

Modeling and analysis of electrochemical hydrogen compression

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Abstract

One of the challenges to realizing the hydrogen economy is hydrogen compression and storage issues. Recent developments in proton exchange membrane (PEM) technology have offered possibilities for efficient electrochemical compression of hydrogen. This alternative method offers operational and efficiency benefits over the conventional mechanical compressor. Efficient hydrogen compression can improve the overall efficiency of a renewable hydrogen production system. This paper summarizes the modeling of a PEM electrochemical compression system. Modeling was done using the Mathematica software to calculate the energy requirement of electrochemical compression at different output pressures. The PEM cell compressor can be used as an intermediate step to mechanical compression to reduce the number of compression stages and energy usage. Results from the theoretical calculations are used to compare energy use for the combination of PEM cell and mechanical compression with mechanical compression alone, over a wide pressure range.

Key words: hydrogen compression, hydrogen storage, PEM-cell.

1. Introduction

The need for clean sustainable energy system and the advancements in fuel cell technologies in recent years has attracted more attention to a efficient renewable hydrogen production and compression technology. Hydrogen as an energy carrier suffers from its low volumetric energy density in transition to a hydrogen economy. The most technically challenging barrier to building a hydrogen economy is the development of safe, compact and cost effective hydrogen storage technology [1]. Hydrogen can be stored by several methods including gaseous hydrogen storage, as a liquid, in metal, in glass micro spheres or in carbon nanotubes. Each storage method has different advantages and disadvantages. Gaseous hydrogen has low volumetric energy density [about 25% of that of the gasoline] but remains the preferred method to store the hydrogen for specific applications. The low volumetric energy density of hydrogen can be improved by compressing it at high pressure. This compression achieved with an energy efficient hydrogen compressor can improve energy efficiency of the system [2]. Compressed gaseous storage is a well-known and economical method to store hydrogen. The most common approach of mechanical compression is limited due to obstacles such as high energy use, wear-and-tear of moving parts, hydrogen embrittlement, noisy operation, bulky equipment, and contamination of the gas, typically with compressor lubricants [3]. Use of an electrochemical system such as PEM cells offers an alternative means to compress hydrogen. In low power applications, the efficiency of PEM cells is high compared

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to mechanical compression [4]. The other advantages of an electrochemical system approach are noiseless operation, purified hydrogen and simplicity of the system cooling [5]. These advantages make it a promising hydrogen compression technology for future. Electrochemical compressor can also serve as an intermediate step to mechanical compression to increase compression capacity and efficiency by reducing number of compression stages [6].

2. Principle of Electrochemical Compression

Hydrogen feed at the anode as shown in figure 1 is oxidized to protons (H^+) by the application of a potential difference. These protons transport through the polymer membrane and reduce to hydrogen again at the cathode. The hydrogen being produced by proton reduction in the confined cathode space is compressed and discharged at high pressure. As the polymer membrane is selective for hydrogen, inert gas components can not cross the membrane and are thus removed from the compressed gas. Moreover, since the electrochemical compressor does not have any moving parts, it minimizes maintenance. Flexibility in sizing of cells allows this compressor to achieve a high efficiency.

