HYDROGEN PURIFICATION WITH HYDROGEN SELECTIVE CERAMIC MEMBRANES

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1.INTRODUCTION

There will be a transition between nowadays energy structure and the situation in which hydrogen, which is foreseen by many as an important energy carrier in the future sustainable energy society, becomes an important part of it. In this transition the use of existing natural gas pipelines infrastructure to transport hydrogen will be profitable. Hydrogen can be produced by different ways. There are sustainable processes, as water electrolysis from excesses from solar and wind energy. In other processes, as natural gas or biomass reforming, hydrogen is generated mixed with other compounds as CH_4, CO, CO_2, N_2, etc. It is necessary to purify this hydrogen for two main reasons. First of all, pure hydrogen is needed to be converted by fuel cells into electricity with high efficiencies and very low pollutant emissions. Secondly, it is advisable to not introduce undesired gases in the pipelines. In this scenario with the use of natural gas pipelines, hydrogen purification units will also be needed to separate hydrogen from natural gas, due to the fact that they usually have different uses.

The main objective of this work was to test hydrogen selective Pd-based membranes for hydrogen purification from gas mixtures obtained from natural gas conversion to hydrogen.

2.EXPERIMENTAL METHODOLOGY

PdCu membranes were tested to analyse their hydrogen permeance, purification capacity and the influence of thermal cycles in embrittlement problems.. The membranes were prepared by sequential electroless plating method at ECN facilities in The Netherlands and surface morphology was characterized during the process using SEM images.

Hydrogen permeance tests were performed at different feed pressures, with 2 bar of pressure difference and at 673 K and 773 K. Thermal cycles were performed cooling down the membrane to 423 K in inert atmosphere and also in hydrogen atmosphere. Some tests were done to analyse the hydrogen permeance, purification, capacity and the influence of thermal cycles at 673 K and 773 K with 2bar of pressure difference. Once permeability of membranes were characterized, tests with diluted hydrogen were done.

Finally, hydrogen dilution tests were performed. Due to the fact that the aim objective of the membranes is to purify hydrogen from a mixture obtained from the hydrogen conversion from natural gas via catalytic partial oxidation (CPO) or wet-CPO. In the product mixture obtained from these processes hydrogen composition is around 20-40 %. In these operational conditions the influence of sweep gas flow is very important, as it increases the hydrogen pressure difference through the membrane. It was tested the optimal sweep gas flow with different hydrogen composition feed flows to the membrane.

$$CPO \rightarrow CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 \quad \Delta H = -36 KJmol^{-1}$$

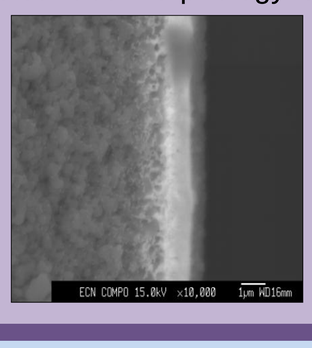
$$Wet-CPO \begin{cases} OPC \rightarrow CH_4 + \frac{1}{2}O_2 \rightleftharpoons CO + 2H_2 & \Delta H = -36 KJmol^{-1} \\ SR \rightarrow CH_4 + H_2O \rightleftharpoons 3H_2 + CO & \Delta H = +206 KJmol^{-1} \end{cases}$$

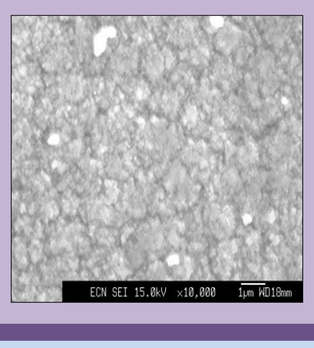
3.RESULTS

3.1 SEM images

PdCu membranes after the Cu electroless plating

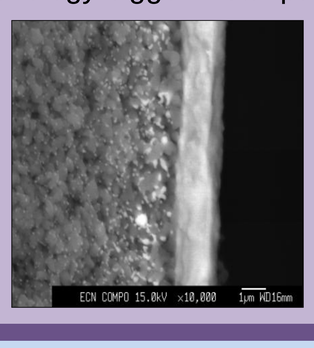
In the image from the left the ceramic support, the Pd metal layer and finally the Cu metal layer can be observed. In the image on the right the surface morphology is shown.

