

III.C.5 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 heat transfer in the metal matrix,
- Additional contribution by physical adsorption, and
- 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:

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

Approach

- Use zeolites as templates on a cathode surface
- Employ electrochemical deposition of metal cations in zeolite pores to grow sub-nanostructured metal grids
- Dissolve zeolite mold, leaving intact the metal grid
- Characterize the metal grid for hydrogen storage

Accomplishments

- Initial efforts concentrate on copper deposition in faujisite for proof of concept
- Hydrothermal faujisite synthesis is performed to control morphology for better adhesion to the cathode

- Necessary chemistry is identified to fully exchange the faujisite to copper form
- High-pH (=10) electrolytic solution for copper deposition is shown to not detrimentally affect faujisite structure
- Physical compaction of powder on cathode surface showed mixed results with respect to powder coat integrity
- Direct in-situ faujisite film growth on cathode material is being evaluated

Future Directions

Just a few months into the project, there are no problems identified yet to change project direction(s). Future directions remain same as proposed with the following first-year milestones:

- **Milestone 1:** Demonstrate fabrication of cathode with layered zeolite where only pathway for cations to reach cathode surface is through zeolite crystal micropores
- **Milestone 2:** Proof of pure metal sub-nanostructured grid growth in the zeolite layer by standard characterization techniques [i.e., high-resolution transmission electron microscope (HRTEM), scanning electron microscope (SEM), energy dispersive X-ray (EDAX), scanning transmission electron microscope (STEM), atomic force microscope/scanning tunneling microscope (AFM/STM), etc.] before zeolite removal

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 sub-nanostructured metal grids (about 1 nm metal thickness) with about 50% microporosity (pores about 1 nm wide). This will increase the overall hydrogen dissociation reaction rate (since the external metal area is enhanced) and decrease the diffusion time constants (since the diffusion path is greatly reduced). In addition, the high mass transfer rates through the pores will enhance the heat transfer. 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, 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:

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

This approach is generically applicable to any pure or mixed metal system, although the electrochemistry is considerably complicated for electrodepositing 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.

Results

The main tasks during the first year involve cathode preparation and pure metal electrodeposition. During the initial start-up period of the project over the past few months, we concentrated on three areas.

Auxiliary Techniques

Many of the auxiliary experimental techniques have been developed during the initial start-up period. No major roadblocks were encountered. These include:

1. **Hydrothermal synthesis:** The zeolites being used are commercially available, but commercial products are optimized for different purposes (mostly for separations). The crystal and particle (agglomerate) morphology of commercial products are not suitable for our purpose. We have developed experimental protocols to synthesize faujisite (1.5 Si/Al ratio by EDAX) and Engelhard titanium silicate - 10 (ETS-10) in our labs with controlled morphology (narrow particle size distribution – around 2 micrometers). X-ray diffraction (XRD) and SEM analysis were used to confirm crystal structure and morphology.
2. **Ion Exchange:** As synthesized, most zeolites contain Na^+ as the cation. In our application, sodium will be reduced in the pores, interfering with the reduction of the desired metal. Therefore, it is necessary to exchange the zeolites to the cationic form of the metal to be electrodeposited. All necessary techniques for ion exchange are implemented in our labs for copper exchange. XRD and SEM analysis of exchanged zeolites do not show any detrimental effect of ion exchange.
3. **Electrolytic Bath Chemistry:** Most electrodeposition solution chemistry involves acidic solutions. Particularly copper deposition is usually performed at low pH (3-5) from copper sulfate/sulfuric acid solution. This causes two

major problems: 1) partial loss of crystallinity of the zeolite (as we observed by XRD analysis) and 2) excessive hydrogen gas evolution at the cathode surface (which causes the zeolite layer to detach from the cathode surface in our experiments). An alkaline electrolyte chemistry (pH=10) has been identified for copper electrodeposition. This solution does not affect faujisite (which is synthesized at similar pH). It also substantially reduces hydrogen evolution, although it does not prevent it completely.

Cathode Preparation with Mechanical Compaction

Copper-exchanged faujisite powder was compaction coated on nickel mesh as the electrode for electrodeposition. The film is intact under normal conditions, but it is detached from the electrode during copper deposition. The delamination occurs mainly because of hydrogen gas evolution. We are pursuing two avenues to prevent the delamination: 1) changes in electrolyte chemistry as described above and 2) direct in-situ zeolite growth on the electrode as explained below. A third remedy of using “polymer patching” will also be tried next quarter for mechanically compacted cathodes.

In-situ Zeolite Growth on the Cathode Metal

Preparation of the cathode coated with a zeolite without any macroscopic defects is a major technical challenge for the success of this project. In-situ zeolite growth is an alternative to mechanical compaction to produce such a coating.

Initially, we tried to grow zeolites (faujisite) on metal (nickel) surface by simply placing the metal in the hydrothermal synthesis chamber. Although the zeolite powder covers the metal, it is not grown “on” the surface. The zeolite layer can be easily removed. Zeolites, being metal oxides, do not have good adhesion on flat metal surfaces.

Recently, we switched to micro-scale “roughening” of the metal surface to serve as nucleation sites during zeolite synthesis and thus to provide better adhesion between the metal and zeolite film. One particularly promising approach based on chemical treatment of titanium has been

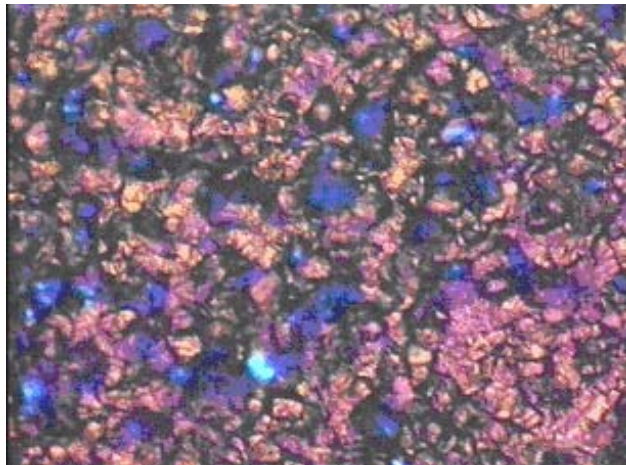


Figure 1. Anatase (TiO_2) on Titanium Surface (Blue regions are titanium metal for electric conductivity. Brown regions are anatase features about 1 micron thick and high.)

identified. A TiO_2 layer (anatase structure) is formed on the Ti surface, as shown in Figure 1. There are several advantages to this approach:

1. TiO_2 , being an oxide, should provide better nucleation for zeolite growth.

2. The surface is very rough, which should provide micrometer-scale adhesion by “locking” between growing zeolite crystals and the metal.
3. Bare Ti metal is still available at the surface (blue regions in the figure) for electric conductivity during electrodeposition.

At present, we are in the process of growing zeolites on these surfaces.

Conclusions

- Mechanical compaction of zeolite powder to prepare the cathode does not work.
- Compaction followed by polymer patching will be tried.
- In-situ zeolite growth on plain cathode metal without any treatment does not work.
- A method to chemically roughen titanium surfaces without completely covering the surface with an oxide layer has been accomplished.