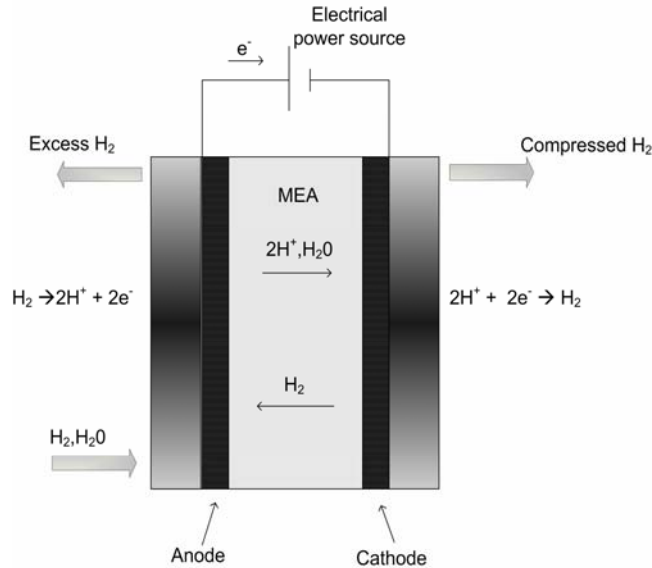


Figure1: Polymer electrolyte membrane (PEM) hydrogen compressor

3. Future Experimentation

The proposed experimental setup for electrochemical compression of hydrogen from University of North Dakota's (UND) PEM electrolyzer system is shown in figure 2. The membrane of the electrochemical cell must be well hydrated to maintain the ionic conductivity; hence the hydrogen must be humidified before feeding to the anode. This can be achieved by using the product hydrogen gas from the PEM electrolyzer system, conditioned to compress electrochemically. The product hydrogen from PEM electrolyzer can be assumed to be 100% saturated. It is

conditioned using a thermoelectric cooling system to the required humidity level to electrochemically compress using a PEM cell assembly [7]. Results from testing on this system will allow validation of the modeling results presented in this paper.

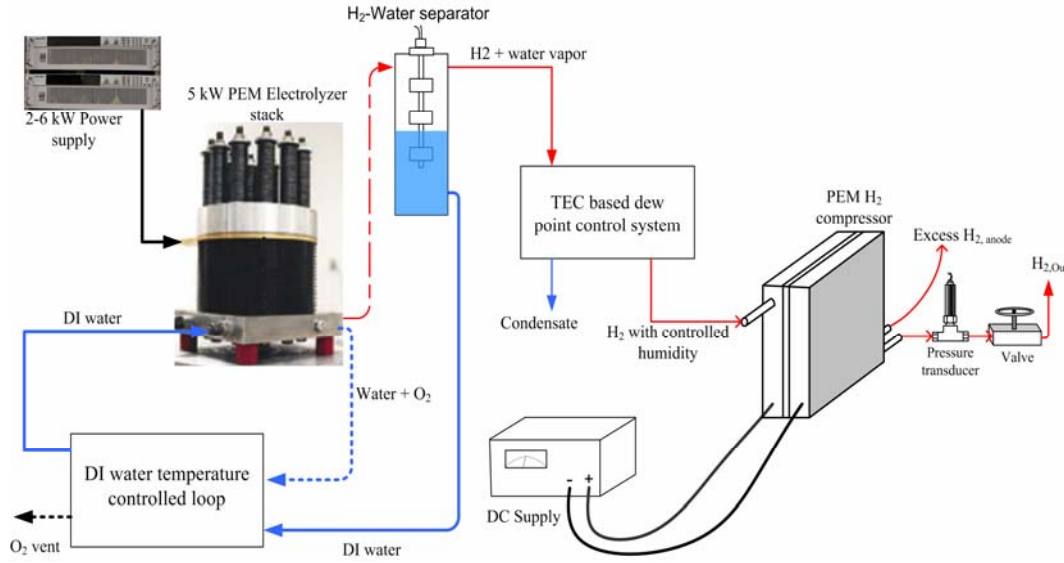


Figure 2: Proposed experimental set up

4. Mathematical Modeling

A. Nernst Potential:

The total voltage of the PEM cell includes the Nernst potential, the polarization voltage and the IR drop or ohmic resistance. The Nernst potential depends on the pressure difference between the cathode side and the anode side. This equilibrium potential is given by eq

$$E_{\text{Nernst}} = E_0 + \frac{RT}{2F} \ln \left(\frac{P_C}{P_A} \right) \quad (1)$$

where P_C is cathode pressure and P_A is anode pressure.

