Modeling and control strategies for solid-state hydrogen storage system in fuel cell

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Abstract. Given the disadvantageous factors of the currently prevalent high-pressure hydrogen cylinder storage technology for providing hydrogen to proton exchange membrane fuel cell (PEMFC), such as bulky systems, significant energy losses, and high costs, this study adopts a novel and efficient solid-state hydrogen storage technology as the hydrogen supply method for PEMFC. Through the design of the topological structure of the metal hydride hydrogen storage system, a simulation model of the metal hydride hydrogen storage system is built on the MATLAB/Simulink platform based on this structure. The research focuses on designing corresponding control methods for the hydrogen release process of the solid-state hydrogen storage device. The simulation results demonstrate that the designed controller achieves rapid response within 15 seconds, exhibiting excellent dynamic performance, and effectively realizes the objective of supplying hydrogen to the fuel cell system rapidly and stably.

1 Introduction

Due to the extensive use of fossil fuels such as coal, oil, and natural gas, the issues of global warming and environmental pollution are becoming increasingly severe, posing new demands for the utilization of clean energy. Hydrogen energy, characterized by its high-quality energy density, pollution-free byproducts, and abundant sources, is hailed as the most promising secondary energy source for the 21st century, serving as a long-term substitute for fossil fuels [1]. Proton exchange membrane fuel cell (PEMFC) is crucial device for harnessing hydrogen energy, efficiently and cleanly converting the chemical energy of hydrogen into electrical energy.

As the hydrogen energy industry is still in its nascent stage, hydrogen storage technology faces challenges in achieving high efficiency, safety, and economic feasibility. Traditional hydrogen supply systems primarily employ high-pressure hydrogen storage technology, which result in drawbacks such as bulky systems, significant energy losses, and high costs. Therefore, solid-state hydrogen storage technology has been proposed as a novel and efficient indirect hydrogen storage method. Among various solid-state hydrogen storage materials, metal hydrides possess immense application potential due to their mature preparation processes, high hydrogen storage capacity, excellent hydrogen absorption-desorption platform, and safety.

A solid-state hydrogen storage device based on metal hydrides can provide hydrogen for fuel cells, forming a Metal Hydride Hydrogen Storage Tank-Proton Exchange Membrane Fuel Cell (MH-PEMFC) system. Currently, numerous studies focus on the control of fuel cell systems. For instance, O'Keefe et al. [2] designed a time-varying PI controller for a 5 kW water-cooled fuel cell, regulating the battery temperature by controlling the flow rate of cooling water, and verified the controller's performance through simulations. Saygili et al. [3] developed three distinct control strategies based on the PI control strategy, using water pumps and radiator fans as actuators, and compared their control effects, concluding that controlling the water pump voltage via a PI controller while minimizing fan operation time achieved the best results. However, there is a paucity of research on the control of metal hydride hydrogen storage systems. Therefore, this study focuses on a multi-stack fuel cell system, employing metal hydride hydrogen storage tanks to provide effective and timely hydrogen supply for the fuel cell system, with hydrogen storage alloy selected as the hydrogen storage material. The present study establishes a simulation model of a metal hydride hydrogen storage system on the MATLAB/Simulink platform and achieve the objective of continuously and stably supplying hydrogen to the fuel cell system by controlling the hydrogen release process of the solid-state hydrogen storage device.

2 Modeling

In this section, the topological structure of the metal hydride hydrogen storage system is first designed, and

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then a model is built based on this structure. Regarding the structural design of the metal hydride hydrogen storage tank, the focus lies on the heat exchange method. Common heat exchange methods for hydrogen storage tanks include air heat exchange and liquid heat exchange. Since the hydrogen storage tank requires excellent heat transfer capability to facilitate the absorption/release of hydrogen reactions, this study adopts a liquid forced convection heat exchange method with higher heat transfer efficiency for the design of the hydrogen storage tank's thermal management system. The structural design is illustrated in Figure 1.

In this system, the heat exchange fluid exists in two circulating circuits as follows: the small circulation circuit is: circulation pump–hydrogen storage tank (convective heat exchange)–diverting valve–mixer–heat exchange fluid storage tank; the large circulation circuit is: circulation pump–hydrogen storage tank (convective heat exchange)–diverting valve–heat exchanger–mixer–heat exchange fluid storage tank.

