Fuel Cell Technologies Office (FCTO)

Hydrogen Storage R&D

Core Characterization Capabilities

An NREL-led National Laboratory Collaboration between NREL, LBNL, PNNL, and NIST

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NREL CORE CHARACTERIZATION CAPABILITIES

The National Renewable Energy Laboratory (NREL) will offer specialized characterization for hydrogen storage materials through its DOE-FCTO core-capability validation laboratory. We offer PCT analysis of hydrogen storage materials to determine their gravimetric and volumetric capacities, and thermal conductivity/thermal diffusivity determination of hydrogen storage materials.

PCT Analysis. NREL has all the requisite equipment, capabilities, and expertise in order to continue to offer specialized analysis of materials specifically for their hydrogen gravimetric and volumetric capacities. We have optimized techniques that enable rapid throughput with accurate and precise measurements on samples from 200 mg to grams. We will be upgrading a commercial Sieverts instrument, a PCTPro 2000, to allow for variable sample temperatures for PCT measurements at arbitrary temperatures from ~50 K to 350 K and pressures up to 160 bar hydrogen. This new capability will:

- Allow measurements for determination of the hydrogen isosteric heats of adsorption.
- Facilitate determining the parameters of universal isotherm equations such as the Dubinin-Astakhov (DA) model.
- Allow for desorption at specific temperatures for quantification of sorbed hydrogen at specific temperatures. (For materials with multiple binding sites)

Thermal Conductivity and Heat Capacity. Measurements of the thermal conductivity (TC) of hydrogen-storage materials will be critical in establishing the most practical tank/systems designs. In addition to providing design criteria for storage vessels, such as the heat capacity influencing the amount of insulation required for low-temperature storage, knowledge of the thermal conductivity will aid in understanding how the heat associated with the sorption/desorption of hydrogen is distributed throughout the storage material. The thermal properties of the powder materials used for hydrogen storage can differ significantly from those of the bulk materials because heat transfer within a powder is achieved through (1) conduction through both the solid particles and through the gas in the interstices; (2) convection through the gas; and (3) radiation. The effective thermal conductivity, therefore, depends not only on the temperature-dependent bulk thermal conductivity of the powder particles, but also on the compaction of the powder and the morphology-dependent interfacial resistance, as well as the thermal conductivity of the surrounding gas, which in turn depends both on its temperature and pressure. Therefore our new system will:

- Allow for the measurement of the thermal conductivity of sorbent materials at temperatures from 77 K to 400 K and gas overpressures up to 150 bar.
- Be able to measure materials ranging from loose powders to packed powders to densified pucks.
- Both the pressure and temperature will be computer controlled, allowing one to establish a preset matrix of temperatures and hydrogen pressures at which to perform measurements.
- Evaluation of three-dimensional heat flow.
- Evaluation of heat capacity.
- Allow for expansion/contraction of materials for multi-cycle sorption/desorption TC experiments.

LBNL CORE CHARACTERIZATION CAPABILITIES

DRIFTS. Lawrence Berkeley National Laboratory (LBNL) will offer specialized DRIFTS analysis with a new instrument equipped with a controllable environment and variable temperature. The new system is designed for the study of H_2 in a variety of materials such as metal-organic frameworks, zeolites, and graphene aerogels, among others. Infrared spectroscopy provides valuable information on the nature of H_2 bound within the cavities of microporous materials. Adsorbed H_2 vibrates at lower frequencies as compared to the vibrational frequency of the molecule in gas phase with a strong correlation between the magnitude of the redshift and the binding energy of a particular site. Adsorbed H_2 gains a dipole moment and becomes IR active, thus is amenable to be investigated by IR spectroscopy.

Specifically in this new DRIFTS spectrometer system:

- With this setup, materials can be characterized by individual or simultaneous variable pressure and temperature *in situ* gas loading experiments.
- This setup will provide precise control of the gas pressure initially up to 30 bar with subsequent efforts to increase the upper limit to 100 bar.
- This setup is designed to operate from 77 K to 500 K. The temperature range will then be extended to as low as 10 K (using liquid helium) in order to increase the amount of adsorbed gas, obtain better resolution, and collect data over a larger temperature range.
- The enthalpy change upon adsorption at a given binding site can be established by variable-temperature experiments.
    - Variable-pressure and variable-temperature IR spectra can give insights into the binding energies of specific sites.
    - By precise control of the gas pressure, different binding sites could be selectively and consecutively populated.
- The measurements will be completely non-destructive.