B. Overpotentials :

These are the irreversibilities that have to be overcome by applied potential to a PEM cell before oxidation and reduction of hydrogen can begin. For PEM cell working as an electrochemical compressor only activation and ohmic overpotentials are significant. The activation polarization is the overpotential that has to be overcome by an electrochemical reaction before the reaction can occur. This process is modeled by Tafel equation. The Tafel equation for an electrochemical process with non zero activation polarization at each electrode can be described by following equations

$$E_{Act\ Anode} = \frac{RT}{2\alpha_a F} \ln\left(\frac{i}{i_{oa}}\right) \quad (2)$$

$$E_{Act\ Cathode} = \frac{RT}{2\alpha_c F} \ln\left(\frac{i}{i_{oc}}\right) \quad (3)$$

where, i is the operating current density in A/cm^2 , α is the charge transfer coefficient at anode and cathode and is assumed equal to the symmetry factor (ie 0.5) for both electrodes. The magnitude of activation overpotential is a function of the exchange current density at the anode (i_{oa}) and exchange current density at the cathode (i_{oc}). The exchange current densities are a measure of the activity at the anode and cathode prior to the application of potentials. Generally, the kinetics of hydrogen electrodes are rapid, but in the case of PEM cell compressor, a slightly slower kinetics of the reduction at the cathode can be observed as compared to the oxidation at the anode [5]. This can be explained due to slower kinetics of the Volmer-Tafel mechanism [5].

The constant resistance experienced across the applied voltage to the PEM cell is represented as ohmic overpotential. The magnitude of ohmic loss depends on electrode material, electrolyte material and interface between electrode and electrolyte. Manufacturing processes and techniques are an important factor in keeping this overpotential minimal.

The ohmic overpotential is modeled by the following equation

$$E_{Ohmic} = \frac{\varphi}{\sigma} i \quad (4)$$

where, φ is the membrane thickness (cm), σ is the cell conductivity (S/cm), and i is the operating current density. The membrane conductivity is a function of temperature. For this work, the conductivity is estimated using following equation [8]

$$\sigma = 0.0007 \times t + 0.0574 \quad (5)$$

where, t is temperature in $^{\circ}C$.

The total cell voltage of PEM cell compressor includes Nernst potential, the polarization voltage and the ohmic losses and therefore can be represented theoretically by equation (6).

$$E_{Total} = E_{Nernst} + E_{Act} + E_{Ohmic} \quad (6)$$

Combining equations (1)-(4) the cell potential is given by

$$E_{Total} = E_0 + \frac{RT}{2F} \ln\left(\frac{P_C}{P_A}\right) + \frac{RT}{2\alpha_a F} \ln\left(\frac{i}{i_{oa}}\right) + \frac{RT}{2\alpha_c F} \ln\left(\frac{i}{i_{oc}}\right) + \frac{\varphi}{\sigma} i \quad (7)$$

where membrane thickness (φ) used is 178 μm (for Nafion™ 117) and the charge transfer coefficient at anode and cathode is 0.5. The calculations were done at 60°C.

5. Model Results

Theoretically calculated anode and cathode overpotentials using equation (2) and (3) respectively, increase with increasing current densities as shown in figure 3. The anode exchange and cathode exchange current densities from the literature [9,10] are used for this modeling work.