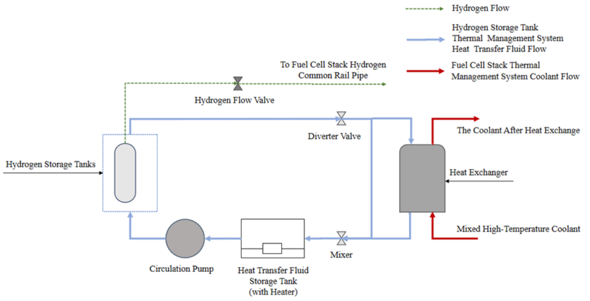

Fig. 1. The Metal Hydride Hydrogen Storage System.

2.1 Solid-state hydrogen storage device

The model of the solid-state hydrogen storage device is used to describe the mass and heat transfer processes within the device during hydrogen absorption or desorption. It primarily follows the principles of the chemical kinetics equations for hydrogen absorption or desorption reactions, as well as the mass and energy balance equations of the hydrogen storage material.

The chemical kinetic equations characterize the chemical reaction properties of the selected hydrogen storage material. Parameters that affect the reaction rate between hydrogen storage alloy and hydrogen include the internal pressure, temperature, and SOC (State of Charge) value of the device [4, 5]. For the reaction kinetics of LaNi5 hydrogen storage material [6], an acceptable model that has been experimentally fitted and widely used is as follows:

$$\begin{cases} \dot{m}_a^{MH} = C_a \cdot e^{-E_a/RT_{MH}} \cdot \ln(P_g / P_{eq,a}) \cdot (m_s^{sat} - m_{MH}), & P_g > P_{eq,a} \\ \dot{m}_{a,d}^{MH} = 0, & P_{eq,d} < P_g < P_{eq,a} \\ \dot{m}_d^{MH} = C_d \cdot e^{-E_d/RT_{MH}} \cdot \ln(P_g - P_{eq,d} / P_{eq,d}) \cdot m_{MH}, & P_g < P_{eq,d} \end{cases} \tag{1}$$

In equation (1) , $\dot{m}_a^{MH}$, $\dot{m}_d^{MH}$ represent the change in mass of MH during hydrogen absorption and desorption processes; C_a and C_d are the reaction rate constants for hydrogen absorption and desorption; E_a and E_d are the activation energies for the hydrogenation reactions; P_g, $P_{eq,a}$, and $P_{eq,d}$ are the pressure within the device, the equilibrium pressure during hydrogen absorption and desorption; R is the gas constant; and T_{MH} is the internal temperature of the device.

The mass balance equations for hydrogen storage tanks are primarily categorized into the mass balance of the hydrogen storage material within the tank and the mass balance of the hydrogen gas contained within the tank [7]. The specific expressions are presented as follows:

$$S_m = (1-\varepsilon)\frac{\partial \rho_s}{\partial t} \tag{2}$$

$$S_m * Vol - f_{out} = [Vol - (1-\varepsilon)V_{MH}]\frac{\partial \rho_s}{\partial t} \tag{3}$$

In Equations (2) and (3), S_m represents the rate of change in mass per unit; ϵ denotes the porosity; ρ_s is the real-time average density; Vol is the volume of the hydrogen storage tank; f_{out} is the mass flow rate; and V_{MH} is the volume occupied by the hydrogen storage material within the tank.

The energy balance of hydrogen storage tanks is primarily manifested in the heat balance equation during their operational processes. The sources of heat variation within the tanks are primarily categorized into three main mechanisms: firstly, the enthalpy change resulting from the reactions of the hydrogen storage materials; secondly, the heat exchange occurring between the tank and the external environment; and thirdly, the heat exchange induced by forced convective heat transfer between the tank and the heat exchange fluid[8, 9]. The specific expression is presented in the following equation:

$$\frac{\partial[(\overline{\rho c_p})T_{MH}]}{\partial t} = s_m \frac{\Delta H}{M_{H_2}} + \frac{\dot{m}_\omega C_{p\omega}}{V_{MH}}(T_\omega - T_{MH})(1-e^{-\partial}) - \frac{\varepsilon\sigma A_{rad}}{\mathrm{v}_{MH}}(T_{can}^4 - T_{amb}^4) \tag{4}$$

In equation (4), $\overline{\rho c_p}$ represents the effective volumetric heat capacity within the hydrogen storage tank; m_ω denotes the mass flow rate of water that is undergoing real-time heat exchange with the hydrogen storage tank; $C_{p\omega}$ is the specific heat capacity of water, which is 4200 J/(kg·K); and T_ω represents the average temperature of the water involved in the heat exchange process.

