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Triply Periodic Minimal Surface-Based Heat Exchanger as Metal Hydride Hydrogen Storage Reactor

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Sustainable energy production growth tends to move toward hydrogen as energy carrier. Metal hydride (MH) has been considered as a promising technology to store hydrogen effectively due to relatively low-pressure working condition and high energy density, unlike compressed and liquid hydrogen. Heat exchanger (HE) that is required to manage and provide the heat during hydrogen adsorption and desorption influences the performance of the MH reactor. Recently, due to significant advancements in manufacturing technology, triply periodic minimal surface heat exchanger (TPMS-HE) has been developed in order to enhance the heat transfer and improve the cycle efficiency. In this study, TPMS-HE is implemented as the main structure of MH hydrogen storage to improve its performance, especially in terms of adsorption rate, storage capacity, and mechanical properties. Modelling and analysis using computational fluid dynamics conducted in this research is validated with experimental data. The influence of cooling conditions is studied and increase of heat transfer coefficient to 500 $W/m^2 \cdot K$ and above leads to the increase of hydrogen fraction generated per time compared to natural convection. The improvement comparison between each parameter is reported as nonlinear correlation, with forced air convection cooling condition shows as the preferable solution.

1. Introduction

Hydrogen as a secondary energy source was found as the most promising candidate to further replace the fossil fuel to meet the energy demand used for sustaining the growth of human's life quality and recovering the environmental damage due to the use of non-renewable energy resources. Recent study shows that the ability to use hydrogen in a system with zero-carbon emission becomes a key as it could satisfy the condition that accelerates the transition, in terms of both economy and policy, in order to realize environmentally friendly and sustainable energy system (Muthukumar et al., 2012).

Hydrogen is produced from various forms of sources and technologies, including biomass gasification, methane decomposition, electrolysis, and chemical looping (Akhlaghi and Najafpour-Darzi, 2020). Although hydrogen has many advantages, it faces a problem with its storage due to low volumetric energy density. Well-adapted methods of hydrogen storage are liquefaction and compressed gas. However, these methods have drawback of stability, safety, and efficiency, although their volume-per-energy storage ratio is considered high (Abe et al. 2019). Promising solutions for high-safety of hydrogen storage are using either catalytic or non-catalytic $\mathrm{NH_3}$ synthesis (Juangsa et al., 2021) or Metal Hydride (MH)-based hydrogen storage. MH-based storage has been investigated and found attractive with its properties of safety aspect and energy density based on volumetric value (Afzal et al., 2017). This adsorbed element in metal hydride offers ambient temperature, low pressure, and high volumetric hydrogen density. The biggest concern on the usage of MH is due to its low gravimetric hydrogen density. MH utilization for hydrogen storage on mobility sector is limited.

The relationship of adsorption and desorption performance of hydrogen to heat exchanger (HE) layout have been investigated, including pipe (Patil and Ram Gopal, 2013), finned spiral pipe (Wang et al., 2012),and finned multi tubular tank HE (Ma et al., 2014). The results demonstrated that high surface area that leads to uniform temperature distribution on the metal hydride bed is correlated strongly with higher sorption kinetics efficiency. The recent research from Yang et al. (2012) on HE performance of helical type and Tong et al. (Tong et al. 2019) that compared straight tube with coiled HE reflected the approaches in implementing uniform temperature distribution across metal hydride bed. Combined with the need of HE designs to further improve the hydrogen

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sorption kinetics, the implementation of a complex geometry, like lattice (Yan et al., 2014), and mathematically-constrained cellular structure (Thomas et al., 2018) to improves heat transfer area is very crucial.

A triply periodic minimal surface (TPMS) is one form of complex geometries in cellular structure that is created based on mathematically-constrained cell shape patterned asymmetrically in 3D space. It has various forms, including gyroid, Schwartz-p, Schwartz-D, Lidinoid, Neovius, split-P, and I-WP, as shown in Figure 1. A study conducted by Panesar et al. (2018) showed that TPMS has high strength, while it has a lightweight structure. Based on the nature of TPMS, the ratio of surface-area-to-volume is also high. Therefore, TPMS can be optimised for lightweight, high strength, and high surface area density of heat exchanger for various purpose (Li et al., 2020). TPMS can be manufactured through additives manufacturing (AM) and layer-by-layer manufacturing methods. The latter has become an industrial standard for manufacturing of high density printed circuit HE (Panesar et al., 2018).

