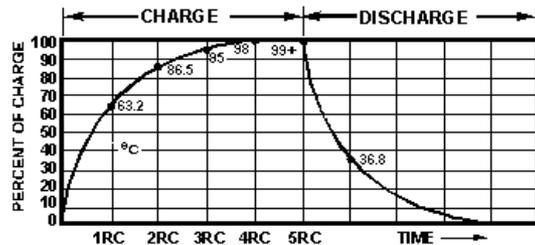
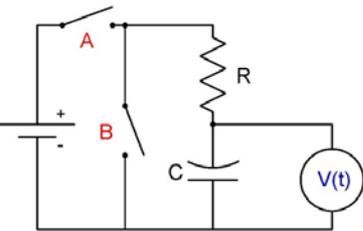
- (1) Dielectric sample is sandwiched between two electrodes to form a capacitor.



**Capacitance:  $C = Q / V = \epsilon_0 \epsilon_r A / d$**

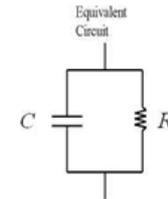
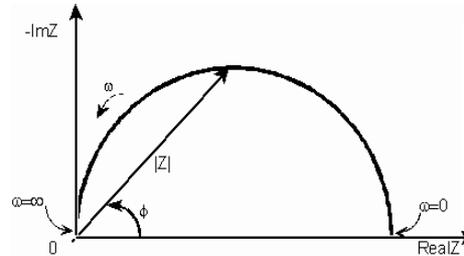
- $\epsilon_0$  : Dielectric constant of the free space
- $\epsilon$  : Dielectric constant of the material
- $\epsilon_r$  : Relative dielectric constant of the material:  $\epsilon_r = \epsilon / \epsilon_0$
- A** : Area of electrodes
- d** : Distance between electrodes

## (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:
 
$$V_C(t) = V_C(t=0) e^{-t/RC} \quad (RC = \text{time constant})$$
- e) Capacitance C is measured from the discharging curve and  $\epsilon_r$  is calculated from:  $C = \epsilon_0 \epsilon_r A / d$

## (3) AC Impedance method to calculate capacitance, C



$$\epsilon'_r = \frac{d * C}{A * \epsilon_0}$$

$$\epsilon''_r = \frac{d}{\omega * R * A * \epsilon_0}$$

- 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 ( $\epsilon'_r$ ) and Imaginary ( $\epsilon''_r$ ) 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:

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

# CHARACTERIZATION

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## EXPERIMENTAL VALIDATION OF TECHNIQUE: Static Relative Dielectric Constant Measurements

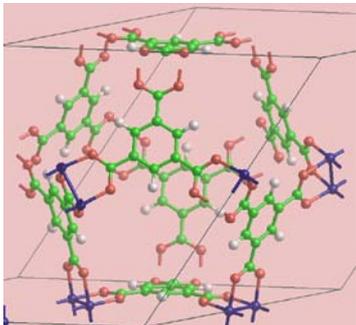
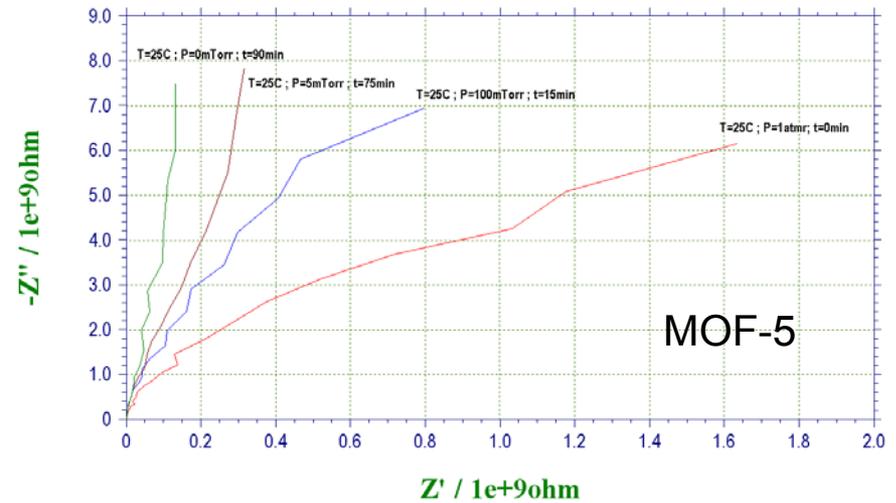
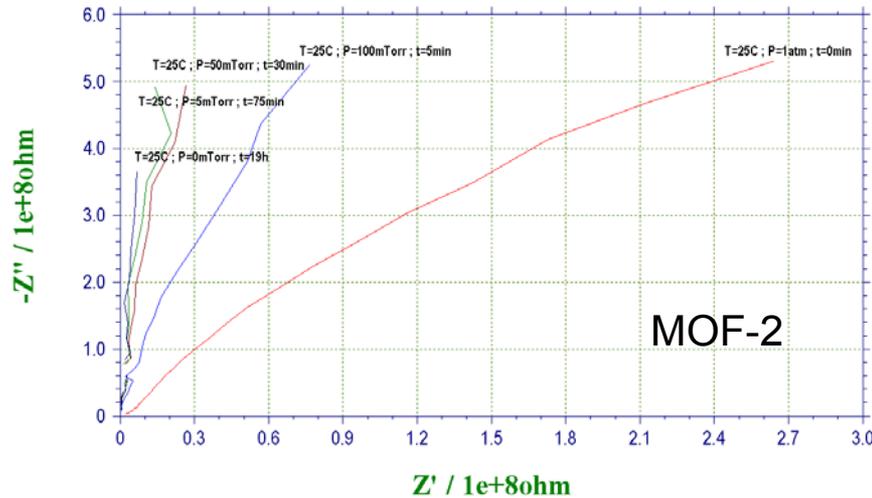
Condition	Measured	Literature Reference
Vacuum	$0.96 \pm 0.05$	1
Teflon	$2.29 \pm 0.05$	2.1

