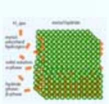
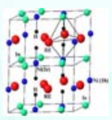
Modeling and Optimization of Hydrogen Solid Storage Systems

E.S. Kikkinides[1], M.C. Georgiadis[2], M. Konstantakou[1,3] and A.K. Stubos[3]

[1] Department of Engineering and Management of Energy Resources, University of Western Macedonia, Kozani, Greece
[2] Process Systems Enterprise Ltd, P.O. Box 60053, Thermi-Thessaloniki 57001, Greece
[3] National Center of Scientific Research "DEMOKRITOS", 15310 Ag. Paraskevi Attikis, Greece

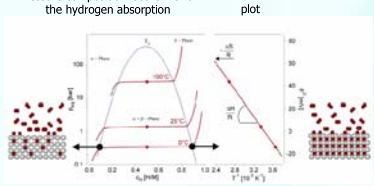
Abstract: An integrated modeling and optimization based approach is presented for the efficient, safe and economic hydrogen storage using advanced solid materials. First, recent advances on dynamic optimisation are utilized to develop optimal operating policies and novel cooling systems design options for hydrogen storage in metal hydride. The approach takes into account realistic operating constraints related to maximum allowable tank temperature, maximum pressure drop and cooling fluid availability. A multiscale modelling and optimisation framework is also investigated to explore the synergistic benefits between material design and storage processes design and operation using nanoporous carbon. The framework relies on a novel iterative strategy between formal molecular simulation techniques and advanced macro-scale optimisation methodologies. Results indicate how process operating constraints, potentially expressing safety concerns, can affect the material design.

Metal Hydrides (LaNi5)

Pressure composition isotherms for the hydrogen absorption

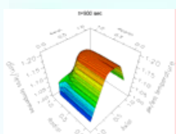
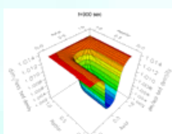
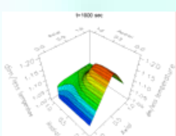
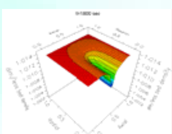
Van 't Hoff plot



solid solution (a-phase)

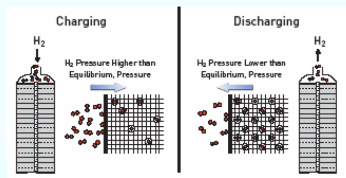
the coexistence of both phases

hydride phase (b-phase)

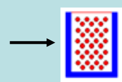
Time-space evolution of temperature profiles in the bed

Time-space evolution of solid density profiles in the bed



Macroscopic Simulation

2D Cylindrical Geometry

Conservation of mass

$$\varepsilon\frac{\partial\rho}{\partial t}+\nabla\cdot(\rho\mathbf{u})+(1-\varepsilon)\rho_s\frac{\partial q}{\partial t}=0$$

Conservation of Momentum (Darcy's law)

$$\mathbf{u}=-(\mathbf{K}/\mu)\cdot\nabla P$$

Conservation of Energy

$$\frac{d}{dt}\left(\varepsilon\rho C_{pg}T+(1-\varepsilon)\rho_s C_{ps}T-\varepsilon\frac{\rho RT}{M_{H_2}}\right)+\nabla\left(\rho C_{pg}\mathbf{u}T-\lambda\nabla T\right)+(1-\varepsilon)(-\Delta H)\rho_s\frac{\partial q}{\partial t}=0$$

Mass balance for the metal hydride

$$(1-\varepsilon)\cdot\frac{\partial\hat{\rho}_s}{\partial\tau}=C_a\cdot t_{res}\cdot\exp(-\varepsilon_a/\theta)\cdot\ln\left(\frac{\hat{P}}{\hat{P}_{eq}}\right)\cdot(\hat{\rho}_{sat}-\hat{\rho}_s)$$

Definition of Equilibrium Pressure (Jemni and Nasrallah, 1995)

$$P_{eq}=f(H/M)\times\exp\left[\frac{\Delta H}{R_g}\cdot\left(\frac{1}{(T_0\cdot\theta)}-\frac{1}{T_{ref}}\right)\right]$$

Adsorption kinetics (LDF model)

$$\frac{\partial q}{\partial t}=k\cdot(q^*-q)$$

Adsorption Isotherm (Langmuir)

$$q^*=\frac{q_s bP}{1+bP}=\frac{q_s b_0\exp[-\Delta H/RT]P}{1+b_0\exp[-\Delta H/RT]P}$$

