IV.F.4 Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics

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Objectives

To develop storage materials that enable high H_2 loading under more economical temperature and pressure ranges; that have more controllable uptake/release dynamics; and that have moderate losses over a charge/discharge cycle. By using electric field enhanced adsorption, we expect to:

- Enhance adsorption binding energy (10-15 kJ/mole electric-field effect expected).
- Ultimately meet hydrogen loading goals at more practical combinations of temperature and pressure.
- Establish better control over charge/discharge dynamics via field modulation.

Technical Barriers

Several technical barriers from the Storage section (part 3.3) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan are addressed by this project:

(C) Efficiency
(E) Charging/Discharging Rates
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

The project centers on the fundamentals of hydrogen adsorption in porous adsorbents under the influence of externally applied electric fields. Electric-field enhancement of binding (capacitive storage) can integrate well with electric drive systems and the insights gained from these studies will be applied toward the design and synthesis of storage materials more likely meet DOE hydrogen storage targets. Outcomes of this work are expected to include:

- New insights into H_2 physisorption/chemisorption at sites of high local polarizability.
- Improvements in net efficiency of storage systems, i.e. acceptable hydrogen wt% at more accessible temperature and pressure.
- Better control over hydrogen charge/discharge dynamics using field strength as a control variable in addition to thermal and/or pressure modulation.

Accomplishments

- Continued of *ab initio* computations exploring effects of external field on electron density in organic constituents typical of metal organic frameworks. Modeling results are being used to guide chemical synthesis effort (e.g. organic linker selection).
- Refined capacitor test-cell design for use in measuring sorption under an applied electric field. Fabricated custom sorption rig – measurements underway.
- Substrate synthesis efforts now include more porlarizable organic linkers. Focus remains on metal organic framework and related substrates.
- Modified dielectric properties of substrates and characterized using electrochemical impedance spectroscopy. Static dielectric constant, loss tangent, and leakage current are being measured and used to estimate time constants and losses over a charge-discharge cycle.
- Conducted experiments where dielectric breakdown was intentionally induced across the capacitor in the presence of hydrogen (addresses an important safety issue).
- Designed a neutron diffraction cell for use with static electric fields. Cell will ultimately provide insight into specific binding site locations.

✧   ✧   ✧   ✧   ✧

Introduction

Capacitive storage involves establishing an electric field across a porous dielectric material designed to adsorb hydrogen. The field acts on localized regions of high polarizability to enhance binding within the cavities of the porous network through induction and dispersion forces (we hope by 10-15 kJ/mol). The enhanced binding energy, induced by the substrate's response to the field, should allow storage goals to be met at more practical combinations of temperature and pressure. Upon discharge of the "capacitor" the electric field is removed, and in turn, the induced electrostatic moment stabilizing hydrogen dissipates. Thus a portion of the thermodynamic driving force for binding can in principle be switched on and off at will. Furthermore, some of the energy required to bind and release hydrogen is reversibly introduced into the system in the form of an electric field. Losses are expected to include dielectric losses and any leakage current through the capacitor during storage. As the field is removed, desorption will be promoted and cooling the substrate is expected. The decrease in temperature provides a larger driving force for heat diffusion into the substrate. Thus, improvements in the release dynamics and improved control over the release are anticipated. Two critical operational issues associated with hydrogen storage are potentially addressed with capacitive storage – hydrogen density and thermal management. Electric field-mediated storage has the ability to enhance the density of stored hydrogen at more practically accessible temperatures and pressures. For example, operating over the range –40 to 60°C should become less onerous. Charging and discharging, system cycling, and transient system response can now involve field modulation in addition to thermal and/or pressure swings and heat exchange within the adsorbent bed. The other outstanding challenges detailed in the On-Board Hydrogen Storage System Technical Targets, such as delivery pressure, charging/discharging kinetics, and system fill time may also benefit directly.