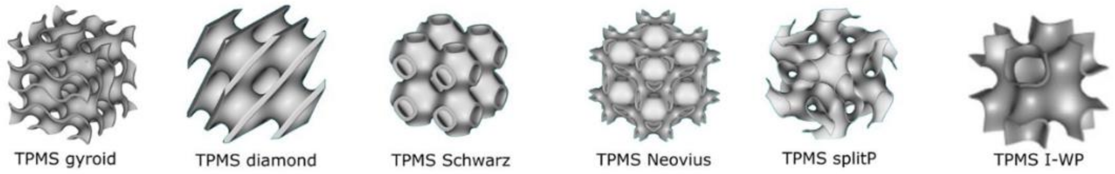


Figure 1: Architecture of lattice structures that based on TPMS (Benedetti et al. 2021)

Application of simple multi zone has been investigated by Eisapour et al. (2021) and they concluded that the number of passages can improve the hydrogen adsorption performance. This simple extruded passage could be adapted with one of TPMS form like Gyroid that has been studied as one of promising structure to be used in HE because of its excellent performance on heat transfer and structure strength.

Based on those studies, it is considered that the implementation of innovative TPMS structure for MH bed design can realize more effective sorption kinetics of hydrogen. However, to the best knowledge of the authors, there is almost no study that investigates the implementation TPMS structure for metal hydride hydrogen storage, including numerical and experimental works. The objective of this study is to analyse the opportunity of TPMS structure to be implemented as effective solid hydrogen storage, as well as its structural strength. The effect of different geometric parameters of the TPMS structure is investigated and compared using CFD and FEA analyses.

2. Numerical model

The governing equations implemented in this study include hydrogen sorption kinetics, heat transfer, HE coolant turbulent flow, and MH bed housing strength. For numerical model simplification purpose, some assumptions are made: (1) hydrogen in gas phase considered as ideal gas, (2) local thermal equilibrium is assumed between hydrogen and MH, (3) MH bed is considered homogenous porous medium and isotropic, (4) MH bed volumetric expansion is neglected and its properties, like porosity, permeability, and thermal conductivity, are considered constant, and (5) MH bed is assumed to be perfectly in contact and packed.

Table 1: Material properties (Singh et al., 2015a)

Properties	Value
Density, ρ $(\mathrm{kg\ m^{-3}})$	8,200
Specific heat, c_p $(\mathrm{J\ kg^{-1}\ K^{-1}})$	419
Thermal conductivity, k $(\mathrm{W\ m^{-1}\ K^{-1}})$	2.4
Porosity, ε $(-)$	0.5
Van 't Hoff constants used in Eq. (2.7), A $(-)$, B (K)	12.99, 3,704.59
Plateau slope, α $(-)$	0.038
Hysteresis factor, β $(-)$	0.137
Initial concentration of MH bed, $\mathrm{c_0}$ $(\mathrm{mol\ m^{-3}})$	18,981.6
Activation energy – Adsorption, $\mathrm{E_a}$ $(\mathrm{J\ mol^{-1}})$	21,170
Initial pressure P_o (Mpa)	2
Material constant used in Eq. (2.6), $\mathrm{C_a}$ $(\mathrm{s^{-1}})$	59.187

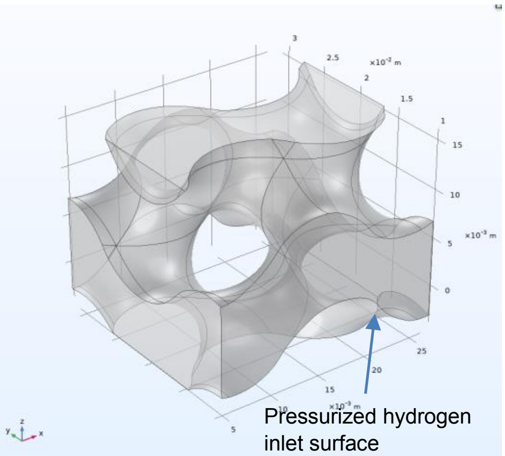


Figure 2: Geometry of studied TPMS MH Gyroid

MH bed was designed to have four cell types of gyroid with the size manufacturable for experiment purpose. Figure 2 shows the geometry of the MH bed with gyroid shell filled with $\mathrm{LaNi_5}$ MH where ambient temperature air passage was determined on other side of the gyroid surface. The parameter of MH properties and bed geometry are shown in Table 1 and Figure 2. Flat surface on the right side is considered as the inlet for the pressurized hydrogen supply with no outlet to simulate a common pressurized vessel of MH container. Other surface of the bed then applied with range of heat transfer coefficient ranging from natural convection with 20 °C ambient temperature, with additional case of 500 and 1,000 $\mathrm{W/m^2 \cdot K}$ to also simulate forced air convection and forced liquid assisted cooling like oil coolant.