## Effects of pelletizing (pressure) on Relative dielectric Constant

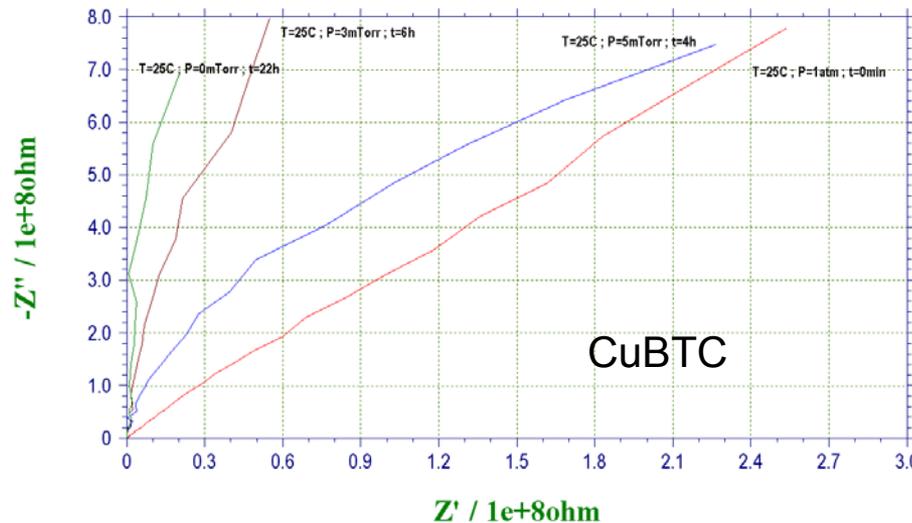
Sample	Pelletized @5000 Lbs	Pelletized @15000 Lbs
Alumina	$5.65 \pm 0.05$	$5.66 \pm 0.05$
CuBTC	$4.91 \pm 0.05$	$4.90 \pm 0.05$

