VI.D New Materials and Concepts

VI.D.1 Sub-Nanostructured Non-Transition Metal Complex Grids for Hydrogen Storage

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Objectives

- Grow sub-nanostructured metal grids to increase dynamic hydrogen storage capacity of metal hydride systems by
  - Increased hydrogen molecule dissociation rate,
  - Increased hydrogen atom transport rate,
  - Decreased decrepitation caused by cycling,
  - Increased energy transfer in the metal matrix,
  - Possible additional contribution by physical adsorption, and
  - Possible additional contribution by quantum effects.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- D. Durability
- E. Refueling Time
- M. Hydrogen Capacity and Reversibility
- N. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental studies on nanostructuring metal hydrides. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L
- Cycle life: 1,000 cycles
- Transient response: 0.75 s
- Start time to full flow at 20°C: 4 s
- Start time to full flow at minimum ambient: 8 s
- System fill time: 3 min

Accomplishments

- Metal grids (copper was used as a proxy) were electrochemically grown in faujisite pores compacted in powder form on a wire-mesh cathode.
- Metal grids were electrochemically grown in faujisite pores where the faujisite was crystallized in-situ on flat anodized titanium cathodes.
- Electrochemical deposition conditions in nano scale were optimized using polycarbonate film (PCF) membranes as proxy-templates to support the research.

Future Directions

- Multicrystal template grown on metals (Ti and Cu) will be continued to increase the thickness of template.
- Oriented large crystals of nanoporous materials (e.g., mesoporous silica) on cathodes will be initiated to prevent any macropore formation.
- Other techniques [e.g., high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM)/scanning tunneling electron microscopy (STM)] will be deployed for better characterization of the metal grid.
- Template removal and metal grid recovery will be initiated.
- Pure palladium and/or magnesium will be grown for hydrogen storage testing.
- Tests with mixed metal electro deposition conditions will be initiated.

Introduction

One major problem with metal hydride systems is the slow kinetics of hydrogen uptake/release due to two reasons: 1) intrinsic reaction rate of the hydrogen molecule dissociation on the external surface of the metal and 2) slow diffusion of atomic hydrogen in the dense metal phase. In this project, we propose to grow nanostructured metal grids (about 1 nm metal thickness) with about 50% micro porosity (about 1 nm wide pores). This will increase the overall hydrogen dissociation reaction rate (since the external metal area is greatly enhanced) and decrease the diffusion time constants (since the diffusion path is greatly reduced). In addition, the high mass transfer rates through the pores and hydrogen dissociation dispersed throughout the metal will enhance the energy transport in the metal. The flexibility of such a grid is expected to lower decrepitation caused by cycling. Hydrogen storage capacity may also increase due to contributions by physical adsorption and through possible quantum effects.

The nanostructured metal grids will be grown from pure and alloyed non-transition metals. The

physical properties will be characterized by imaging [HRTEM, STEM, scanning electron microscopy (SEM), AFM, STM] and by density, thermal conductivity, and electrical resistivity measurements. The metal hydride phase diagram will be measured (P-T behavior). The phase diagrams are expected to be different from the bulk phase diagrams because of the quantum effects that may arise at these length scales. In addition, the hydrogen uptake/release rate data will be collected. These measurements will enable a complete evaluation of these novel metal grids for hydrogen storage application. These nanostructured metal grids are expected to provide significant performance advantage over the same metals in bulk form.

Approach

The technical approach can be summarized in three steps:

- Coat a cathode with nanoporous materials to act as template.
- Employ electrochemical deposition of metal cations in zeolite pores to grow sub-nanostructured metal grids.
- Dissolve the template, leaving the metal grid only.

This approach is generic and applicable to any pure or mixed metal system, although the electrochemistry is considerably complicated for electro depositing metal mixtures. Pure metals (e.g., copper, nickel, titanium) are being used in initial experiments for proof-of-concept. First, hydrogen storage testing will be performed with palladium. Magnesium is also being considered due to its high capacity, but low hydrogen uptake rate.

Results

This is the first year of this project. The project tasks in sequence are:

- Mold/cathode preparation
- Pure metal electro deposition
- Mold removal, grid recovery
- Pure metal hydrogen storage
- Mixed metal electro deposition
- Mixed metal hydrogen storage

This year, research effort concentrated on Tasks 1 and 2 as planned. Main characterization tools used were SEM and HRTEM for imaging, and energy dispersive X-ray analysis (EDX) for composition analysis. Copper was used in electro deposition studies as a stand-in for hydrogen storage metals during these initial proof-of-concept experiments.