2.2 Hydrogen flow valve

The function of the hydrogen flow valve is to supply an appropriate amount of hydrogen to the hydrogen common rail of the fuel cell stack. In this study, a variable opening proportional valve is selected, which controls the outlet opening of the valve through electrical signals to regulate the hydrogen flow into the stack. The flow characteristic of the proportional valve used in this paper is determined by the Sanville flow-pressure equation, which can be expressed as follows:

$$\dot{m}_{valve} = \begin{cases} \frac{kC_D A_{valve} p_{valve}^{in}}{\sqrt{RT_{valve}}}\left(\frac{p_{valve}^{out}}{p_{valve}^{in}}\right)^{1/\gamma}\left\{\frac{2\gamma}{\gamma-1}\left[1-\left(\frac{p_{valve}^{out}}{p_{valve}^{in}}\right)^{(\gamma-1)/\gamma}\right]\right\}^{1/2}, & \frac{p_{valve}^{out}}{p_{valve}^{in}} > Ac \\ \frac{kC_D A_{valve} p_{valve}^{in}}{\sqrt{RT_{valve}}}\gamma^{1/2}\left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/(2\gamma-2)}, & \frac{p_{valve}^{out}}{p_{valve}^{in}} \le Ac \end{cases} \tag{5}$$

In equation (5), $\dot{m}_{valve}$ represents the mass flow rate through the valve; k is the set opening coefficient; C_D is the discharge coefficient; A_{valve} is the valve orifice area within the valve; p_{valve}^{in} and p_{valve}^{out} are the inlet and outlet pressure of the valve; T_{valve} is the hydrogen temperature at the valve; γ represents the specific heat ratio of the gas; and A_c is the critical pressure ratio, which is taken as 0.528.

2.3 Diverter valve

In the thermal management system of hydrogen storage tanks, the flow divider valve can regulate the heat exchange fluid flow into the large and small circulation loops. The specific calculation formula is as follows:

$$\begin{cases} \dot{m}_{out,big}^{therm} = \varphi_{therm} \dot{m}_{in}^{therm} \\ \dot{m}_{out,small}^{therm} = (1-\varphi_{therm}) \dot{m}_{in}^{therm} \end{cases} \tag{6}$$

In equation (6), $\dot{m}_{out,big}^{therm}$, $\dot{m}_{out,small}^{therm}$ are the heat exchange fluid flow distributed by the divider valve to the large circulation loop and the small circulation loop; $\dot{m}_{in}^{therm}$ is the heat exchange fluid flow at the inlet of the divider valve; and φ_{therm} is the opening degree of the divider valve, ranging from 0 to 1.

2.4 Circulation pump

The role of the circulation pump is to drive the heat exchange fluid from the storage tank to circulate in the thermal management loop, controlling the flow rate of the heat exchange fluid passing through the hydrogen storage tank. In the modeling process, it is assumed that there is a linear relationship between the flow and the rotational speed of the pump, as shown in the following equation:

$$\dot{m}_{pu} = n_{pu} k_{pu} \tag{7}$$

In equation (7), $\dot{m}_{pu}$ is the output flow of the circulation pump; n_{pu} is the rotational speed of the circulation pump; k_{pu} is the dimensionless linear conversion coefficient between flow and rotational speed. In this article, the flow range of the circulation pump is set to 0.01 kg/s to 2 kg/s.

3 Control research

The hydrogen storage tank is a crucial component of the PEMFC gas supply system, achieving rapid and stable hydrogen release from the tank is a key factor in ensuring the stability of the PEMFC. Therefore, this section focuses on the hydrogen release reaction process of the hydrogen storage tank and its effective control.

3.1 Controller design

PID (Proportional Integral Derivative) control is one of the earliest developed control strategies, and due to its simple principle and convenient calculation, it is widely adopted in the industrial application of fuel cell systems.

For the solid-state hydrogen storage device designed in this paper, the control objectives are the hydrogen supply rate, internal pressure, and temperature of the hydrogen storage tank. The control primarily consists of three parts, corresponding to actuators including the hydrogen flow valve, flow divider valve, and circulating pump. Therefore, a control model is implemented using a parallel configuration of three PID controllers. The specific control structure is shown in Figure 2.

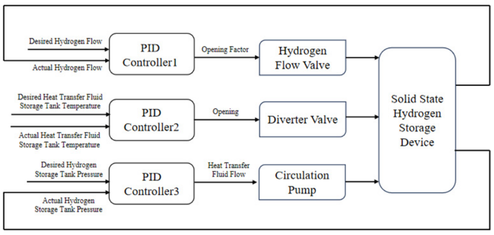

Fig. 2. The PID Controller for the Hydrogen Storage Tank.