Approach

It is well-known that manipulation of temperature and pressure provides benefits in gas storage, however, it appears that combinations of these two intensive variables alone will not likely yield the desired end result, namely, high hydrogen loading under moderate (and economically attractive) conditions. As an alternative, we are examining the effects of also introducing an electric field to enhance hydrogen uptake in porous dielectric substrates. This materials discovery effort is based on the idea that local regions of high electron polarizability will respond strongly to an applied external field. In doing so, the expectation is that the resulting redistribution of electron density should enhance the hydrogen binding energy. This may involve a combination of enhanced binding energies, creation of new binding sites and/or formation of hydrogen clusters (as is reported in both clathrate-hydrate cages [1] and metal organic frameworks [2]). The key challenge is to determine how best to create localized polarizability within porous adsorbents. Electrostatic stabilizing forces can be locally enhanced by judiciously increasing the polarization of the host substrate at specific sites, or within sub-structures (cavities) favorable to molecular clustering. The metal organic frameworks (MOFs) are serving as the starting point for developing the new dielectric materials [3]. MOFs are composed of metal ions with coordinated organic ligands, where the nature of metal-to-organic ligand coordination provides versatility in the design and control of chemical and physical characteristics (of specific interest to us is the local polarizability). Thus in addition to being high surface area structures (>3,000 m^2/g), MOFs can be chemically tailored by modifying the organic linkers between metal centers. This can potentially be done through introduction of more polarizable atoms and functional groups, tuning the band gap, and/or varying core metal electronic properties. Related materials such as the zeolitic imidazolate frameworks are also being examined. Other potential adsorbents include composites constructed by distributing small metal or semi-conducting clusters in porous structures (e.g. xero- or aero-gels) as another means of producing inorganic materials with extreme dielectric properties [4]. Our approach to developing these materials (structured dielectrics) combines both computational guidance and experimental probes/testing.

Results

Our recent computational modeling has focused on simple models for the structural motifs featured in the Cu-1,3,5-benzenetricarboxylate (BTC) MOFs and the effect on an applied electric on their interaction with hydrogen. For this purpose, we chose the copper acetate structure since it shares several structural similarities with Cu-BTC while consisting of discrete molecular units in the solid state. For example, the pinwheel coordination geometry is present about the copper center. Figure 1(a) shows a candidate binding geometry for the hydrogen molecule at the copper site. Quantum chemical calculations have been performed on this model in vacuum and with an applied electric field. In Figure 1(b), the calculated electrostatic potential has been projected onto the calculated total electron density for the molecule. It can be clearly seen that applied electric field induces a dipole in the molecule, and the calculated binding energy is enhanced by around 5 kJ/mol for an applied field of 20 MV/cm. The computations suggest that in order to effect the desired change at more modest field strengths, higher polarizability and/or low band gap ligands (linkers) are needed (Figure 2). Thus, new

(a)

(b)
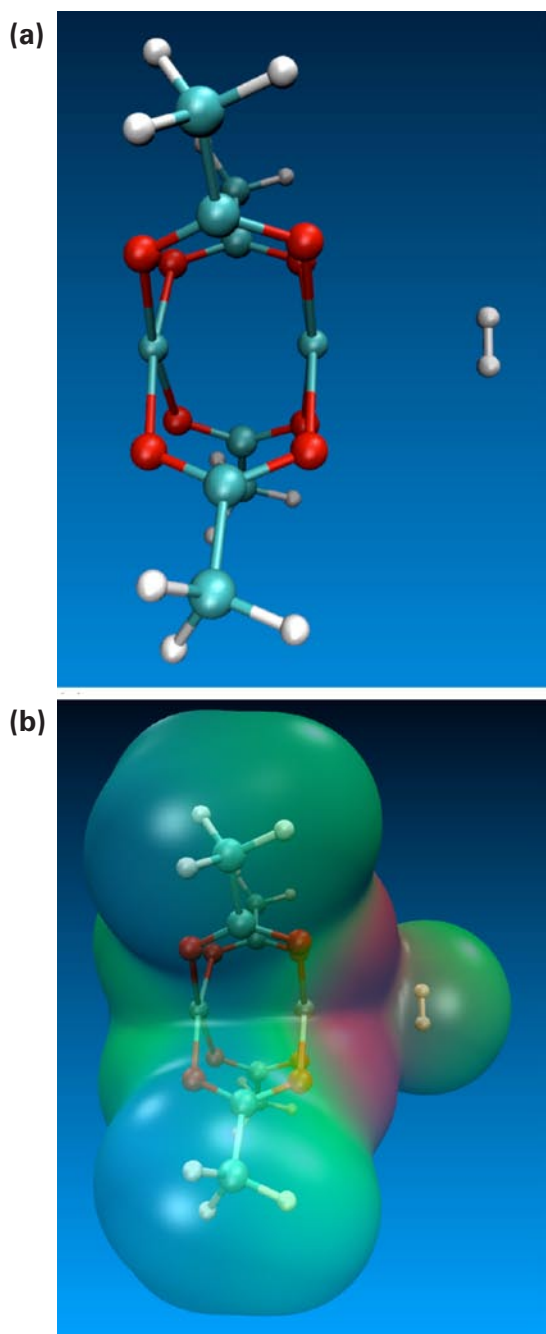
FIGURE 1. (a) Candidate binding geometry for hydrogen at the copper site. (b) Calculated total electron density for the hydrogen molecule interacting with a copper acetate structure.