# CHARACTERIZATION

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



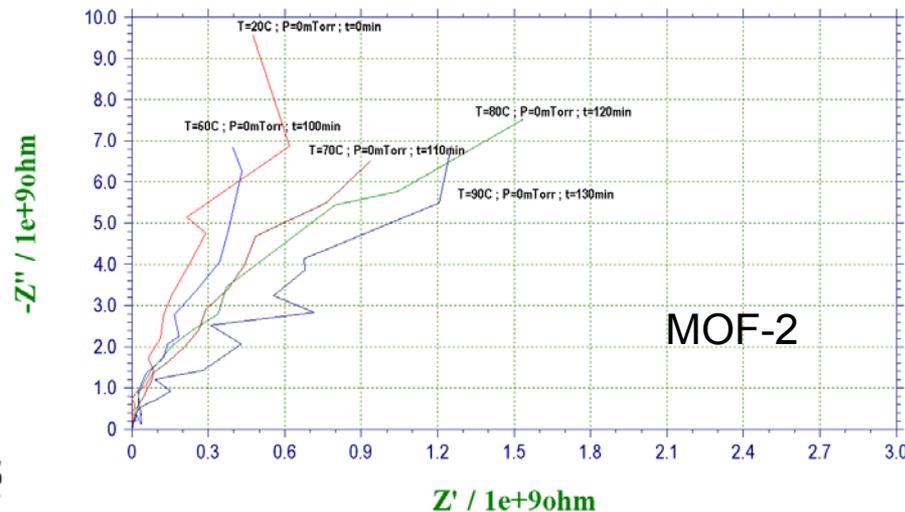
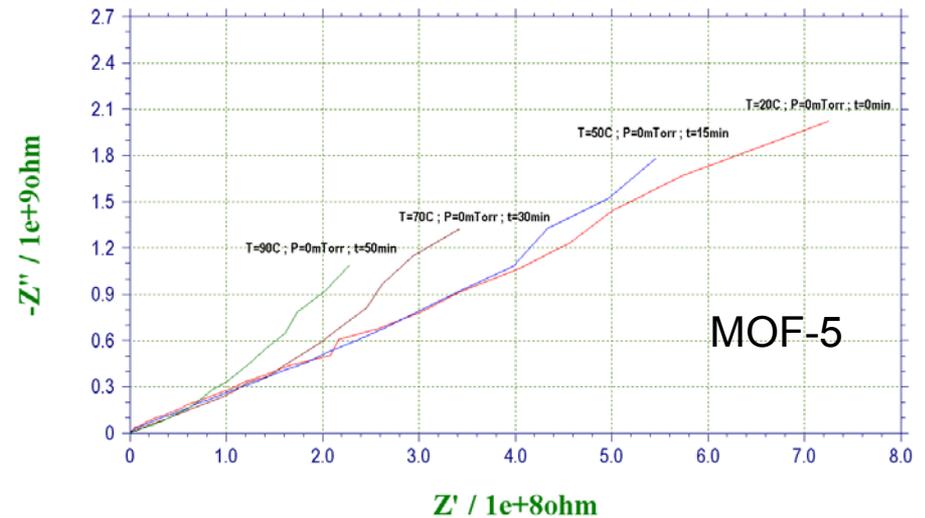
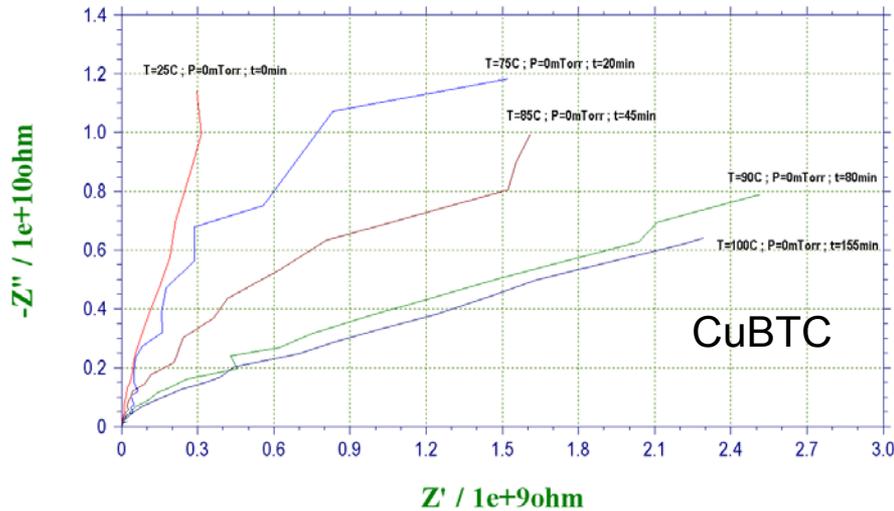
Cu(II)-BTC MOF