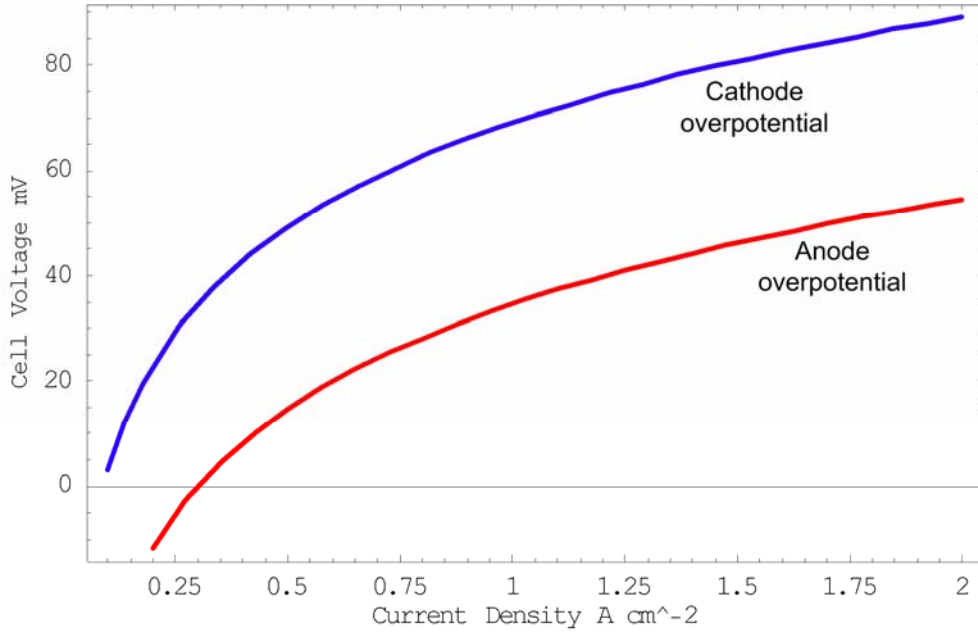


Figure 3: Polarization of PEM compressor electrodes

The calculated total cell voltage and Nernst potential versus pressure is shown in figure 4. To simplify modeling work, the anode pressure is assumed to be constant at 1 atm (14.7 psi). However, in real situation the assumption of constant anode pressure can not be true. The high pressure difference across the membrane promotes back diffusion of molecular hydrogen from cathode to the anode side. The back diffusion rate is important for efficiency calculations, as the compressor efficiency decreases with increasing back diffusion. The back diffusing hydrogen which increases the pressure at the anode side varies with cathode pressure and cell

temperature. This back diffusion increases linearly with increasing pressure difference [4].

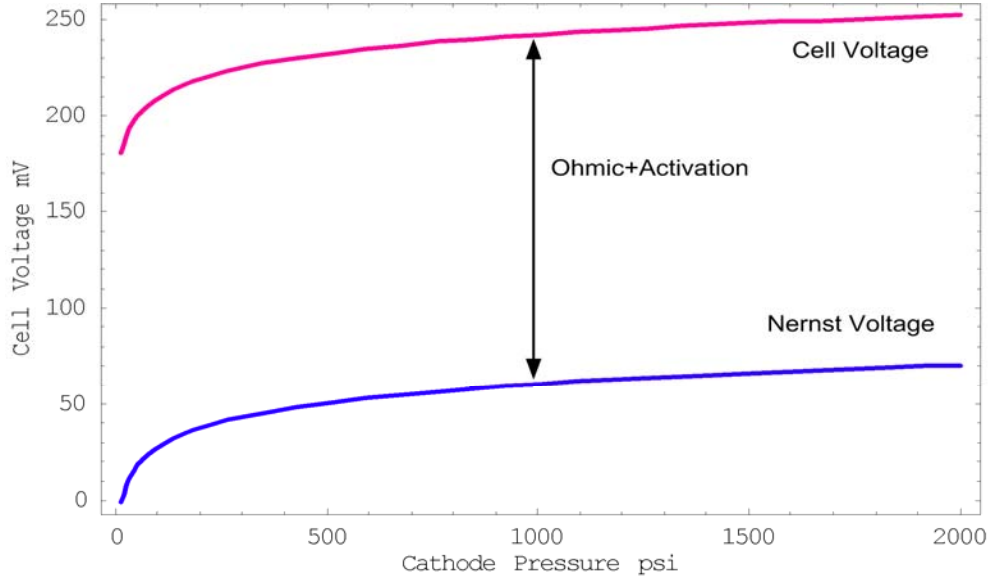


Figure 4: Cell voltage versus hydrogen pressure at the cathode.