ligands are being incorporated into MOFs with the aim of altering framework polarizability (e.g. replacing the 1,3,5-benzenetribenzoate [BTB] links in MOF-177 with more polarizable ring motifs or phosphazene derivatives). Known MOFs were also synthesized for baseline testing. A custom gas adsorption rig was also commissioned. Experiments are now underway using this rig and the matching capacitor assembly (Figure 3). We will also explore the role played by the electrostatic

(a)

(b)
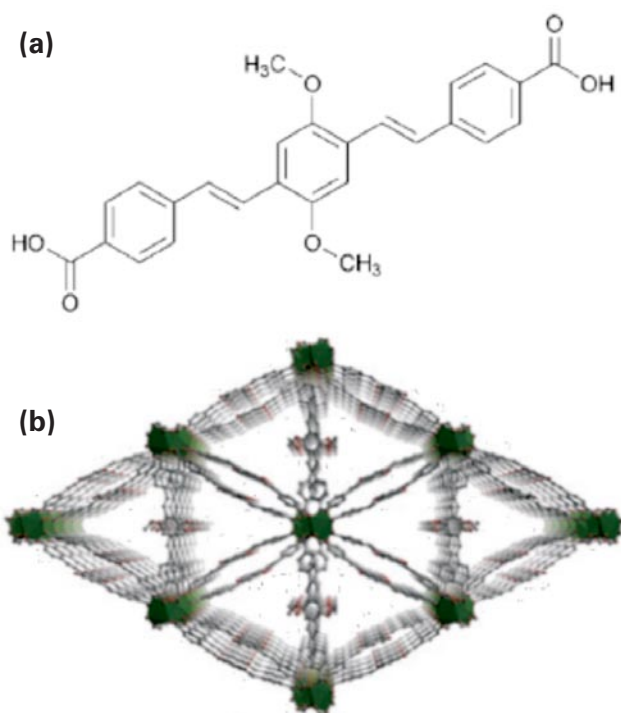
FIGURE 2. (a) A poly-vinylidene dichloride (PVDC) linker. PVDC represents a ligand class that shows a non-linear optical response under an electromagnetic field. In addition to the facile electromagnetic response of the PVDC structural motif, it has a low highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) band gap and the ability to conduct charge between adjacent metal centers in certain charge transfer complexes. The H_2-PVDC structural characteristics are being modified to control the HOMO-LUMO band gap and electron mobility between metal centers. (b) The PVDC ligand has shown the ability to bond with trivalent metals (M^{+3}) resulting in the formation of a porous MOF. We are synthesizing isostructural porous MOFs utilizing the basic PVDC ligand motif with trivalent Group 3, Group 13, and lanthanide based metal centers. It is expected that the high-spin non-bonding 4f electrons found in the lanthanide series will have the most facile response to an applied electric field.

moment in the gas by comparing field-induced adsorption of hydrogen and carbon dioxide, which have very different electrostatic moments than hydrogen (e.g. relative quadrupole moments: CO_2 4.3 esu; H_2 0.662 esu [5]). We expect to have a robust quantitative assessment of the electric field enhancement on hydrogen adsorption in selected MOFs next year. Electrochemical impedance spectroscopy is being used to determine dielectric properties and estimate losses. Losses specific to electric field swing adsorption include the dielectric losses upon a charge-discharge cycle, which involves a time-varying (periodic) electric field. A simple (idealized) way to envision these is energy dissipation as a result of dipole rotation generating friction in the time-varying field. Dielectric losses over a charge-discharge cycle for a uniform dielectric in a periodic field can be estimated from classical

(a)

(b)

FIGURE 3. (a) Custom design test rig for sorption experiments under action of an electric field. (b) Spring-loaded parallel plate capacitor test cell with electrical leads. Pressed sample "wafers" are inserted between plates. Notches enable precise measurement of distance between the plates prior to inserting the capacitor assembly into the adsorption test rig (a).