The governing equations used to simulate the sorption kinetics of hydrogen in $\mathrm{LaNi_5}$ MH bed include volume averaged energy balance equation, volume averaged mass balance equation, and reaction kinetics of MH. The energy balance equation is expressed as,

$$(\rho \mathrm{c_p})_{\mathrm{eff}} \frac{\partial \mathrm{T}}{\partial \mathrm{t}} = \frac{\partial}{\partial \mathrm{x}}\left(\mathrm{k_{eff}} \frac{\partial T}{\partial \mathrm{x}}\right) + \frac{\partial}{\partial \mathrm{y}}\left(\mathrm{k_{eff}} \frac{\partial T}{\partial \mathrm{y}}\right) + \frac{\partial}{\partial \mathrm{z}}\left(\mathrm{k_{eff}} \frac{\partial T}{\partial \mathrm{z}}\right) - (1-\varepsilon)\dot{\mathrm{m}}\,\Delta\mathrm{H} \tag{1}$$

$$(\rho \mathrm{c_p})_{\mathrm{eff}} = \varepsilon(\rho \mathrm{c_p})_{\mathrm{gas}} + (1-\varepsilon)(\rho \mathrm{c_p})_{\mathrm{mh}} \tag{2}$$

$$\mathrm{k_{eff}} = \varepsilon\,\mathrm{k_{gas}} + (1-\varepsilon)\,\mathrm{k_{mh}} \tag{3}$$

In addition, the mass balance equation for MH is expressed as,

$$(\varepsilon)\frac{\partial \rho}{\partial \mathrm{t}} = \dot{\mathrm{m}} + (1-\varepsilon)\frac{\partial}{\partial \mathrm{x}}\left(D\frac{\partial \rho}{\partial \mathrm{x}}\right) + (1-\varepsilon)\frac{\partial}{\partial \mathrm{y}}\left(D\frac{\partial \rho}{\partial \mathrm{y}}\right) + (1-\varepsilon)\frac{\partial}{\partial \mathrm{z}}\left(D\frac{\partial \rho}{\partial \mathrm{z}}\right) \tag{4}$$

$$D = D_o \exp\left(\frac{-\mathrm{H_a}}{\mathrm{k_B}T}\right) \tag{5}$$

where ρ, D, ε, and $\dot{\mathrm{m}}$ are density, mass diffusion coefficient, porosity of MH, and hydrogen mass absorbed with time to MH. D_o, $\mathrm{k_B}$, $\mathrm{H_a}$, and T are pre-exponential factors, Boltzmann constant, and activation enthalpy, and temperature, correspondingly.

The hydrogen mass rate during adsorption per volume is expressed as,

$$\dot{\mathrm{m}}_{\mathrm{a}} = C_{\mathrm{a}} \exp\left(\frac{-E_{\mathrm{a}}}{\mathrm{RT}}\right) \ln\left(\frac{P}{P_{\mathrm{eq}}}\right)(\rho_{\mathrm{sat}} - \rho_{\mathrm{t,a}}) \tag{6}$$

where, ρ_{sat} and $\rho_{\mathrm{t,a}}$represent saturated density empty density of $\mathrm{LaNi_5}$ MH. P_{eq} represents pressure equilibrium that can be expressed with Van ‘t Hoff equation as,

$$\ln(P_{\mathrm{eq}}) = A - \frac{B}{T} \tag{7}$$

where A and B denote Van ‘t Hoff constants.

With HE introduced in the system, the coolant at constant flow rate is governed by energy balance equation, shown as,

$$\left(\rho c_p\right)_f \frac{\partial T_f}{\partial t} + \left(\rho c_p\right)_f \vec{u}\, \mathrm{grad} T_f = \mathrm{div}(k_f\, \mathrm{grad} T_f) \tag{8}$$

Initially, the MH pressure, density, and temperature are considered constant.

$$T = T_o,\ \rho = \rho_o,\ P = P_o \quad u_x = u_y = 0, u_z = u_{in}, T = T_{in} \tag{9}$$

$$u_x = u_y = 0, u_z = u_{in}, T = T_{in} \tag{10}$$

2.1 Numerical simulation methodology

3D geometry of TPMS-HE is imported as CAD IGES file into COMSOL Multiphysics (COMSOL Inc.) due to asymmetry nature of TPMS. Global parameter and variables expression of thermophysical for sorption kinetics are set according to Table 1. The study and evaluation of MH storage tank involves three physics components, mass balance, energy balance, and reaction kinetics, and, time dependent study is selected to investigate the time variation of the reaction. From mesh comparison from normal to fine and extra fine, fine and extra fine, both fine and extra fine mesh results show no significant difference, although the computational time increases significantly for the extra fine mesh. The fine mesh is used in this study. Figure 3 visualizes the fine mesh applied in the model.