The back diffusion rate can be measured using the amount of compensating current to keep the anode pressure constant [5]. The relation between gas diffusion rate (dn/dt) and membrane thickness (ϕ) is given by diffusion coefficient (Dn) [5].

$$\frac{dn}{dt} = -DnA \frac{dc}{d\phi} \quad (8)$$

The hydrogen back diffusion can be determined at open circuit voltage and $P_c > P_A$. Because of the additional back diffused hydrogen the pressure at the anode increases. This additional increase has to be compensated by a reduction of total anode pressure. This can be done by pumping of hydrogen from the anode to the cathode via protons (H^+) by adding more current to the anode [5].

As can be seen from figure 4, the main contributor to cell voltage is the ohmic and activation polarizations. Efforts were taken to estimate the contribution of each of these polarizations towards the total cell voltage at various operating current densities. Figure 5 shows these contributions to the total cell voltage. The ohmic voltage almost amounts to the cell voltage.

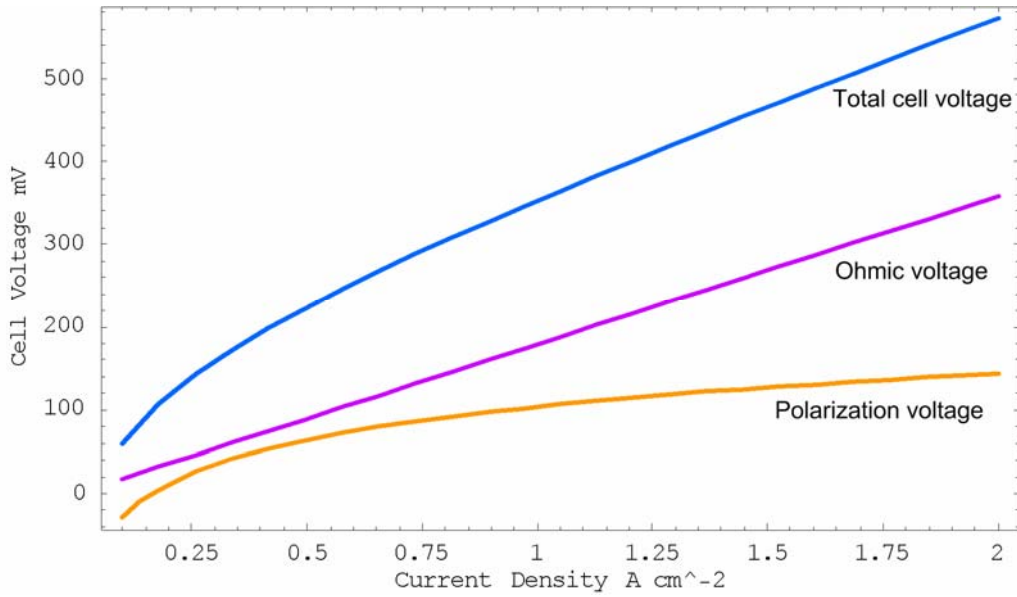


Figure 5: I-V characteristics of PEM cell compressor.

The energy required for compression increases with pressure. Therefore, it is expected that cell voltage increases with increased product pressure. To verify this, cell voltages were calculated at different cathode pressures and plotted versus operating current densities in figure 6. For this calculation the anode pressure is assumed constant at 1 atm (14.7 psi) and the product pressure at the cathode is varied from 250 psi to 2000 psi.

