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Sub-Nanostructured Non-Transition Metal Complex Grids for Hydrogen Storage

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This presentation does not contain any proprietary or confidential information.

* (8th int. conf. Fundamentals of Adsorption)

OBJECTIVE

To develop sub-nanostructured continuous three-dimensional metal alloy grid with improved kinetics of hydrogen storage.

WHY SUB-NANOSTRUCTURE

- Increase hydrogen dissociation rate,
- Increase hydrogen atom transport rate into the metal,
- Decrease decrepitation caused by cycling,
- More efficient heat transfer in the metal matrix,
- Physical adsorption on surface (?)
- Quantum effects (?)

Increase dynamic hydrogen uptake !

BUDGET

DOE FUNDING

Total funding for the project: $1,052,356 (3-years)

Funding in First Year: $350,515

Projected Funding next year: $348,848

Technical Barriers and Targets

- DOE On-Board Hydrogen Storage Barriers
  - -C. Efficiency
  - -D. Durability
  - -E. Refueling Time
  - -M. Hydrogen Capacity and Reversibility
  - -N. Lack of Understanding of Hydrogen Physisorption and Chemisorption
- DOE 2010 Technical Target Hydrogen Storage System.
  - - Usable specific-energy from H_2 -> 0.06 kg H_2/kg
  - - Start time to full flow at 20 C ->0.5 sec
  - - Refueling rate -> 1.5 kg H_2/min

