Thermal and energy balance of a fuel cell during hydrogen supply from metal hydride materials

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Abstract

The present article deals with the material and energy balance of a fuel cell during hydrogen supply from a metal hydride tank. It describes potential utilisation of heat from a fuel cell for heating a tank in order to achieve the required kinetics of the process. The concluding part hereof contains a numerical calculation of the thermal field of the designed tank during the fuel cell operation.

Keywords: hydrogen; metal hydride; fuel cell

1. Introduction

The energy content of one mole of hydrogen is determined by the value of change in enthalpy ΔH which equals the heating value of hydrogen. When hydrogen is used for the production of electric energy, the efficiency of such conversion is limited by the applied production method. For example, in thermomechanical methods of electric energy production, maximum efficiency of a device is determined by the Carnot cycle, as it is with other fuels. Even though it is possible to achieve a higher combustion temperature in hydrogen combustion, the cycle efficiency, which is limited by the thermodynamic laws, is approximately the same as that of fossil fuels. As hydrogen represents a very high-grade type of energy, its chemical properties make it an excellent fuel for fuel cells (FCs). A reaction between hydrogen and oxygen in a fuel cell is a reverse process of water electrolysis, while these two processes exhibit a lot of common theoretical and practical patterns. At present, fuel cells with a PEM (Proton Exchange Membrane) are becoming the most frequently used fuel cell type (Fig. 1). Their mechanism is based on supplying hydrogen molecules through a distribution layer to a catalyser (Pt) where a hydrogen molecule dissociates into atoms. Then electrons leave atoms and a hydrogen cation (proton) is formed. Proton passes through the membrane towards the cathode where it accepts an electron and merges with the supplied oxygen to produce water.

Electric voltage in the fuel cell is produced by electrochemical oxidation of hydrogen:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

and electrochemical reduction of oxygen:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{2}$$

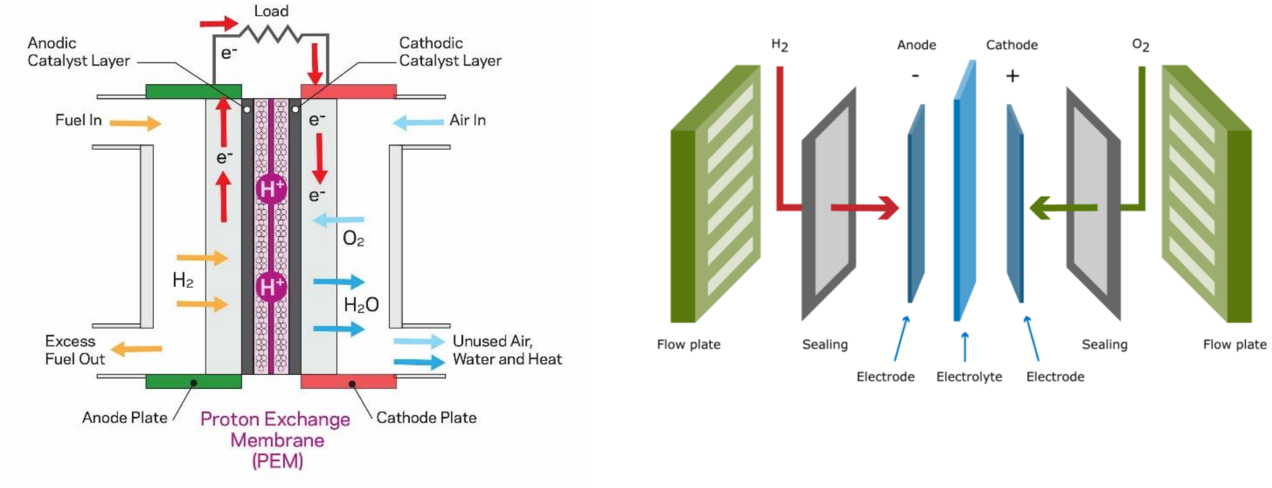

Figure 1. The mechanism of action of a PEM fuel cell and its structure scheme [3] [4].