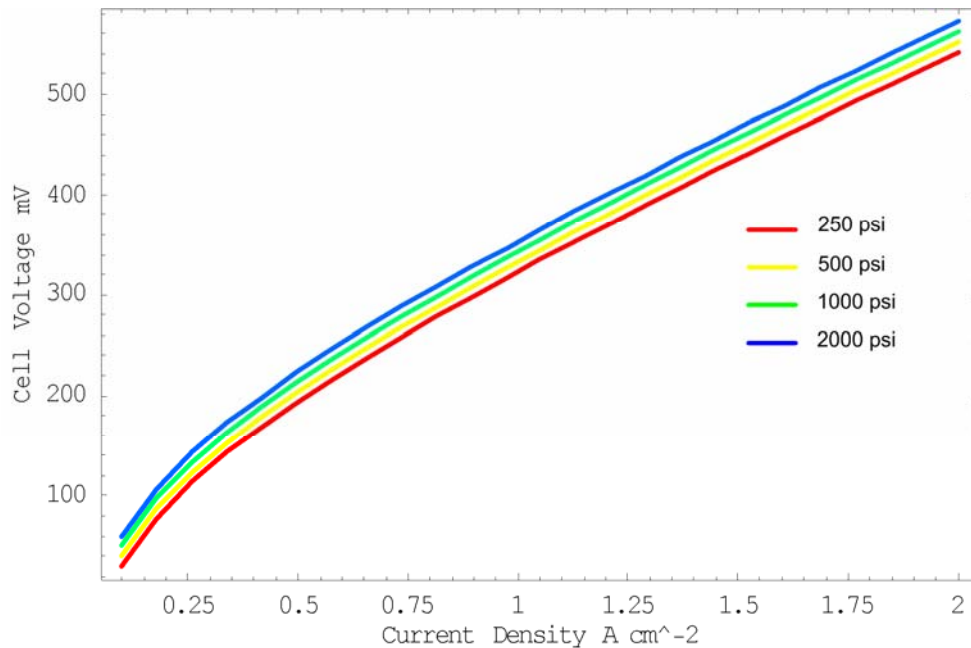


Figure 6: Cell voltage of PEM cell compressor at various product pressures.

As expected, the higher cell voltage at higher pressures shows higher energy requirement to compress hydrogen to an elevated pressure. In real systems, the

voltage differences are small at low current densities and more significant at higher current densities [6]. Also, measured voltage is expected to be greater than that calculated by equations because of increased resistance of the cell. The pressure differential between the anode and cathode causes expansion and contraction of the material inside the cell which results in an increase of contact resistance and therefore leads to the higher voltages [6].

6. Mechanical compression comparison

Mechanical Compression:

Calculating the work required to mechanically compress the hydrogen to the high storage pressure is complicated as hydrogen does not behave as an ideal gas at high pressures and the compression process is done in stages with cooling between these stages. Many investigators consider compression of hydrogen as an isentropic process to simplify the calculations. They assume no heat exchange between the compressor and environment and the process is reversible. Assuming hydrogen behaves as an ideal gas, the isentropic work to compress hydrogen gas from pressure P1 to pressure P2 is given by following equation [11].

$$W_s (isentropic) = \frac{RT_1\gamma}{\gamma - 1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (9)$$

where T1 is the temperature of hydrogen in Kelvin at pressure P1 and γ is the specific heat ratio of the gas (Cp/Cv). The specific heat ratio (γ) is assumed to be independent of temperature. For diatomic gases such as hydrogen, γ has approximate value of 1.4. But, since adiabatic hydrogen compression is not reversible process, isentropic compressor efficiency can be accounted for deviation from ideal behavior. Therefore, the actual compressor work can be given by [11]

$$W_{Actual} = \frac{W_s (isentropic)}{\eta_{adiabatic}} \quad (10)$$

where $\eta_{adiabatic}$ is the adiabatic efficiency of the compression process. Its value is approximately 75% -80% [12]. Finally, the actual energy required by compressor (ie. electrical consumption) is calculated considering the mechanical efficiency of the compressor to be 90% [12] and is shown in figure 7 for product pressure upto 10,000 psi.