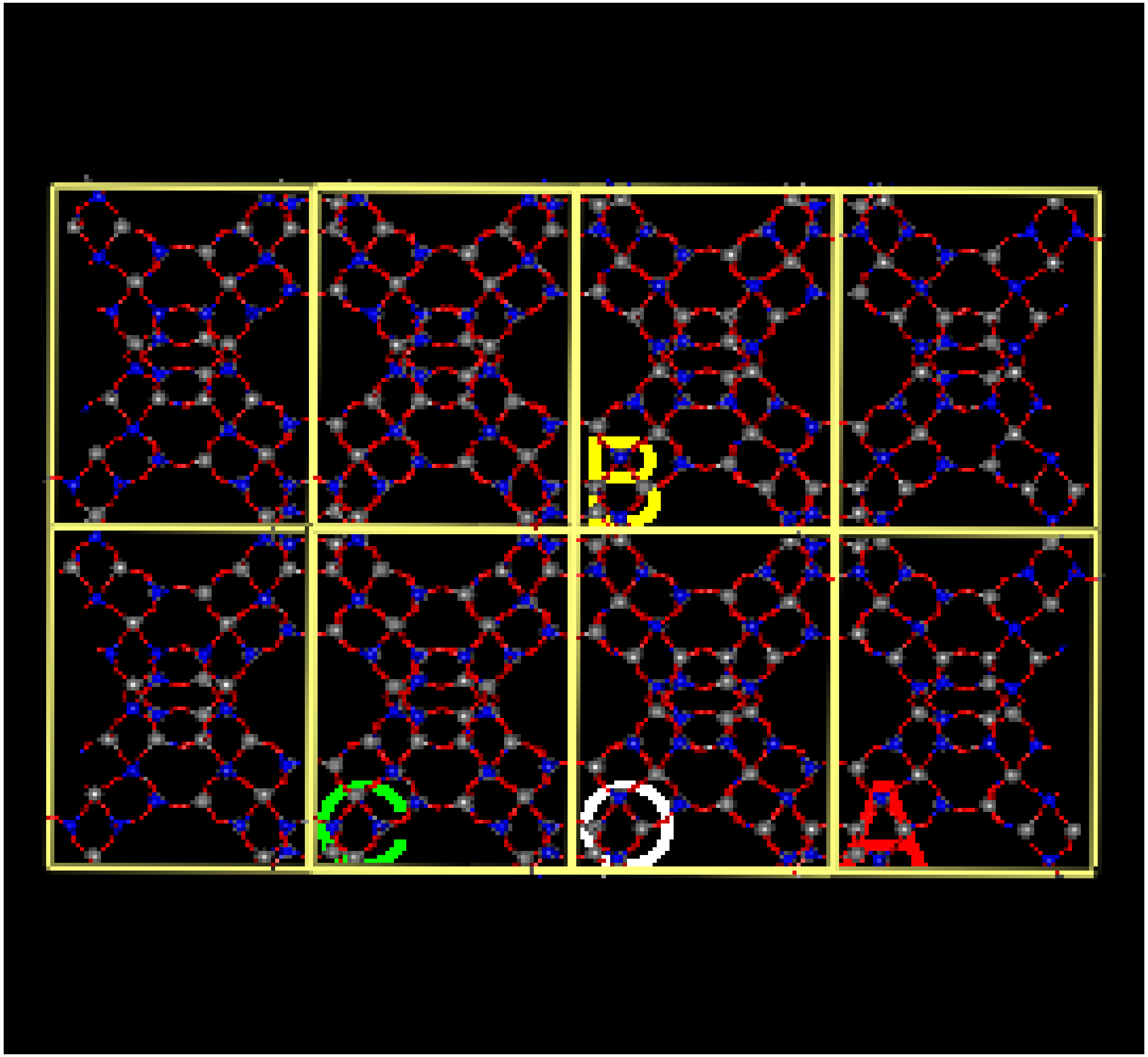
TECHNICAL APPROACH

1. Use zeolites as templates (mold)
2. Employ electrochemical reduction of metal cations in zeolite pores to grow sub-nanostructured metal grids
3. Dissolve zeolite mold, leaving intact the metal grid
4. Characterize the metal grid for hydrogen storage

ZEOLITE SHOULD HAVE:

	ETS-10	Faujasite
• Large void fraction	35 %	50 %
• Well defined nanopore structure	OK	OK
• 3-D pore connectivity	OK	OK
• High exchange capacity (Si/Mx)	10	from 1
• Acid stability (electrolyte soln.)	excellent	depends on Si/Al
• Base stability (mold removal)	excellent	depends on Si/Al
• Cost	high	low

FAUJASITE (Si/Al = 1)



Si = Gray

Al = Blue

O = Red

(Each Al introduces one charge, Na+ cations not shown)