However, the use of hydrogen as a fuel brings several problems, including a low heating value relative to a volume unit caused by low gas density, i.e. 0.08988 $kg \cdot m^{-3}$ (at 101,325 Pa and 0 °C). This negatively affects hydrogen storage as such, whereas the efforts are aimed at achieving the highest possible energy density. The efforts aimed at eliminating the use of extremely high pressures have led to mass investigation of absorption-based method of hydrogen storage in form of metal hydrides (MH). They facilitate hydrogen absorption directly in their structure at lower pressures and ambient temperatures. A commonly available MH type is the intermetallic alloy $LaNi_5$ and especially its related alloys containing cerium. The working pressure of $LaNi_5$ ranges from 0.1 to 1 MPa and the temperature ranges from 20 to 60 °C; these values are compatible with selected types of high-pressure electrolysers and fuel cells. Storing hydrogen which is firmly bound to a metal alloy facilitates significant reduction of the pressure in tanks with the same amount of fuel as in the standard storage in pressure vessels. This results in the reduction of energy demand during hydrogen compression into tanks. Furthermore, during hydrogen combustion in FCs, the relative pressure must be reduced to approximately 50 kPa; this means that the application of high-pressure methods of hydrogen storage is unnecessary.

2. Experimental Section

Hydrogen absorption into metal hydride is accompanied by heat generation. Therefore, during the “tank charging” it is necessary to apply cooling and the heat may subsequently used for heating purposes. While hydrogen is supplied from a MH tank to a FC, hydrogen desorption occurs and this requires supplying heat to the alloy, otherwise the heat is absorbed at the expense of its internal energy. This causes that the temperature of the MH material decreases and so does the kinetics of hydrogen release. For a commonly used alloy $La_{0,85}Ce_{0,15}Ni_5$, absorption heat amounts to 1.01 MJ per 1 m^3 of absorbed hydrogen, representing 7.9 % of the heating value of hydrogen (12.76 $MJ\cdot m^{-3}$).

During hydrogen combustion in the PEM FC, electric energy is produced with the efficiency of approximately 50 %, while the remaining portion of chemically bound energy is transformed into thermal energy. This process may be described using the energy balance as follows:

$$\sum Q_{\text{in}} = W_{\text{el}} + \sum Q_{\text{out}} + Q_{\text{dis}} + Q_{\text{c}} \tag{3}$$

wherein ΣQ_{in} represents the enthalpy of gases at the inlet (J), W_{el} is the produced electric energy (J), ΣQ_{out} is the enthalpy of unused gases at the outlet, including the heat contained in the produced water (J), Q_{dis} is the heat loss into the surrounding environment (J) and Q_{c} is the heat removed by active cooling (J). Active cooling may be achieved through the cooling medium flowing between the fuels, or at the edge of the active part of the FC, or by using the phase transition. Total heat generated in the fuel cell is calculated using the following formula [1]:

$$Q_{\text{gen}} = \sum Q_{\text{out}} + Q_{\text{dis}} + Q_{\text{c}} = \left(1.482 - U_{\text{cell}}\right) \cdot I \cdot n \tag{4}$$

wherein U_{cell} is the voltage in one cell (V), I is the current passing through the FC (A) and n is the number of cells (1).

Equation (4) applies when the produced water is in the liquid state at the temperature of 25 °C. If water leaves the cell in the gaseous state (vapour), Equation (5) is more appropriate [1]:

$$Q_{\text{gen}} = \left(1.254 - U_{\text{cell}}\right) \cdot I \cdot n \tag{5}$$