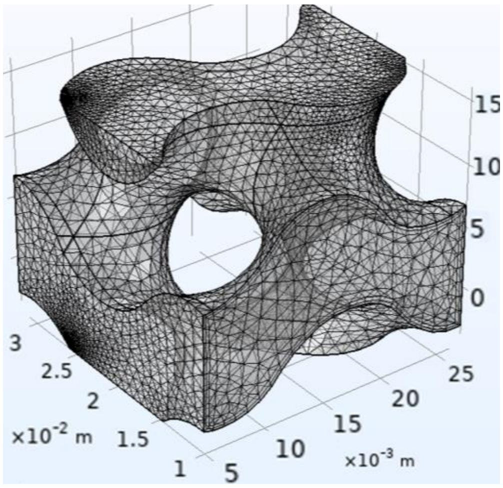


Figure 3: Fine mesh setting generated by COMSOL Multiphysics

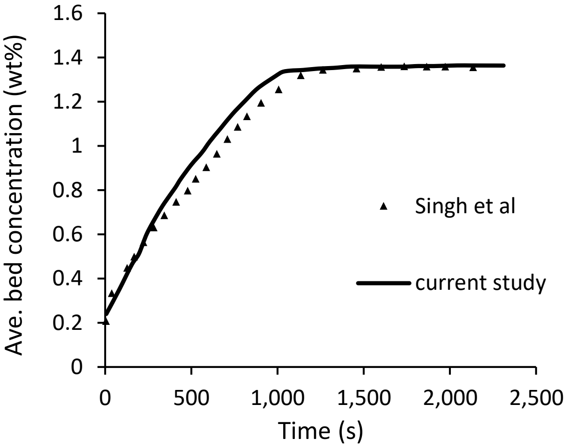


Figure 4: Average bed concentration comparison between current study and existing experiment (Singh et al., 2015)

2.2 Model validation

Numerical simulation study is validated against the existing experimental data to validate the model. Singh et.al (2015) have measured the concentration of MH bed from their model and reacted with hydrogen supply at 15 bar. Figure 4 shows the comparison of average bed concentration between the experiment and conducted numerical study. The comparison shows that the mathematical model represents high validity with the experiment result under the same parameters, and the deviation is assumed to be caused by assumption that being made.

3. Results and discussion

The simulation uses a heat transfer coefficient to simulate the cooling condition, varied from natural convection, 500 W/m^2·K (to simulate forced convection with air), and 1,000 W/m^2·K (to simulate forced cooling with oil-based coolant) with all the mentioned parameters and mesh initialization set up in COMSOL Multiphysics (COMSOL Inc.). Figure 5 shows the correlation of hydrogen fraction and time which is compared to the experimental results obtained by Jiao et al. (2012). The numerical results of this study and experimental works by Jiao et al. (2012) are based on the common design of MH tank, and applied with different heat transfer coefficients. A natural convection cooling is adopted in this study as one of parameter due to the nature of TPMS with high density of surface area per volume. It is shown that the performance of hydrogen adsorption at natural convection almost agrees with the effect of heat transfer performance obtained from experimental works. Figure 6 shows the hydrogen absorption performance on different cooling condition. The increase of heat transfer coefficient to 500 and 1,000 W/m^2·K leads to the increase of hydrogen fraction compared to natural convection. However, there is no significant difference between heat transfer coefficient of 500 and 1,000 W/m^2·K in hydrogen sorption performance, as it only shortens about 120 s to reach 95 % fully charged hydrogen condition. It seems that a forced air cooling condition is more favourable because of its simplicity and competitive performance. However, further model and analysis are required to clarify the impact of air cooling to the scalability of the system, including wall thickness and TPMS ratio.