- $Z'$ ,  $Z''$  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

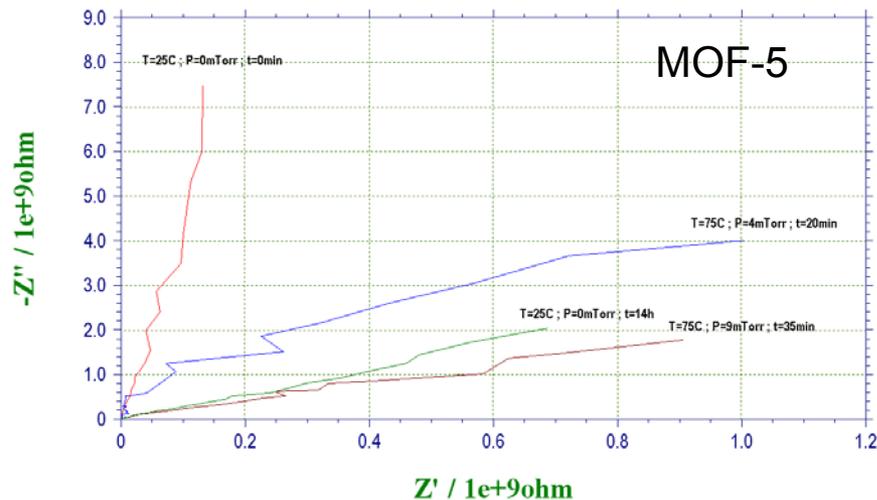
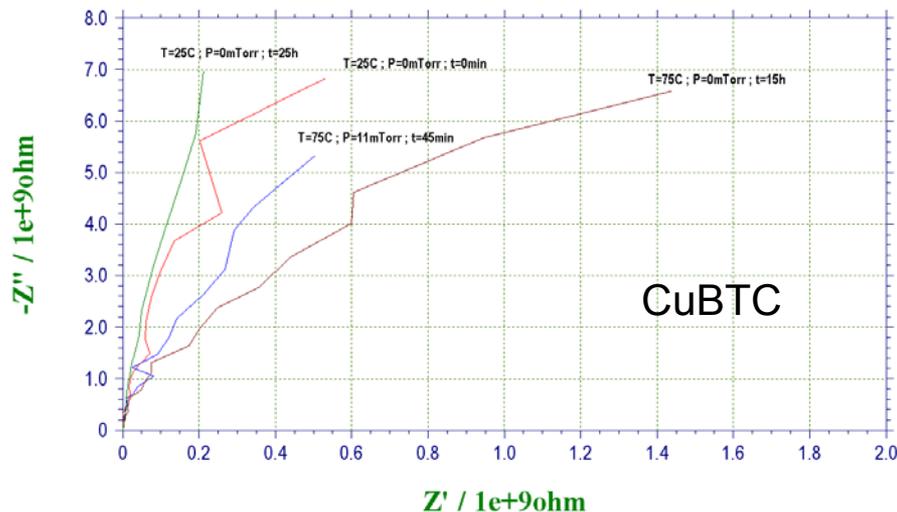
Application of Heat Following Evacuation (i.e. vacuum at ambient T)



- 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?)