Task 1. Mold/Cathode Fabrication

Mold/cathode preparation is the single most challenging task of this project. The cathode needs to be completely covered with the nanoporous mold (e.g., zeolite), with metal ion transport only through the pores, to achieve the main goal of this project. A stepwise series of approaches, from least to most complicated, is being followed to accomplish this task.

- Multicrystal particles pressed/compacted on a metallic cathode.
- Multicrystal film of inter-grown crystals synthesized in-situ on a metallic substrate.
- Multicrystal film containing large oriented crystals synthesized in-situ on a metallic substrate.
- Very large single nanoporous crystal grown on a metallic substrate.

Initial effort concentrated on the first approach. Copper was successfully electro deposited in the pores of a zeolite (faujisite) powder compacted around a nickel mesh cathode. The Cu deposition was confirmed by EDX and electron microscopy, as shown in Figure 1. Although Cu was electro deposited in nanopores (HRTEM shown later), two issues could not be resolved:

- Excessive Cu growth in macropores between zeolite particles could not be completely eliminated. These growths, resembling tree roots in stony soil, have large diameters from 0.1 μm to 1 mm. With such large particle sizes, this portion of metal will act like bulk metal during hydrogen storage.
- The compacted zeolite layer de-laminates (detaches) from the grid at some places because of hydrogen evolution during electro deposition. The powder is simply compacted on the mesh; it does not adhere to the cathode metal. This provides further opportunity for large particle electro deposition.

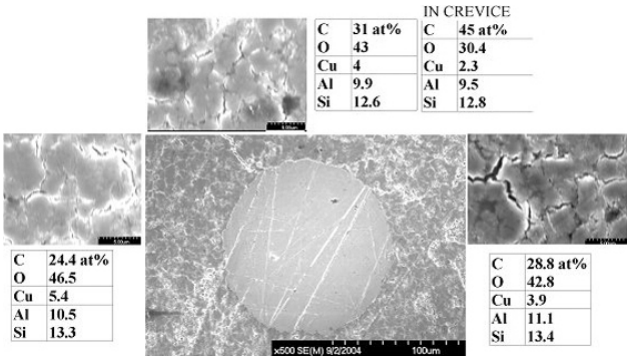

Figure 1. Copper Distribution Around a Cathode Wire - Copper is grown in micropores of faujisite powder compacted around nickel wire mesh. The anode is in solution at far left. The inserts are spatially oriented as left, top and right of the cathode wire.

Later efforts concentrated on the second approach: in-situ synthesis of multicrystal intergrown zeolite crystals on a cathode followed by electro deposition. Micro-scale "roughening" of the metal surface is necessary to provide nucleation sites during zeolite synthesis and thus to provide better adhesion between the metal and zeolite film.

Titanium plates were anodized with NaOH at 60°C, and cured at 500°C in air. This treatment forms TiO_2 (anatase) on parts of the surface, which is necessary for good adhesion of zeolites. Some of the surface remains in metallic form to provide electrical conduction during electro deposition. The non-uniform texture on the surface has characteristic dimensions in the range 0.1 to 10 mm, controlled by treatment conditions. Many different morphologies of faujisite can be grown on anodized titanium surfaces, depending on hydrothermal synthesis conditions. The best coating conditions, giving pinhole-free continuous faujisite layer on the titanium substrate, were used for electro deposition.

The faujisite-coated anodized titanium plates were used as a cathode to electro deposit Cu in the nanopores. Figure 2 shows SEM and EDX results. Gas evolution was not observed during deposition. Large Cu growth in macropores was not observed (unlike compacted powders) since the surface is completely coated with faujisite. After the pores are filled with Cu, the electro deposition proceeds to form "mushroom"-like over-growth. This can be avoided by carefully adjusting the total charge used during electro deposition.

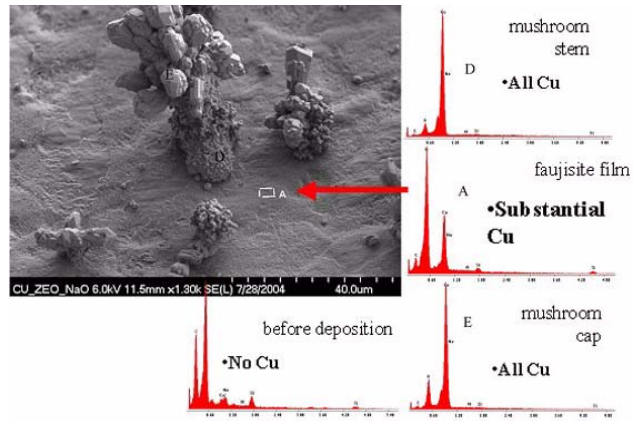

Figure 2. Copper Growth in Micropores of Faujisite Synthesized In-Situ on Anodized Titanium Plate - The "mushrooms" are copper overgrowth. Region A in thin faujisite film shows substantial amount of copper growth.