u.c. 25x15x25 A

ELECTROCHEMICAL METAL GROWTH

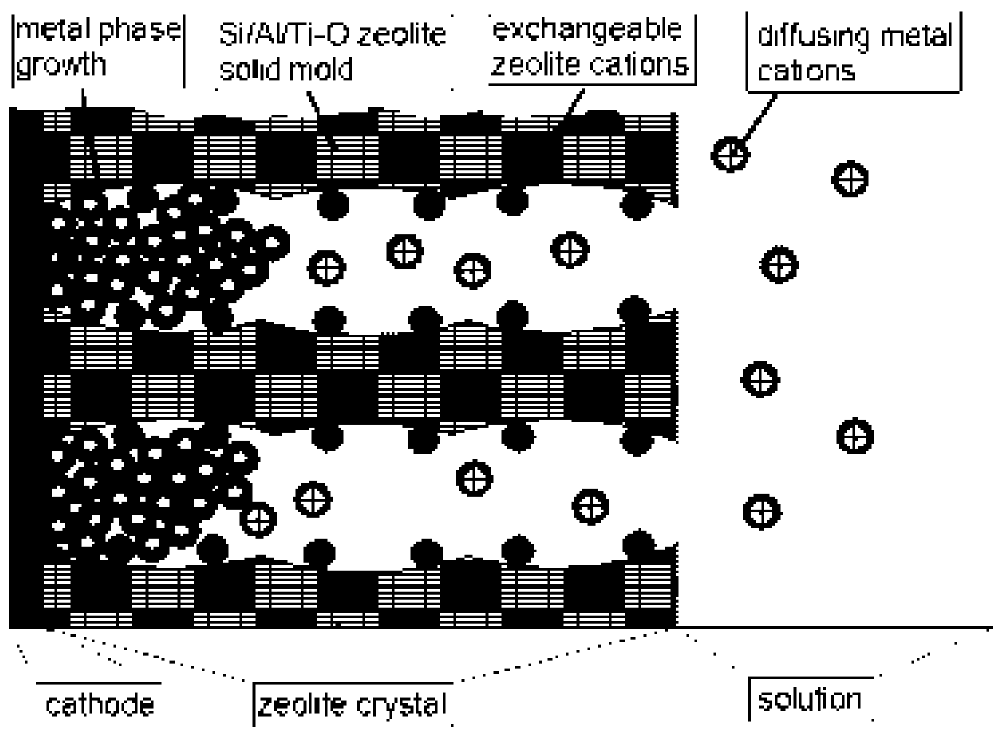


Figure 8. Electrochemical Growth of Sub-nanostructured Metal Grids

ELECTROCHEMICAL METAL GROWTH

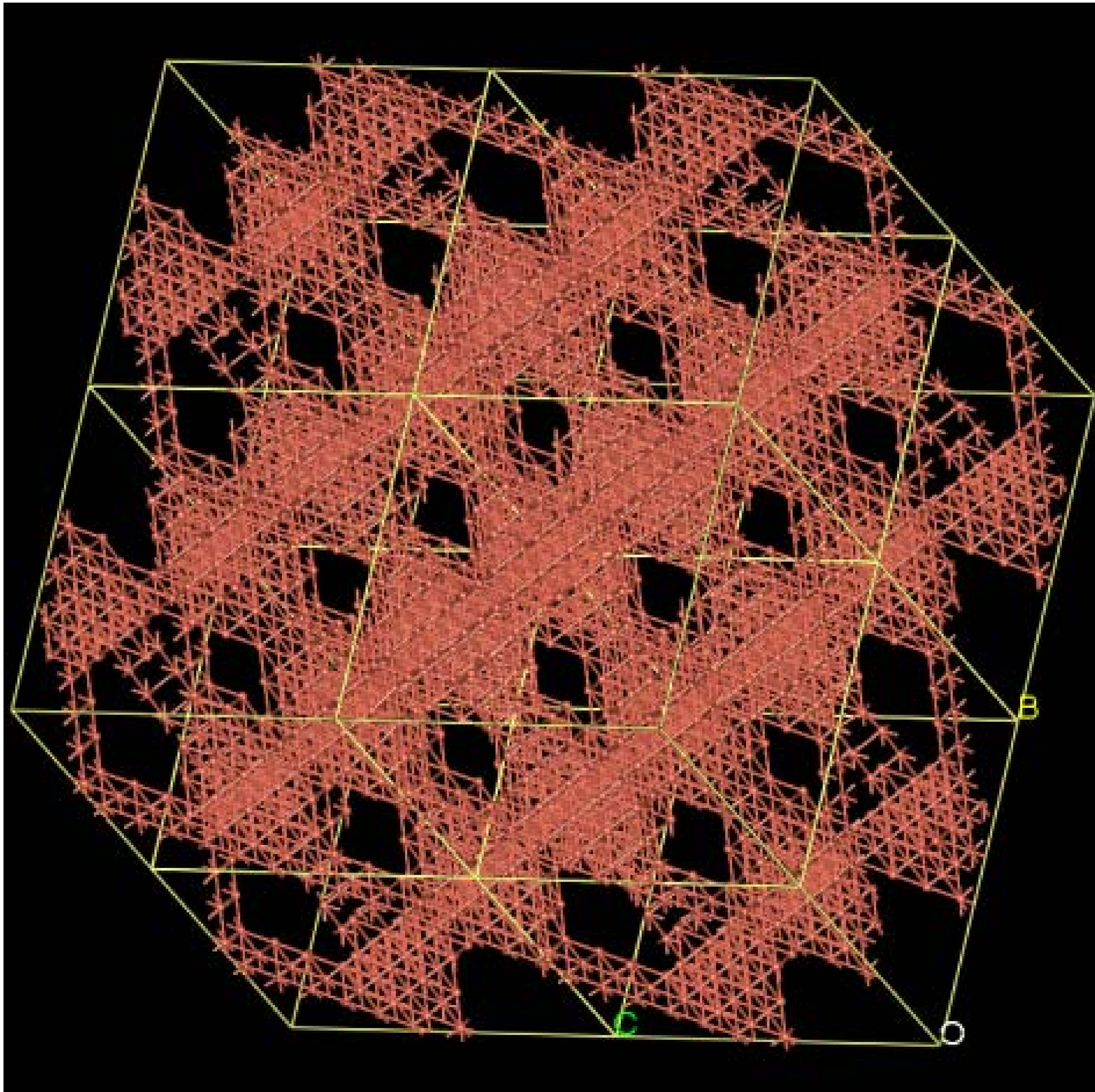
- Applicable to any metal
- Exchange zeolite to the same metal
- Energy efficient reduction to metal

Cathode preparation to prevent macropores !

REMOVE ZEOLITE MOLD

- High pH solution to “melt” the zeolite
- “Dangling” bonds => hydroxide

Will the metal be intact !