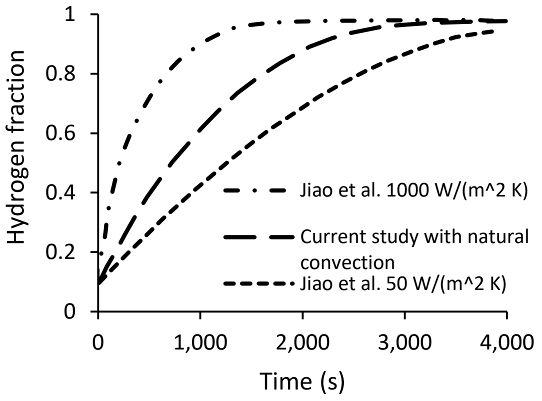


Figure 5: Hydrogen adsorption compared to other studies in heat transfer coefficients.

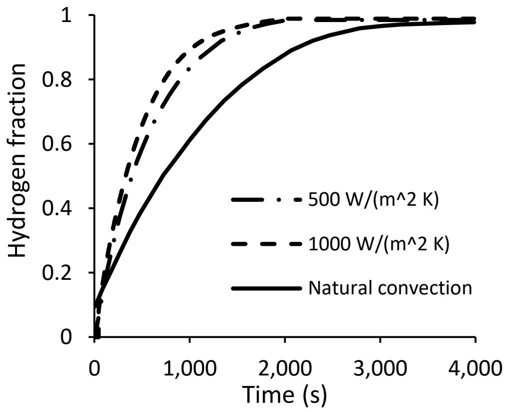
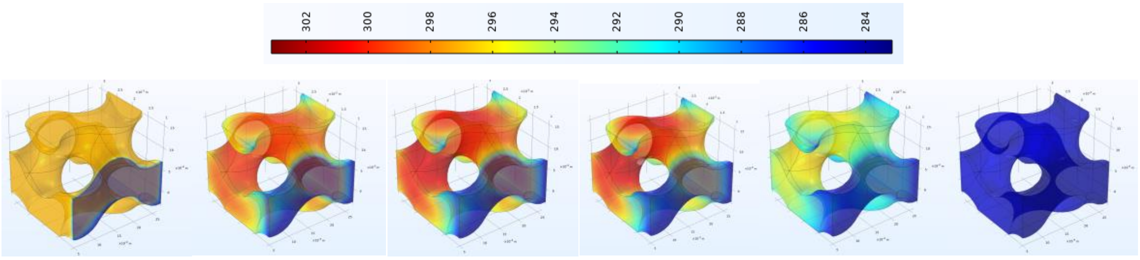


Figure 6: Hydrogen adsorption performance in different cooling condition



1s 5s 10s 20s 100s 1,000 s

Figure 7: Temperature (K) distribution of MH bed over time on heat transfer coefficient of 500 W/m^2·K

Figure 7 maps the temperature distribution in the MH bed over time at heat transfer coefficient of 500 W/m^2·K. This temperature mapping shows that the temperature uniformity is reached before the adsorption kinetics finished completely. This happens because the heat generation rate by the sorption kinetics process is neglected by the rate of heat removed from the system due to high number of heat transfer coefficient. If we consider the two above result, it also shows that with same heat transfer coefficient compared with normal pipe construction bed, due to higher heat transfer area density of TPMS structure, the sorption performance of TPMS is higher.

4. Conclusion

The kinetics of hydrogen adsorption on $LaNi_5$ MH bed with TPMS gyroid under different cooling condition have been numerically investigated with mathematical model that has been validated with the existing experimental results. The result shows a promising usability, and an adsorption performance has been improved by the application of TPMS MH bed compared to traditional MH tank design. The performance of the natural convection air-cooled TPMS MH bed is in par with forced convection in a simple pipe design. The comparison of different cooling conditions show that the increase of heat transfer coefficient improves the hydrogen sorption kinetics to a certain amount (time) although the correlation is non-linear. It is important to note that the biggest advantage of TPMS compared to other structures are its structural high strength. Currently-available manufacturing technology, such as additive manufacturing, is feasible to manufacture the structures of TPMS MH bed reactor, which can also be utilized as a structure of the system due to its strength. The integration of MH bed and system structure, e.g., chassis, case, and body, can compensate the weakness of gravimetric density of MH. As in average, the energy density of MH is higher than current technology of lithium based electric battery, with further development in hydrogen utilization efficiency, the idea of hydrogen car uses MH bed for hydrogen storage is already promising. With current electric car already implemented lithium based electric battery as frame integrity, this implementation of TPMS MH could also be a promising solution to expand the utilization of hydrogen for a safety and clean energy solution without concern of the waste problem caused by hazardous waste.

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