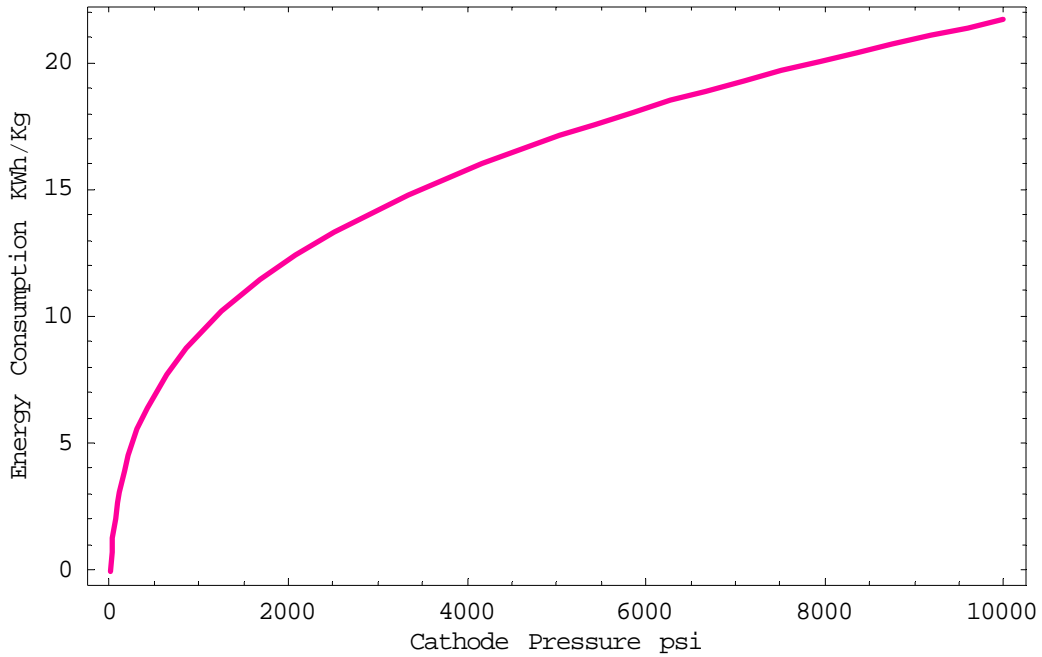


Figure 7: Energy consumption for mechanical compressor.

As can be seen from figure 7, mechanical compression requires more energy to compress the hydrogen gas at lower pressure ranges than at elevated pressure. In other words, mechanical compression is more efficient for compressing gases from 2000 psi to 10000 psi (1.2 wh/kg/psi) than from atmospheric pressure to 2000 psi (6 wh/kg/psi).

Electrochemical Compression:

The total cell voltage for PEM cell compression can be calculated using equation (7). The work required for the compression process can be calculated at different current densities by multiplying the total cell voltage by current density and total active area. The calculations were done for current density of 0.7 A/cm^2 and an active area of 30 cm^2 . The anode pressure is assumed to be constant at 14.7 psi. The calculations were performed for an inlet hydrogen flow rate of 4 kg/h. To account for real time losses the efficiency of PEM cell compressor is assumed to be 70%.

The calculated energy consumption for both mechanical and electrochemical compression for a product pressure range upto 2000 psi is shown in figure 8. The energy consumption for electrochemical compression is lower than for mechanical compression at a low pressure range. Therefore, the efficient electrochemical compressor can serve as an intermediate step between the electrolyzer and mechanical compressor to increase the whole system efficiency. Electrochemical compression can also reduce the number of compression and cooling stages resulting in more efficient compression process.