The faujisite layer is fairly thin with about 50-100 μm thickness. Current effort is concentrating on growing thicker films and on re-using the cathode after the electrodeposited layer is scraped off (or harvested).

Task 2. Pure Metal Electro Deposition

Vast electroplating/electro deposition literature is primarily geared to optimize the uniformity of thin films on large, smooth cathode surfaces of a different metal. We are trying to deposit non-uniform, "thick" bulk metal in small nanopores of a non-conducting material. (The cathode/anode conductor can be the same metal.) A series of experiments was performed to fine-tune electro deposition techniques for nano-scale deposition. These experiments were performed in parallel to cathode preparation studies and are independent on the rate of cathode preparation.

As a stand-in for the zeolite mold, track-etched polycarbonate films (PCFs) are being used. PCF has the following advantages for this work.

- Commercially available and easy to use.
- Non-conducting polycarbonate "mold," like zeolites.
- Pore sizes from 1 μm, down to 0.015 μm = 15 nm, 15x larger than zeolite pores.
- Film thickness up to 10 μm, close to zeolite crystal size.
- Porosity up to 10%, less than zeolites.

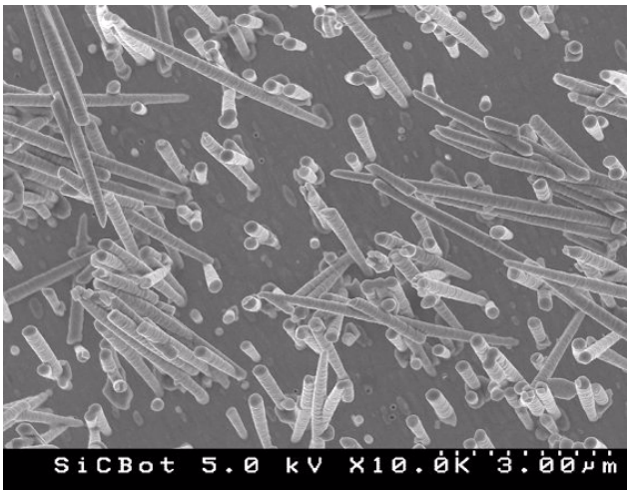

Figure 3. Copper Grown in 100 Nanometer Pores of PCF - The PCF membrane is partially dissolved to expose the metal for imaging. The copper needles are approximately 10 micrometers long, corresponding to length-to-diameter (L/D) ratio of 100.

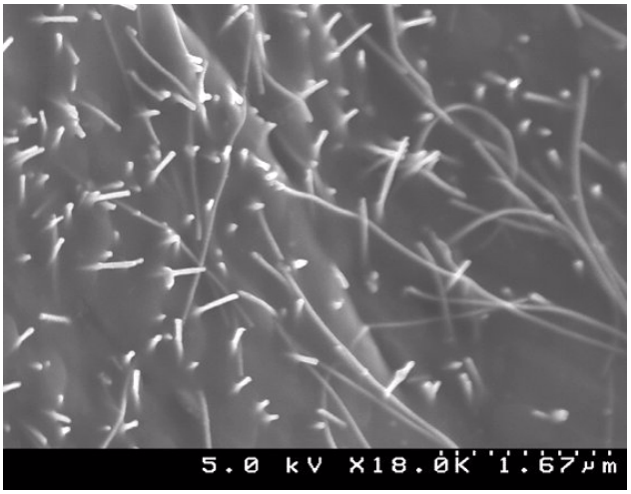

Figure 4. Copper Grown in 15 Nanometer Pores of PCF - The PCF membrane is partially dissolved to expose the metal for imaging. The copper needles are approximately 10 micrometers long, corresponding to L/D ratio of 667.

A series of PCFs is being used; i.e., 10, 1, 0.1, 0.015 µm average pore diameter. The main purpose of this effort is to analyze the effect of pore size. The identified effects will be extrapolated down to 1 nm range to guide electro deposition in zeolite molds. Extrapolation is actually proportional to the square of diameter (proportional to deposition area). The effects of film thickness and porosity are directly scalable; thus, they represent no concern.