Sub-nanostructered
Metal Grid (e.g. Cu)
Grown in Faujasite

(Faujasite
removed)

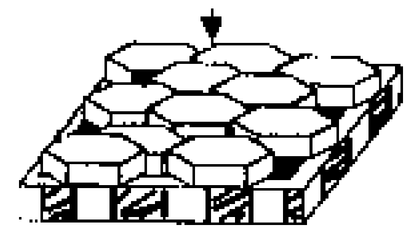
TASKS

1. Fabrication of zeolite (Faujasite/ETS-10) mold on a metallic cathode substrate.
2. Filling of mold with pure metal (Cu/Pd) by electrodeposition.
3. Removal of mold to obtain sub-nanostructured metal grid.
4. Filling of mold with metal alloy (Al/Li?) by electrodeposition, and sub-nanostructured grid preparation.
5. Grid characterization for Hydrogen storage

Task 1. Mold Fabrication on a metallic cathode

Most Attractive

- Very large single crystal of Faujasite.?
- Multicrystal film containing large oriented crystals grown on a metallic substrate.



- Multicrystal film containing large intertgrown crystals grown on a metallic substrate. (High gravity facility, ZSM-5/ETS-10 experience)

- Multicrystal film of crystals pressed on a metallic substrate

Least Attractive

Task 2. Electrochemical Metal Growth in Nanopores

- Only continuous path for metal ions in salt-solution through sub-nanopores all the way to the cathode surface

- Characterize metal filled mould to ensure that three dimensional sub-nanostructured grid has been created. (HRTEM-microstructure comparison between metal filled and unfilled mould samples, STEM-chemical analysis, STM/AFM)

- Perfect the techniques with mostly copper and some palladium

Task 3. Removal of Mold to obtain Sub-nanostructured Metal Grid

- Dissolution of mold in a hydroxide solution
- Grid recovery

  Is GRID truly interlocked in three dimensions over large enough distances for its future characterization?

  Is GRID mechanically stable? (Surface energy driven coalescence and grid collapse !)

  Is GRID chemically stable? (self ignition in air?)

  Special handling environment during and after its removal from the solvent? [$(OH)^-$ ions should provide some stability]

Task 4. Electrodeposition of Mixed Metal/Alloy in Nanopores

- *Assumption: If copper gets into the subnanopores by electrodeposition then other metal alloys, such as, Li/Al alloy can also be introduced!*

Cu/ Pd = > Li - Al? (or state of art alloy)

- Commonly done in electroplating, should work in nanopores but with different chemistry?
- Fill the mold with selected alloy (Establish electrodeposition conditions to achieve desired alloy composition in the metal grid Anode/s? Electrolyte Chemistry?)

SAFETY/HANDLING!!!

Task 5. Grid Characterization For Hydrogen Storage

5.1 Characterize the metal alloy grid for its hydrogen absorption/desorption characteristics.

5.3 Limited cycling data (10-20 cycles)

5.2 Propose a scale-up process for growth of ideal sub-nanostructured metal/metal alloy grid.

SAFETY/HANDLING!!!

Project Safety

- Bench Top experiments using limited quantities of chemicals.
- Labs are monitored by CSU Environmental Health and Safety Office.

MILESTONES; Year 1

Milestone 1: 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 (Cu/Pd) sub-nanostructured grid growth in the zeolite layer by standard characterization techniques (i.e. HRTEM, SEM, EDAX, STEM AFM/STM, etc) before zeolite removal

MILESTONES; Year 2

Milestone 3: Demonstrate zeolite removal process does not damage the metal grid

Milestone 4: Improved equilibrium and/or kinetic hydrogen storage characteristics of a pure metal sub-nanostructured grid with after zeolite removal as compared to the bulk pure metal.

Milestone 5: Proof of mixed metal complex sub-nanostructured grid growth in the zeolite layer by standard characterization techniques (i.e. HRTEM, SEM, EDAX, STEM AFM/STM, etc) before zeolite removal

MILESTONES; Year 3

Milestone 6: Improved equilibrium and/or kinetic hydrogen storage characteristics of mixed metal complex sub-nanostructured grid after zeolite removal as compared to bulk mixed metal complex

Milestone 7: Demonstrate that metal alloy sub-nanostructured grid has durability with limited (10-20) cycles of hydrogenation/dehydrogenation

Milestone 8: Estimate scale-up potential of the zeolite-electrochemical technique based on lab-scale experiments.

CLOSURE

- A very exciting idea/project at cutting-edge of material science (high-risk/high-gain)
- Will the grids be metallic?
- There is no scientific evidence that it can not be done!!