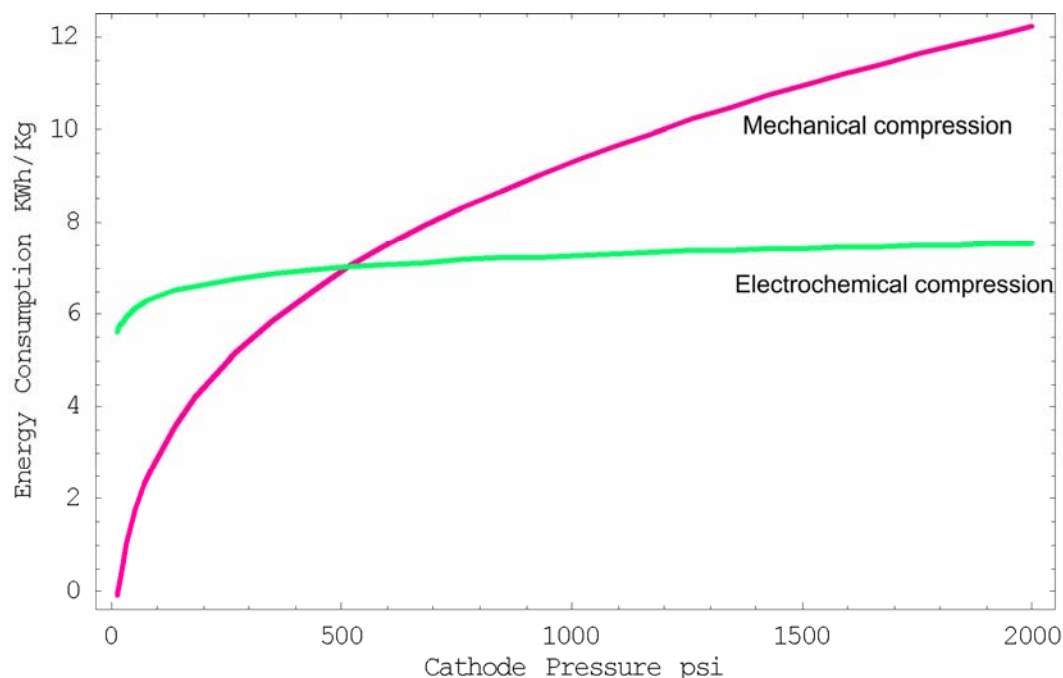


Figure 8: Comparison of energy consumption by mechanical and electrochemical compressor.

To compress the hydrogen from atmospheric pressure to 10000 psi using mechanical compression alone theoretically requires 22 KWh/Kg of H_2 as shown in figure 7. Calculations showed that electrochemical compression requires 7.5 KWh/Kg of H_2 energy to compress hydrogen from atmospheric pressure to 2000 psi. If the electrochemical compressor is used as an intermediate step between electrolyzer and mechanical compression to compress hydrogen upto 2000 psi and then mechanical compression from 2000 psi to 10000 psi, the energy saving can be as high as 5 KWh/Kg (23%) according to theoretical calculations. The energy required for cooling stages during mechanical compression have not been considered for these calculations.

7. Conclusions

Several studies [4-6] support the technical and economical feasibility of electrochemical compression of hydrogen as an alternative to mechanical compression. In addition to increased efficiency, electrochemical compression has several benefits over mechanical compression including selective permeability for hydrogen. The stack active area can be reduced by operating at high current density; hence a lower number of cells are required. Therefore, operating at high current density can reduce the stack cost. Thin membranes allow efficient operation at high current density because of low resistance, although poor mechanical properties limit its operation at high pressure differences. The limiting factors to the high pressure electrochemical compression are construction of the cell assembly, perfect sealing, internal cell resistance and hydrogen back diffusion from cathode to anode through membrane. Optimizing the cell hardware packaging can minimize the losses due to an increase in contact resistance at higher pressures. The current research focused on

building a high pressure PEM electrolysis system using advanced seal and endplate design [13] may help in designing membrane electrode assembly for hydrogen compressor to achieve high pressure compression.

8. Acknowledgment

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9. List of symbols

F	Faraday's constant, 96486 C/mol
A	Active area, cm^2
T	Temperature, K
E_0	Standard potential, V
R	Gas constant, 8.314 J/mol K
I	Current, amp

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