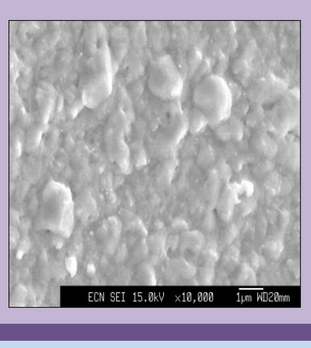




PdCu membranes after the alloying step for PdCu metal mixture

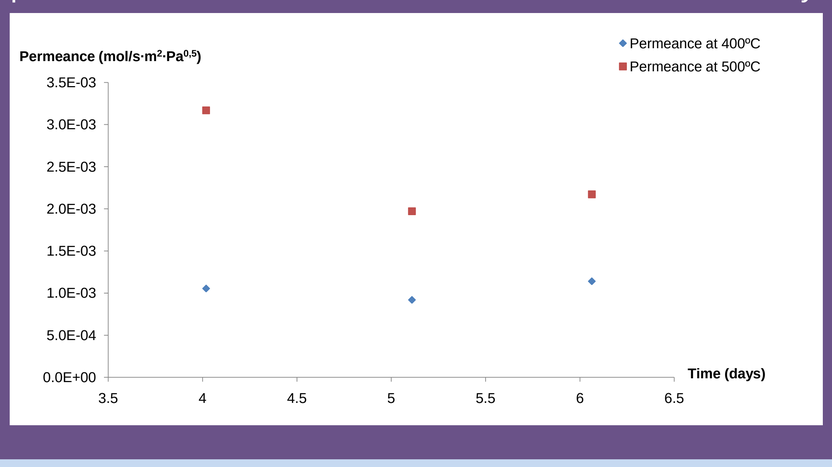
In the image on the left it is still possible to distinguish the Pd-rich and Cu-rich areas. But the permeance changed. In the surface morphology bigger metal particles can be observed.





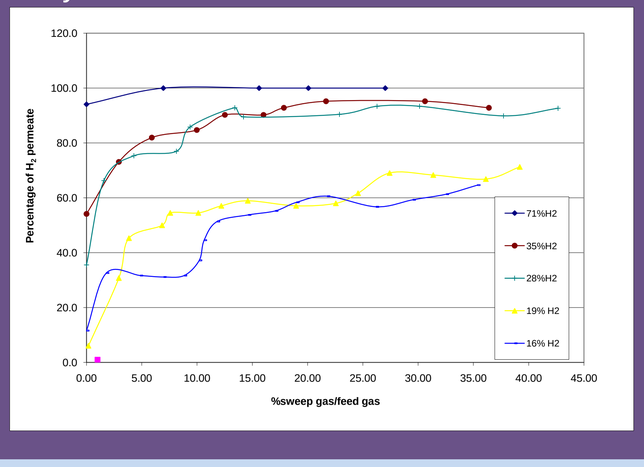
3.2 Hydrogen permeance and temperature cycle

With pure hydrogen flow permeance values at two temperatures were measured. Between the first and the second values the cooling down in inert gas was performed and between the second and the third value in hydrogen.



3.3 Hydrogen dilution effect

Sweep gas flow was varied according to the flow fed to the membrane module. With diluted hydrogen flow the sweep gas flow was very critical for the hydrogen recovery.



4. CONCLUSIONS

The prepared membranes showed high permeance values and good behaviour. Temperature cycles did not affect the permeance of the membranes, even the ones performed in hydrogen atmosphere that are critical for embrittlement due to metal phase transition. With the addition of sweep gas to the membrane module hydrogen recovery from a mixture flow was higher than 60 % even in diluted flows with less than 20 % of hydrogen. The optimal sweep gas flow was around a 15-20 % of the flow fed to the membrane module.

ACKNOWLEDGEMENTS

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