Pacific Northwest
NATIONAL LABORATORY

PNNL CHARACTERIZATION CAPABILITIES

Pacific Northwest National Laboratory (PNNL) will offer specialized characterization for hydrogen storage materials through its Physical Sciences Laboratory and its User Facility EMSL, which hosts a wide range of characterization facilities. We will concentrate on three signature capabilities: Nuclear Magnetic Resonance, Transmission Electron Microscopy, and Reaction Calorimetry.

NMR Spectroscopy. PNNL has more than 15 multinuclear spectrometers suitable for both liquids and solids and ranging from 100 to 850 MHz. Many of these have wide-bore magnets accepting specialized sample probes for *in-situ* environments. The specialized facilities include:

- High pressure solution NMR (to 500 MHz)
  - Pressure to 70 bar
  - Temperatures -100°C to +100°C (+150°C at lower pressure)
- High pressure MAS solid NMR (to 850 MHz)
  - Pressure to 200 bar
  - Temperatures ambient to +100°C
  - Pressurizing gases—include H_2, CO_2, CH_4, He, and N_2
  - Uses standard commercial solid-state NMR probes in 5 mm, 7.5 mm, and 6 mm OD rotors, using the full internal diameter for increased volume and sensitivity

The ability to make measurements at higher temperatures and pressures is also under development. A new capability to probe H_2 gas adsorption by NMR as a function of temperature and pressure will be developed as part of the AOP project. This strategy will be used to measure *H_2-specific* pore size and adsorption energies by using H_2 gas as the probe. At the end of FY16, ^{1}H NMR measurements at H_2 pressures up to 8 MPa and temperatures down to 200 K will be available.

Transmission Electron Microscopy. Three aberration-corrected TEMs, including STEM, are available with optimum resolution ca. 0.7 Å. Key features of this capability include:

- Heated sample stages with temperatures to 700°C
- Environmental TEM with 10 mbar gas pressure (including H_2) at the sample
- Si_3N_4 window sample stage for 1.5 bar gas pressure and 500°C with reduced resolution
- Elemental and chemical state information by EDS and EELS

Reaction Calorimetry. Reaction calorimetry can be used to measure *in-situ* heats of reaction during a reaction in isothermal as well as temperature-ramp mode. The C-80 calorimeter can be coupled to a GC to analyze evolved gases and the reversal mixing vessels allow for a range of reaction conditions. Liquid/liquid, solid/liquid, and even gas phase reactions can be measured.

- Temperature range: ambient to +300°C
- Pressure range: 1 to 100 bar

NIST CHARACTERIZATION CAPABILITIES

The National Institute for Standards and Technology (NIST) Center for Neutron Research investigates/characterizes a range of materials of different classes that have unique physical and chemical characteristics. As such, the range of neutron-scattering tools available at NIST is available to address specific issues depending on the material properties. We specifically perform state-of-the-art, neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of hydrogen in hydrogen-storage materials that show the most promise to meet the project milestones and goals.

Spectroscopic Neutron Scattering Tools. Isotopic ratios of carbon/metals to hydrogen may be extracted from bulk materials using the technique of Prompt Gamma Neutron Activation Analysis. The Filter Analyzer Neutron Spectrometer (FANS) measures vibrational modes similar to DRIFTS. In addition, we have the capability to measure the relevant diffusivity of hydrogen in these materials (comparable to NMR) and perform macroscopic imaging of hydrogen distribution in large-scale samples that can be correlated with the thermal conductivity measurements at NREL.

Experimental Limits: Generally 1.5 K – 325 K temperatures under up to 100 bar of hydrogen.

Neutron Diffraction. For crystalline materials, the most powerful tool is neutron diffraction, which allows the determination of the locations of deuterium (D) atoms, independent of whether they are atomic or molecular. This tool would be used to provide direct evidence of dual-D_2 bound species to one metal center in a crystalline framework, for instance.

Experimental Limits: Generally 1.5 K – 325 K temperatures under up to 100 bar of hydrogen. Typically lowest temperatures are best for determining atom locations.

Small-Angle Neutron Scattering (SANS). For more disordered materials, structural information from nanoscale structural studies of porous materials and surfaces can be obtained from the use of small-angle neutron scattering instruments (SANS) and reflectivity.

Experimental Limits: Generally 1.5 K – 325 K temperatures under up to 100 bar of hydrogen.

Depending on the nature of the experiments the above experimental limits can be exceeded if required. Engineering higher pressure environments is possible, but usually the same setup would not be best for all experiments.