A thin layer of gold is sputter coated on one side of the PCFs to provide electrical contact. The membranes are placed in a custom-designed electrochemical cell. Cu is electro deposited in the pores. The electro deposition conditions (solution concentration, voltage, total charge, temperature, etc.) are varied. The type of growth is controlled by a complicated interplay between electro deposition conditions. We now have a complete understanding of this interplay, as exemplified in SEM pictures in Figures 3 and 4. The results will be submitted to a journal.

Conclusions

The two milestones for the first year of the project were as follows:

- Milestone 1: Demonstrate fabrication of cathode with layered zeolite where only pathway for cations to reach cathode surface is through zeolite crystal nanopores
- Milestone 2: Proof of pure metal sub-nanostructured grid growth in the zeolite layer by standard characterization techniques (i.e., HRTEM, SEM, EDAX, STEM AFM/STM, etc.) before zeolite removal

As explained under Task 1 above, the first milestone has been reached with in-situ synthesis of the nanoporous mold on micro-structured metal cathodes.

As per Milestone 2, we present the results of two HRTEM studies. Figure 5 shows copper electro deposited in faujisite particles (recovered from mechanically compacted cathodes). Considering EDX results in Figure 1, we are confident that 1 nm spaced lines in these images correspond to copper metal electro deposited in the nanopores (although mechanical compaction is not a viable choice). A second HRTEM study was performed on particles scraped from an in-situ grown mold layer on a cathode. Figure 6 shows copper electro deposition in the nanopores and the beginning of "mushroom" over-growth in nanometer scale. Milestone 2 has also been accomplished, as evidenced by these two HRTEM studies.

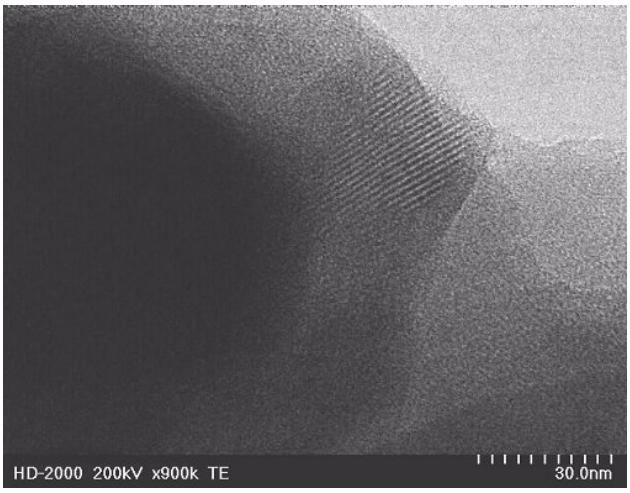

Figure 5. HRTEM of Copper Grown In Faujisite Micropores - The faujisite powder was compacted around a nickel wire mesh cathode. The ridges spaced at 2 nanometers are copper growth, as substantiated by EDX analysis in Figure 1.

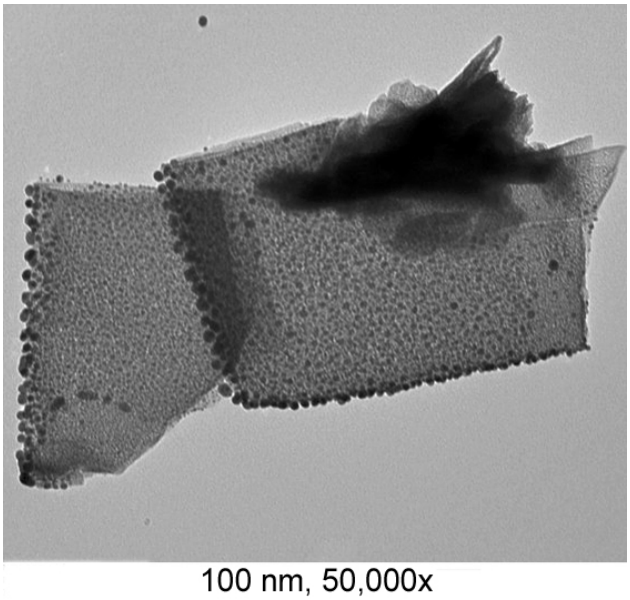

Figure 6. HRTEM Image of Copper Grown in Micropores of a Mold - The mold was synthesized in-situ on an anodized titanium plate as the cathode. The mushroom-like over-growth is on the external surface of the mold crystals.

FY 2005 Publications/Presentations

1. Freedom Car presentation, Washington, D.C., March 17, 2005
2. Program Review presentation, Washington, D.C., May 23, 2005