Validation of impedance spectroscopy technique		
Condition	Measured dielectric constant	Accepted Value
Vacuum	0.96 ± 0.05	1
Teflon	2.29 ± 0.05	2.1
Effects of pelletizing (pressure) on dielectric constant		
Sample	Pelletized @5,000 lbs	Pelletized @15,000 lbs
Alumina	5.65 ± 0.05	5.66 ± 0.05
CuBTC	4.91 ± 0.05	4.90 ± 0.05
Effects of decorating MOF structure		
Sample	Dielectric constant (vacuum)	
CuBTC	5.21 ± 0.05	
CuBTC + Ferrocene	40.61 ± 0.05	

FIGURE 4. Summary of results from characterization using electrochemical impedance spectroscopy. Results of validation experiments, effects of pelletizing, and intentionally altering dielectric properties are shown. As a demonstration, ferrocene (structure shown below the table) was used to infiltrate the MOF CuBTC (the infiltrated powder is shown above). As a result of introducing a more polarizable entity, the static dielectric constant increased eight-fold.

electrostatics [6] as: dielectric loss $= (\varepsilon'' \, E^2 \, \omega) / 8\pi$ where ε'' is the imaginary part of the complex dielectric constant, E the electric field strength (e.g. MV/m), and ω is the frequency of the periodic electric field. Calculations suggest that dielectric losses should be small (<1 watt/liter of dielectric) in the hydrogen storage systems, due primarily to the low frequency variation in the electric field over a charge-discharge cycle. Estimates of the leakage current have been made using electrochemical impedance spectroscopy and results fit to the Randles "equivalent circuit" model for a real capacitor. Initial estimates of leakage in MOFs placed in our current test rig were too high, but by increasing dielectric constants (via molecular design) and altering the electrode area to electrode gap ratio in the capacitor, it appears be possible to maintain charge for days. The ability to favorably modify the dielectric properties

of MOFs were demonstrated (Figure 4). A capacitor cell for use in neutron diffraction experiment was also built. It will ultimately allow us to monitor hydrogen adsorption at specific sites. Hydrogen bonding sites will be refined from the neutron diffraction data and used to improve the next iteration in materials design/synthesis.

Conclusions and Future Directions

- Capacitive storage appears to offer a practical means of enhancing hydrogen storage. The approach is expected to result in more economical combinations of temperature and pressure in hydrogen storage systems. Higher efficiencies and better control over the charge/discharge dynamics are expected (via proper modulation of the field)
- The energy used to establish the field can largely be recovered upon discharge (the dielectric losses, and leakage currents are within acceptable limits).

Work in progress:

- Conducting quantitative demonstration of enhanced hydrogen loading.

- Further assessments of H_2/substrate compatibility under dielectric breakdown.
- Design/synthesis of high polarizability porous adsorbent frameworks.

Results will ultimately position us for design and testing of an integrated storage system.

Special Recognitions & Awards/Patents Issued

1. A US Patent Application was submitted in 2010: "Apparatus and Method for Gas Storage and Separation" R.P. Currier, S.J. Obrey, J.-M. Sansiñena, and D.J. Devlin.

FY 2010 Publications/Presentations

1. "Capacitive Hydrogen Storage Systems: Molecular Design of Structured Dielectrics" D.J. Devlin, R.P. Currier, N. Henson, S.J. Obrey, B.M. Patterson, J.-M. Sansinena, Q. Wei, Y. Zhao. Presented at the DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, Washington, June (2010).

2. "Metal-organic Aerogels: a Family of Hierarchical Architectures of Aerogels Bridging the Amorphous and Crystalline Frameworks " Q. Wei, H. Kim, D.Yang, K.A. Obrey, G. Zou, P. Chupas, Z. Lin, R. Zou, Y. Wang, S. Obrey, R.P. Currier, T.E. Proffen, H. Xu and Y. Zhao. Submitted to *J. Materials Chemistry* (2010).

3. "Electrochemical Characterization of the Dielectric Properties of Metal Organic Frameworks" J.-M. Sansiñena, R.P. Currier, S.J. Obrey, D.J. Devlin, N. Henson, Y. Zhao, and Q. Wei. In preparation (2010).

4. "Influence of Adsorbed Species On the Dielectric Properties of MOF's" J.-M. Sansiñena, R.P. Currier, S.J. Obrey, D.J. Devlin, N. Henson, Y. Zhao, and Q. Wei. In preparation (2010).

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3. Rowsell, J.L.C. et al."Hydrogen Sorption in Functionalized Metal-Organic Frameworks" *J. Am. Chem. Soc.* **126**: 5666-5667 (2004).

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5. Hanna, M.W. "Bonding in donor-acceptor complexes. I. Electrostatic contributions to the ground-state properties of benzene-halogen complexes" *J. Am. Chem. Soc.* **90**: 285 (1968).

6. Theory of Dielectrics by H. Frohlich, Second Edition, Oxford (1958).