The material balance of the FC is determined by the mass of hydrogen, oxygen and produced water per unit time:

$$m_{\mathrm{H_2}} = m_{\mathrm{H_2}}^{1\mathrm{C}} \cdot I \cdot \tau \cdot n \qquad m_{\mathrm{O_2}} = m_{\mathrm{O_2}}^{1\mathrm{C}} \cdot I \cdot \tau \cdot n \qquad m_{\mathrm{H_2O}} = m_{\mathrm{H_2O}}^{1\mathrm{C}} \cdot I \cdot \tau \cdot n \tag{6}$$

wherein $m_{\mathrm{H_2}}^{1\mathrm{C}}$ is the mass of hydrogen used during the passage of electric charge 1 C ($10.441 \cdot 10^{-9}$ kg·C^{-1}), $m_{\mathrm{O_2}}^{1\mathrm{C}}$ is the mass of oxygen used during the passage of electric charge 1 C ($82{,}914 \cdot 10^{-9}$ kg·C^{-1}), $m_{\mathrm{H_2O}}^{1\mathrm{C}}$ is the mass of water produced during the passage of electric charge 1 C = 1 A·s ($93.355 \cdot 10^{-9}$ kg·C^{-1}) and τ is the operation time (s). If the power at FC terminals is 1 kW, efficiency is 50 % and the operation time is 1 hour, the fuel cell receives 0.403 kg of oxygen and 0.0502 kg of hydrogen, and 0.453 kg of water is produced; however, such water must be removed from the fuel cell [2].

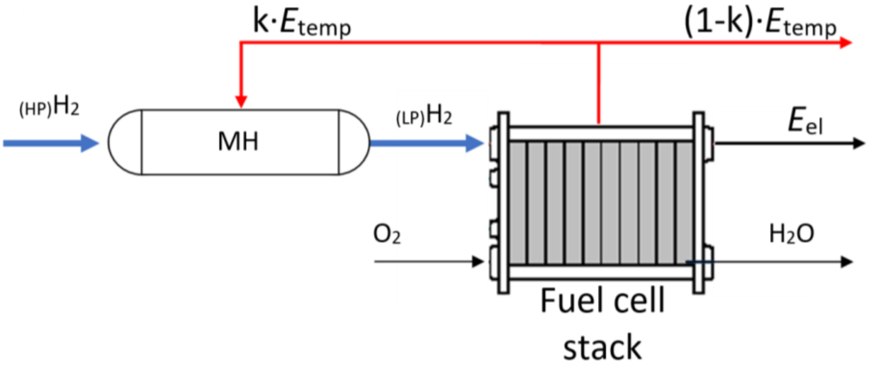

Figure 2. Scheme of material and energy flows when H_2 is supplied from MH.

Fig. 2 shows the material and energy balance of the fuel cell while hydrogen is supplied from a MH tank. As already mentioned above, a MH tank needs a supply of heat while hydrogen is released. With the use of a FC with the power of 1 kW, hydrogen must be desorbed from the alloy at the flow rate of $1.56 \cdot 10^{-4}$ m^3·s^{-1}. In the case of $La_{0,85}Ce_{0,15}Ni_5$ alloy, 158 W of heat output is needed.

3. Results and Discussion

As the fuel cell produces approximately 500 W of heat output, a certain portion may be used to heat up the tank. However, in a real operation it is possible to supply a lower heat output because the internal energy of the tank may be used as well. In this case, hydrogen temperature and pressure decrease, but it does not constitute a problem, unless the pressure falls below the minimum operating pressure in the FC. The purpose of the simulation was to verify the use of heat from cooling the FCs and optimise tank parameters. The numerical calculation was based on the expected power of FC of 1 kW while hydrogen was desorbed from 0.955 kg of $La_{0,85}Ce_{0,15}Ni_5$ alloy, and this facilitated covering the FC consumption for 1,000 seconds of operation. In order to ensure the required kinetics of a hydrogen desorption process, it was necessary to use a ground MH material. This facilitated achieving a large surface area of the material. However, there is a disadvantage of a low value of heat transfer coefficient which impairs the heat supply to the tank's core. Therefore, the tank material extends to the core of the MH material because the inner space of the tank was divided into several chambers (Fig. 3). In order to intensify the heat transfer, the aluminium tank was chosen, and the chambers were created by drilling. The outer diameter of the tank was 130 mm and its height was 200 mm. 26 ribs were formed along the perimeter and they were washed by the heated air from the system cooling the fuel cell. The speed of the flowing air was 1.31 m·s^{-1} at a temperature of 35 °C (average values obtained by measuring the cooling of the FC, type MES DEA 0.5). The baseline temperature of the tank was 35° C. Thermal conductivity of the powder MH material was 0.45 W·m^{-1}·K^{-1}.