3.1.1 Hydrogen flow valve

When designing the controller for the hydrogen flow valve, the control signal is the opening coefficient of the valve. The input signal is the difference between the actual hydrogen flow at the valve outlet and the theoretical hydrogen flow required by the fuel cell stack. The feedforward value is obtained by referencing a table that considers the pressure on both sides of the valve and the flow characteristics of the valve, thereby deriving the actual opening coefficient. The corresponding PID controller is expressed as follows:

$$u_1(t) = K_{p1} \cdot e_1(t) + k_{i1} \cdot \int e_1(t)dt + K_{d1} \cdot \frac{de_1(t)}{dt} \tag{8}$$

wherein, K_{p1} , K_{i1} and K_{d1} are the coefficients of the proportional, integral, and derivative components in the PID controller; $u_1(t)$ denotes the output of the controller at time(t); and $e_1(t)$ signifies the difference between the theoretical hydrogen demand flow and the actual hydrogen flow at time(t).

3.1.2 Diverter valve

For the controller design of the flow divider valve, the control signal is the opening of the valve. The input signal is the difference between the desired temperature and the actual temperature in the heat exchange fluid storage tank of the hydrogen storage tank. Based on the water temperature after heat exchange at the outlet of the hydrogen storage tank and the parametric characteristics of the heat exchanger, a feedforward value is obtained by referencing a table, which is then used to determine the actual opening of the flow divider valve. The corresponding PID controller is expressed as follows:

$$u_2(t) = K_{p2} \cdot e_2(t) + k_{i2} \cdot \int e_2(t)dt + K_{d2} \cdot \frac{de_2(t)}{dt} \tag{9}$$

wherein, $e_2(t)$ signifies the difference between the desired tank temperature and the actual tank temperature at time(t).

3.1.3 Circulation pump

For the controller design of the circulation pump, the control signal is the water flow at the outlet of the pump. The input signal is the difference between the desired hydrogen pressure inside the hydrogen storage tank and the actual hydrogen pressure. Based on the stack load current, the reaction enthalpy changes of the hydrogen storage material, and the temperature difference between the water flowing through the inlet and outlet of the hydrogen storage tank, a feedforward value for the circulation pump flow is obtained by referencing a table. This allows for determining the actual water flow rate participating in heat exchange for the circulation pump.The corresponding PID controller is expressed as follows:

$$u_3(t) = K_{p3} \cdot e_3(t) + k_{i3} \cdot \int e_3(t)dt + K_{d3} \cdot \frac{de_3(t)}{dt} \tag{10}$$

wherein, $e_3(t)$ signifies the difference between the desired hydrogen pressure and the actual hydrogen pressure measured within the hydrogen storage tank.

The PID controller parameters corresponding to each actuator in the solid-state hydrogen storage device are presented in Table 1.

Table 1. System Controller Parameters for the Solid-State Hydrogen Storage Device.

Acutator	Parameters	Values
Hydrogen Flow Valve	K_{p1}	0.005
	K_{i1}	0.378
	K_{d1}	0
Diverter Valve	K_{p2}	0.214
	K_{i2}	0.099
	K_{d2}	0
Circulation Pump	K_{p3}	4.255
	K_{i3}	0.0488
	K_{d3}	14.805

3.2 Simulation analysis

Simulation analysis of the established controller was conducted using the MATLAB/Simulink platform, requiring the setting of stack load currents to simulate operating conditions of the fuel cell stack. While traditional verification conditions commonly adopt step-change conditions to observe the control effect of the controller, ideal step-change conditions do not exist in real-world operating environments. Therefore, in the design of operating conditions, a short duration was set for the rising and falling edges of the step-change conditions, referred to as "quasi-step-change conditions." When the rising edge duration of the "quasi-step-change conditions" is 0.1ms, the accuracy in analyzing system characteristics with frequencies lower than 1kHz can be greater than 99% [10]. Hence, in this paper, when examining the control effect of the solid-state hydrogen storage device, a quasi-step-change condition as shown in Figure 3 was adopted.

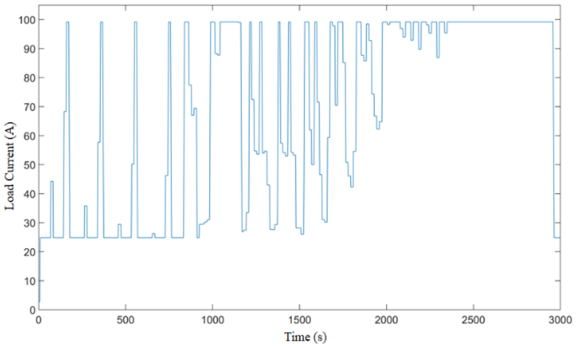

Fig. 3. Quasi-Step Current Profile Diagram.

