Separation of hydrogen from natural gas in distribution pipelines using electrochemical reaction based cells

Elisa Zanella*, Giulia Tonsi, Arian Grainca, Alberto Vertova, Mariangela Longhi, Carlo Pirola

Università degli Studi di Milano, Dipartimento di Chimica – via Golgi, 19, 20133 Milano (MI), Italy
**Corresponding author: elisa.zanella@unimi.it*

Highlights

- Electrochemical purification of hydrogen from methane-hydrogen mixture with a view to deblending was studied.
- Comparing different Nafion membranes, it was found that the best one for this application is Nafion 212, owing to its lower thickness and higher ion-exchange capacity.
- From a methane-hydrogen gas mixture a purity higher than 99.9% was obtained

1. Introduction

Nowadays energy plays a fundamental role in our society and hydrogen seems to have a key role in a scenario dominated by depletion of fossil fuels, global warming, and rising energy demand[1]. However, its use is limited by storage and transport problems[2]. A possible solution is blending hydrogen into natural gas pipeline network. The separation, purification, and potential storage of this energy vector are therefore important challenges. There are different methods for hydrogen purification, e.g. cryogenic[3], Pressure Swing Adsorption (PSA), and membranes, but one of the most promising technologies is based on the Electrochemical Hydrogen Compressor (EHC) because it combines purification with hydrogen compression due to the electrochemical principle on which it is based, namely, the oxidation of impure hydrogen at the anode and the evolution of pure, high-pressure hydrogen at the cathode. Rhandi et al.[4] demonstrate that the EHC has many advantages: high gas recovery, low operating temperature, compatibility of the process with continuous operation, low energetic cost of the process, and high purity of the gas that can be reached, higher than 99.9%[5]. The core of this device is the membrane electrode assembly (MEA), that is based on two gas diffusion electrodes (GDEs) and a proton exchange membrane (PEM). This component is crucial for EHC system performance, due to its electrical resistance and proton conductivity. Therefore, a membrane with high ionic conductivity is required to reduce ohmic losses. In addition, the membrane must have high mechanical, thermal and chemical stability to withstand working conditions.
In this study, low-temperature EHC with Nafion membrane was investigated and tested in hydrogen separation from different methane-hydrogen mixtures, evaluating the influence of different type of membranes on the efficiency of the EHC system.

2. Methods

The EHC used in this study presents a single cell with an active area of 10 cm^2. The core of the cell is a 5-layer commercial membrane electrode assembly (MEA), supplied by Fuel Cell Store. Specifically, three different MEAs were tested, whose characteristics are reported in Table 1.

Table 1: 5-layer Membrane Electrode Assembly (MEA) characteristics.

	MEA 1	**MEA 2**	**MEA 3**
Anode Catalyst	0.3 mg/cm² PtC (20%)	0.3 mg/cm² PtC (20%)	0.3 mg/cm² PtC (20%)
Cathode Catalyst	0.5 mg/cm² PtC (60%)	0.5 mg/cm² PtC (60%)	0.5 mg/cm² PtC (60%)
Membrane	Nafion 212	Nafion 115	Nafion 117
Gas diffusion Layer	Carbon Cloth	Carbon Cloth	Carbon Cloth

The supplied inlet gases are methane and hydrogen. For each of the three streams, pressure, temperature, dew point and mass flow are monitored. Hydrogen or different H_2-CH_4 molar ratio (from 90-10 to 10-90) were investigated. The gas mixture has been humidified and circulated in the cell maintaining a constant inner hydrogen flow of 20 mL/min. To determine the resistance and the associated overvoltage of the system, the potential has been monitored as a function of a set current value. The current has been varied between 0-1.5 A. The efficiency of the system was determined by monitoring the purge flow and the output flow. The purity of the output gas was checked using a microGC.