# CHARACTERIZATION

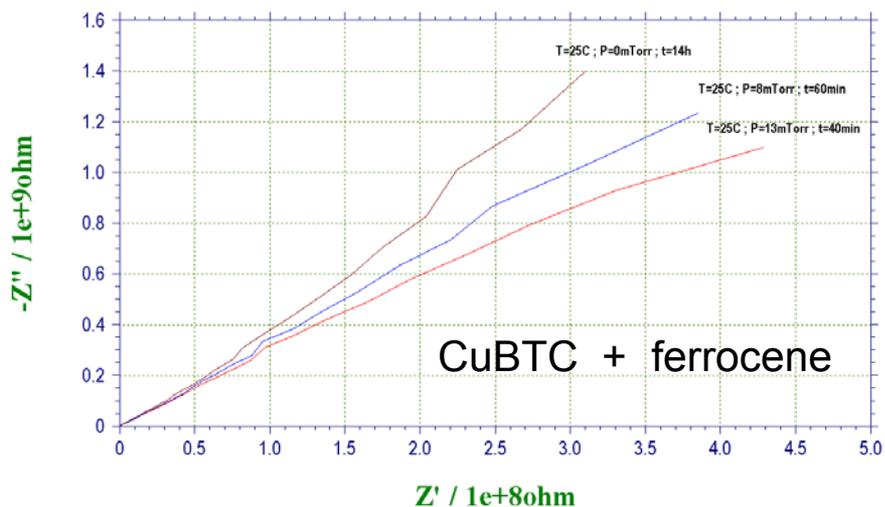
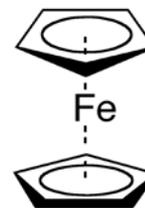
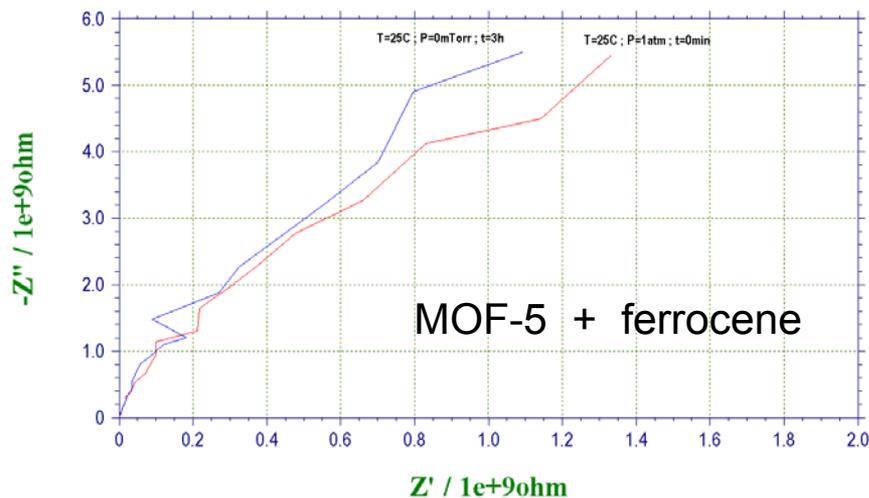
## Results of a Initial Heating Cycle Under Vacuum



- 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



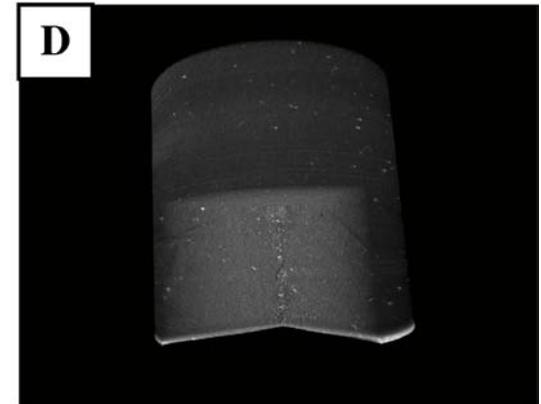
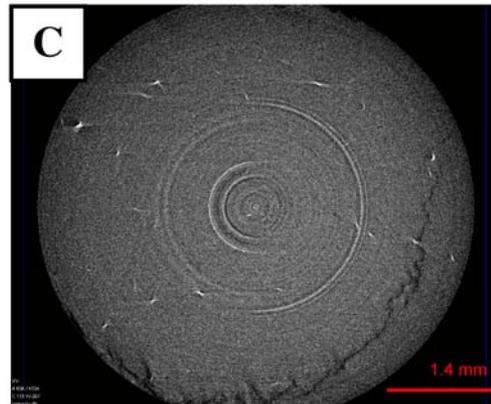
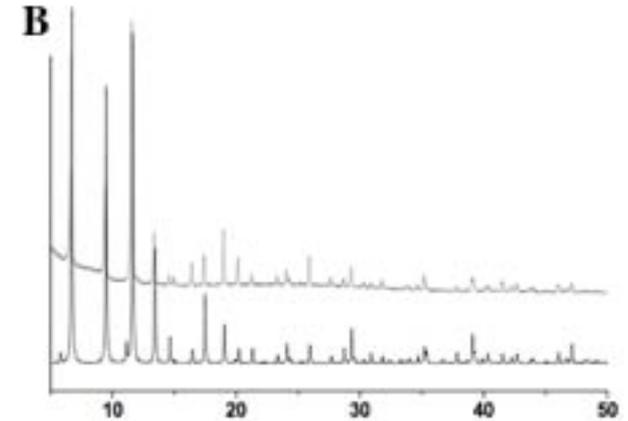
- Must be careful in interpretation - while ferrocene provides additional polarizable electron density, it is also volatile

# 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

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**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                    |
| <br>            |  |
| Q. Wei          | - Synthesis/Characterization (Post-Doc)            |