Maximize hydrogen storage capacity
t,P(t)

Constrains

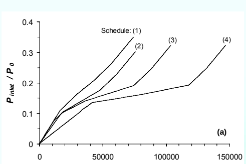
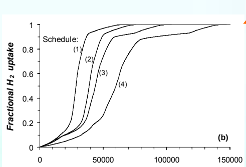
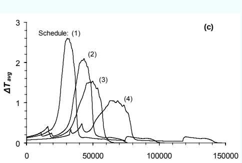
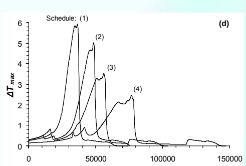
$$m_{fraction}\geq 0.99$$
$$P^{in}(t)\leq P^{max}$$
$$\Delta P(t)\leq\Delta P^{max}$$
$$\Delta T_{average}\leq\Delta T^{max}$$
$$M_{cooling}^{total}\leq M^{max}$$

Maximize hydrogen storage capacity
t,q_s,b_0

Constrains

$$m_{fraction}\geq 0.99$$
$$\Delta T_{average}\leq\Delta T^{max}$$
$$q_s^{min}\leq q_s\leq q_s^{max}$$
$$b_0^{min}\leq b_0\leq b_0^{max}$$

Solve using advanced dynamic Optimisation techniques in gPROMS™

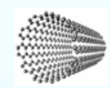
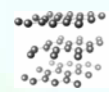





Optimal time scheduling of the pressure history, (a), and time evolution of: (b) H_2 mass uptake in the metal hydride reactor, (c) ΔT_{avg} and (d) ΔT_{max} in the metal hydride reactor

Conclusions:

- Significant improvements in the total storage time can be achieved when optimising the design of cooling systems in metal hydride beds.
- Optimal hydrogen charging rate is an important control variable to ensure satisfaction of maximum temperature limitations inside the bed.
- Process operating constraints, expressing safety considerations, can significantly affect Pore Size Distributions in nanoporous carbons.
- Material and Process design should be simultaneously modelled, designed and optimised in hydrogen storage systems to achieve an efficient, safe and economically attractive operation

Nano-Porous Carbons (graphite structure)

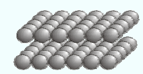



Adsorbate-Adsorbent

Steele's potential

$$u_w(z)=2\pi\rho_s\varepsilon_{CH}\sigma_{CH}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{CH}}{z}\right)^{10}-\left(\frac{\sigma_{CH}}{z}\right)^4-\frac{\sigma_{CH}^4}{3\Delta(0.61\Delta+z)^3}\right]$$

Surface model



Adsorbate-Adsorbate

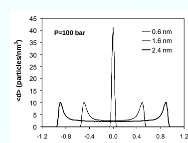
Lennard-Jones

$$u_{ij}(r)=\sum_{\alpha\beta}\left\{4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^6\right]+\frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r_{\alpha\beta}}\right\}$$

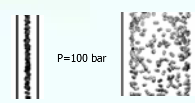
Adsorbate model

H_2

GCMC Simulation-Construction of a Database

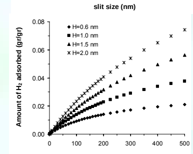
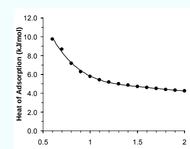


P=100 bar



0.6 nm

2.4 nm

Iterative Process

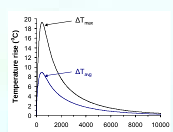
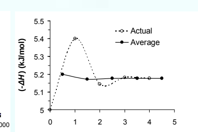
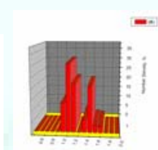
A • x = B

GCMC

PSD

Optimum Isotherm

✓Heat of adsorption, *ΔH*, depends on pore size

Optimum PSD for different constraints on the temperature rise

Case	ΔT_{bound} (°C)	q_s gr/gr	b_0 bar^{-1}	m_{total} gr/gr	Time horizon (sec)	(-ΔH) (kJ/mol)
1	10	0.05	6.4x10⁻⁴	0.02174	16312	5.18
2	8	0.05	5.8x10⁻⁴	0.01882	14579	4.84
3	6	0.05	5.1x10⁻⁴	0.01552	15935	4.42