3. Results and discussion

Following this methodology, the three different MEAs (Table 1) were tested, and the results are shown in Figure 1a. At the same condition the membrane that show the best results is the Nafion 212. In Table 2 it is possible to notice that this membrane presents the lowest thickness and the higher ion-exchange capacity.

Table 2: Comparison of the characteristics of the three Nafion membranes used for the tests.

	Nafion 212	Nafion 115	Nafion 117
Thickness, µm	50.8 (2)	127 (5)	183 (7)
Basis weight, g/m^2	100	250	360
Water uptake, %	50.0 ± 5.0	38	38
Ion-exchange capacity, meq/g	0.92	0.90	0.90
Experimental resistance (Figure 1a), mΩ	98.7 ± 0.3	142.9 ± 0.4	183.6 ± 0.5

Once the best membrane was found, the purification of hydrogen from a gas mixture was tested. Methane/hydrogen molar ratio ranging from 10/90 to 90/10 was investigated. In Figure 1b some results with the higher amount of methane in the stream are reported. It may be observed that as the amount of methane in the stream increases, so the system's resistance does, as indicated by the slope of the polarization curve. The current efficiency of the system was also evaluated and it stay steady at 90-100%. The purity of the hydrogen obtained was quantified using the microGC. A percentage of methane of 0.08 was revealed for every trial, confirming the effective purification efficiency of the system.

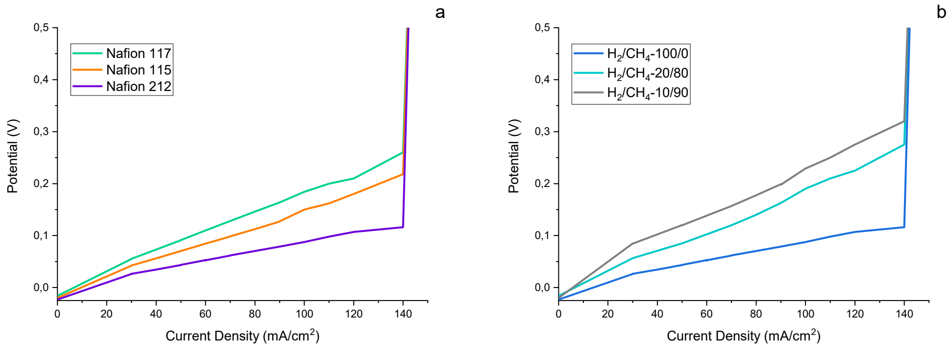

Figure 1. (a) Polarization curves and resistance value obtained for the tested MEAs and (b) polarization curves at different methane/hydrogen molar ratio. Process conditions: ambient pressure for both cathode and anode, 30°C, hydrogen inner flow 20 mL/min, humidity of the gas constant over 90%.

4. Conclusions

Electrochemical hydrogen compressor (EHC) can be considered a suitable system for hydrogen separation from methane, especially in the case of small units of purification. The best membrane among the ones tested is the Nafion 212 which presents the higher conductivity, the lowest thickness, and the higher ion-exchange capacity. Further studies will focus on the study of the compression step to also evaluate this aspect of EHC technology.

References

[1] U.S. Energy Information Administration, "U.S. Energy Information Administration's (EIA), International Energy Outlook 2019.," can be found under https://www.eia.gov/todayinenergy, **2019**.

[2] R. K. Ahluwalia, J. K. Peng, *Int. J. Hydrogen Energy* **2009**, *34*, 5476–5487.

[3] W. Liemberger, M. Groß, M. Miltner, M. Harasek, *J. Clean. Prod.* **2017**, *167*, 896–907.

[4] M. Rhandi, M. Trégaro, F. Druart, J. Deseure, M. Chatenet, *Chinese J. Catal.* **2020**, *41*, 756–769.

[5] G. N. B. Durmus, C. O. Colpan, Y. Devrim, *J. Power Sources* **2021**, *494*, 229743.

Keywords

Hydrogen, hydrogen deblending, purification, electrochemical hydrogen compressor.