IV.G.1 HGMS: Glasses and Nanocomposites for Hydrogen Storage*

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*Congressionally directed project

Fiscal Year (FY) 2012 Objectives

- Fabricate glasses and nanocrystalline composites: improve materials composition by introducing functional dopants
- Demonstrate controlled nucleation of nanocrystals
- Quantify the nanocrystallization processes
- Identify best glass systems, compositions and nanocomposites with interest in H-storage

Technical Barriers

This is a fundamental research project in physics and chemistry of glasses and glass-based nano-crystalline composite materials with potential interest in H-storage. As such, this project does not directly address any H-storage technical barriers. However, the insights gained from these studies could help to answer fundamental questions necessary for considering glass-based materials as H-storage media and could be of interest for the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume
(B) System Cost
(D) Durability/Operability

Technical Targets

In this project basic studies are being conducted aimed to answer fundamental questions essential for considering glasses and glass-based materials as H-storage media. As such, this project does not address any H-storage technical targets. In particular, H-sorption and desorption tests or kinetics measurements are not part of the project scope. Though, results of these studies could contribute toward the design and synthesis of new hydrogen storage materials that could potentially be applied towards the following DOE hydrogen storage technical targets:

- Weight and Volume: 0.045 kg H_2/kg system; 0.028 kg H_2/L system
- Energy density: 0.9 kWh/L

FY 2012 Accomplishments

- Demonstrated fabrication of glass materials and nanocrystalline composites with potential interest in H-storage.
- Performed microstructural studies using a multi-technique experimental approach.
- Demonstrated tunability of size and density of nanocrystals in glass matrices.
- Improved UNLV research infrastructure through state-of-the-art experimental instrumentation acquisition.
- Established two new research laboratories and jump-started glass and glass-ceramic composites research on campus.

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Introduction

Proposed previously, but never practically implemented, one of promising concepts for storing hydrogen are micro-containers built of glass and shaped into hollow microspheres. Drawing inspiration from that concept we have expanded it to the exploration of bulk glass materials and glass-derived nanocrystalline composites as inert H-storage media. It is commonly accepted that the most desirable materials for H-storage do not interact chemically with hydrogen and possess a high surface area to host substantial amounts of hydrogen. Glasses are built of disordered networks with ample void spaces that make them permeable to hydrogen even at room temperature. Glass-derived nanocrystalline composites, hybrids of glass and nanocrystals, appear to be promising candidates for H-storage. Key advantages of glasses include simplicity of preparation, flexibility of composition, chemical durability, non-toxicity and mechanical strength, as well as low production costs and environmental friendliness.

Our goal is to propose glass systems and glass-derived nanocrystalline composites with potential interest in H-storage. These materials with flexible void spaces are able to precipitate functional nanocrystals capable to attract hydrogen. However, for the concept of glass-based materials to be practically implementable as H-storage media, a substantial amount of basic research is still required into physics and chemistry of bulk glasses.

Approach

The research was focused on synthesis of previously pre-selected oxide glass systems and glass compositions with emphasis on their fabrication route and characterization using a multi-technique experimental approach. These studies were directed at the nucleation of nanocrystals in glass matrices and qualitative evaluation of the kinetics of the crystal growth. The use of dopants was essential for effective progress of nanocrystallization.

Results

Research on optimization of glass compositions was continued. New glasses were synthesized and these add to the pool of those previously synthesized (2010) based on titanium- and tantalum-doped silica. To test the effect of dopants and molecular ratios of glass formers to glass modifiers that result in different glass micro-structures (voids, bridging/non-bridging oxygens), several silica-based glass compositions doped by IIIB oxides were investigated. Research on these glasses has been reported [1]. Microstructural characterization of glasses was performed using micro-Raman spectroscopy, synchrotron radiation-based X-ray absorption fine structure (XAFS), transmission electron microscopy and X-ray diffraction.

The glass systems optimal for the project were identified. These are based on silicate glasses variably doped by IIIB oxides. Only some compositions showed formation of desired - from hydrogen storage point of view - functional nanocrystals. From those compositions a number of glass-crystal hybrids (complex nanocrystalline composites) were fabricated and their microstructure was determined using a multi-technique experimental approach. Glass ability to nucleate nanocrystals was monitored using differential scanning calorimetry and Raman spectroscopy, complemented by X-ray diffraction. Local structural environment around atoms of dopants in glass matrices was evaluated using synchrotron radiation-based XAFS spectroscopy.

Analysis has shown that nucleation of nanocrystals is preceded by, and also governed by, a change of local structural environment in the vicinity of the atoms of dopants. The change of coordination number of dopant atoms (from 4 to 6) precedes the structural transition from as-quenched glass to nano-crystalline composite and it occurs prior to nucleation of nanocrystals.

Finally, it was concluded that the use of IIIB oxides as glass dopants results in enhancing overall glass ability to nucleate nanocrystals. These dopants are critical in the progress of crystallization processes that rule nuclei formation and growth within host glass matrices. Also the presence of IIIB oxides as silicate glass dopants is essential in formation of glass-crystal composites with nanocrystals virtually capable to attract hydrogen.

Conclusions and Future Directions

- Complete the synthesis and microstructural characterization of glasses: determine the best glass compositions for nanocrystallization.
- Complete synthesis and microstructural characterization of glass-derived nanocrystalline composites: determine the best nanocomposites compositions.
- Select the most promising materials for further exploration in the H-storage field.
- Even though H-sorption and desorption tests or kinetics measurements were not part of the project, if time permits additional work is being planned in terms of H-sorption measurements on selected glass materials at a collaborator's facility.

FY 2012 Publications/Presentations

1. Kris Lipinska: "Glasses and Nanocomposites for Hydrogen Storage", Presentation at 2012 DOE Annual Merit Review & Peer Evaluation Meeting, Washington, D.C., May 2012.