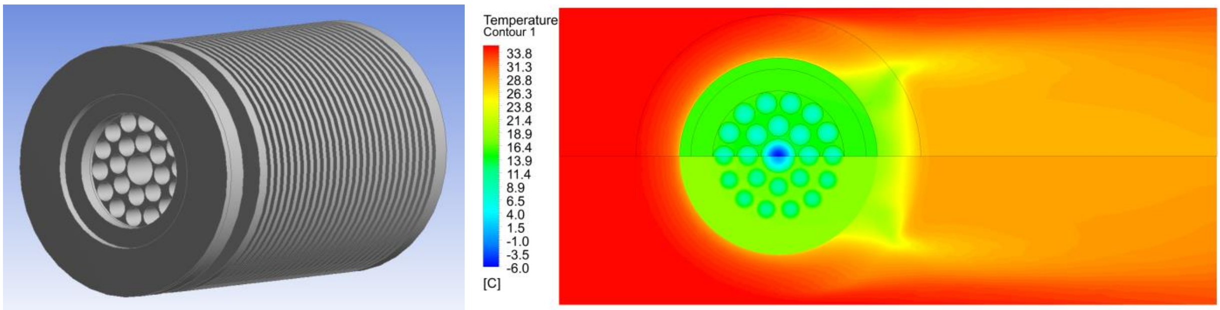

Figure 3. Model of a MH tank and thermal field in the transversal cross-section at time 1,000 s.

The simulation duration was 1,000 seconds with 5-second calculation increments. Fig. 4 shows the curve of average temperatures of MH and the aluminium tank changing over time.

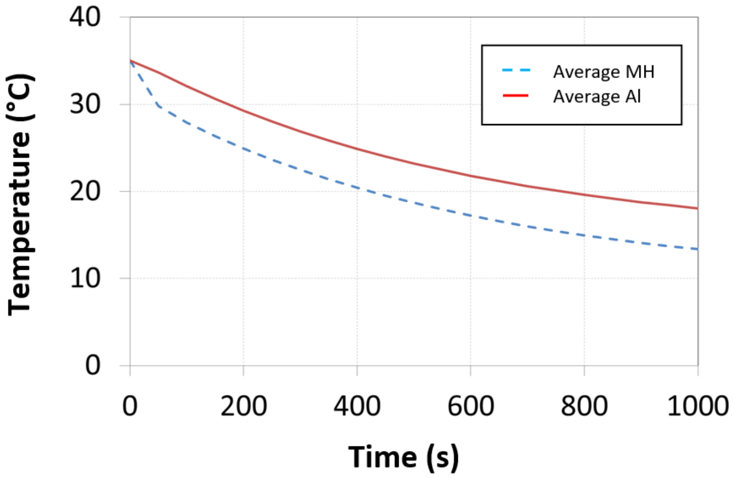

Figure 4. Curve of temperatures of MH and the Al tank changing over time

The curve clearly shows that the average temperature of MH did not fall below 10 °C, i.e. the point when the equilibrium pressure of the alloy is approximately 100 kPa which is sufficient for a stable operation of FCs. By making an analytical calculation of the material and energy balance, followed by a numerical calculation, it is possible to design and optimise MH-FC systems which will use the combined thermal management.

3. Conclusion

The article deals with thermal and energy balance of a fuel cell during the supply of hydrogen from a MH tank into which the required heat was supplied for the purpose of desorption using the cooling air from FCs. A numerical calculation was made to identify thermal fields of the tank over time and this facilitated the assessment of the appropriateness of the used system for real operations.

4. Acknowledgement

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