The initial conditions set for all simulations are listed in Table 2 below:

Table 2. Initial Environmental Conditions for Controller Simulation.

Parameters	Values/Units
Initial Pressure	5/bara
Initial Temperature	293/K
SOC of Hydrogen Storage Material	100%
Initial Coolant Temperature of the PEMFC	333/K

In this section, the desired inlet water temperature of the storage tank was set at 60°C (333K), and the desired pressure of the hydrogen storage tank was set at 4 bara. Figure 4-6 illustrate the control simulation results under the quasi-step condition. It is evident from the figures that the solid-state hydrogen storage device achieves a good following effect in terms of hydrogen flow supply control. When the current of the fuel cell stack undergoes a step change, the theoretical demand for hydrogen also experiences a step change, and the supply from the hydrogen flow valve is able to respond rapidly, with a response time of less than 15s. Similarly, good performance is demonstrated in controlling the pressure within the hydrogen storage tank, with the internal pressure stabilizing mostly between 3.8-4.2 bara, maintaining an error of within 0.2 bara. Compared to the other two parameters, the response time for controlling the inlet temperature of the heat exchange water storage tank is slightly slower, but it is still within an acceptable range with a small overshoot. In summary, the controller designed for the solid-state hydrogen storage device ensures not only the rapid and stable supply of hydrogen, but also excellent control over the pressure within the hydrogen storage tank and the temperature within the storage tank.

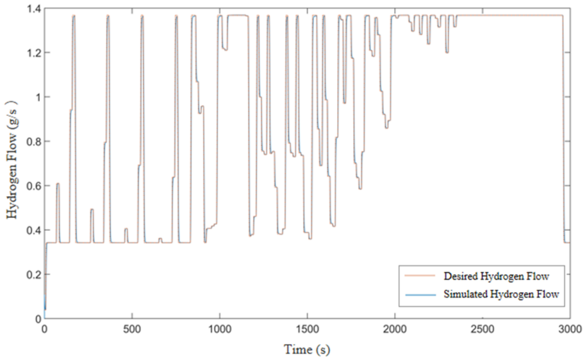

Fig. 4. Simulation Results for Hydrogen Flow Valve under Step-like Operating Conditions.

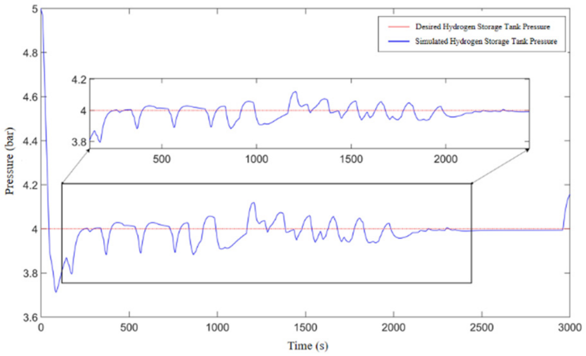

Fig. 5. Simulation Results for the Circulation Pump under Step-like Operating Conditions.

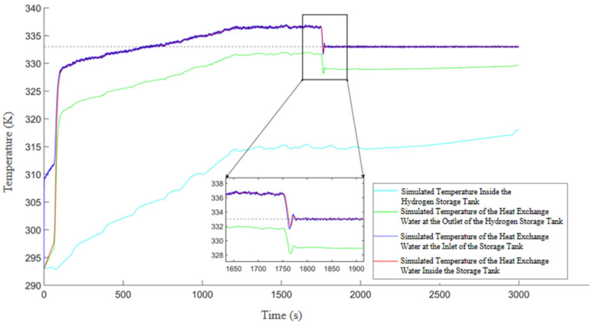

Fig. 6. Simulation Results for the Circulation Pump under Step-like Operating Conditions.

4 Conclusion

In this study, a solid-state hydrogen storage and supply method is employed, and a corresponding metal hydride solid-state hydrogen storage device is designed for the application scenario of PEMFC. This device, along with the fuel cell system, forms an MH-PEMFC system. The research focuses on the modeling and control methods of the metal hydride hydrogen storage system. A corresponding model is built on the MATLAB/Simulink platform, and simulations are conducted to verify that the controller designed for the solid-state hydrogen storage device can achieve the goal of continuously and stably supplying hydrogen to the fuel cell.

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