SHEHU, H., ORAKWE, I., ABUNOMAH, O., OGUNLUDE, P., RAMALAN, M., WILLIAMWEST, T., IGBAGARA, W., OGOUN, E., HASHIM, I., AISUENI, F. and GOBINA, E. 2022. Dense metallic membranes for high-density hydrogen production from different feedstocks for PEM fuel cells power generation. In Dincer, I., Ratlamwala, T.A.H. and Kamal, K. (eds.) *Proceedings of the 13th International conference on hydrogen production (ICH2P 2022): hydrogen for a green future*, 11-14 December 2022, [virtual event]. Hosted on ICH2P [online], pages 203-205. Available from: http://www.ich2p.org/wp-content/uploads/2023/01/Conference-Proceedings.pdf

Dense metallic membranes for high-density hydrogen production from different feedstocks for PEM fuel cells power generation.

SHEHU, H., ORAKWE, I., ABUNOMAH, O., OGUNLUDE, P., RAMALAN, M., WILLIAMWEST, T., IGBAGARA, W., OGOUN, E., HASHIM, I., AISUENI, F. and GOBINA, E.

2022

DENSE METALLIC MEMBRANES FOR HIGH-DENSITY HYDROGEN PRODUCTION FROM DIFFERENT FEEDSTOCKS FOR PEM FUEL CELLSPOWER GENERATION

Habiba Shehu[1] *Ifeyinwa Orakwe*[1], *Ofasa Abunomah*[1], *Priscilla Ogunlude*[1], *Muktar Ramalan*[1], *Tamunotonye Williamwest*[1], *Woyintonye Igbagara*[1], *Evans Ogoun*[1], *Idris Hashim*[1], *Florence Aisueni*[1] *and* ***Professor EdwardGobina***[1]*

[1]Centre for Process Integration and Membrane Technology, School of Engineering, Robert Gordon University,Aberdeen AB10 7GJ, UK

*****Corresponding Author: E-mail: e.gobina@rgu.ac.uk; Phone: +44(0)1224262348

ABSTRACT

The International Electrotechnical Commission (**IEC**), through Technical Committee 105 Fuel Cell Technologies, operates to prepare international standards regarding fuel cell technologies for all fuel types and various associated applications such as stationary fuel cell power systems for distributed power generators and combined heat and power systems, fuel cells for transportation such aspropulsion systems, range extenders, auxiliary power units and portable power systems, micro power systems; reverse operating power systems and general electrochemical flow systems and processes. The aim of this research is to develop a more compact design for hydrogen production from a variety of feedstocks to offer a viable means for the supply of high-density hydrogen for polymer electrolyte membrane fuel cells (PEMFC). Importantly, we will present results demonstrating our world-class expertise in membrane development in hydrogen transport through metallic membranes.

Keywords: High-density, hydrogen, metallic, membrane, fuel cell.

INTRODUCTION

The public acceptance of hydrogen as a constituent in energy provision depends on its practical and commercial appeal, and on its safety record of widespread use. The special flammability, buoyancy, and permeability of hydrogen present huge challenges to its safe use that are different from, but not necessarily insurmountable when compared to those of other energy sources. Scientific research is exploring several issues including: (1) hydrodynamics of hydrogen−air mixtures, (2) the combustion ofhydrogen in the presence of other gases, and (3) the embrittlement of materials by exposure to hydrogen, for example carbon steel pipelines and palladium thin film membranes. Key to public acceptance of hydrogen is the development of robust safety standards and practices that are widely known and routinely used—like those for self−service gasoline stations or plug-in electrical appliances.The technical and educational components of the hydrogen economy and transition to net zero need tobe carefully considered. The great potential of the reactions for palladium thin film deposition by micro-and nanofabrication is demonstrated by coating an alumina porous tubular membrane with a uniform Pd film of approximately 6 μm thickness. The as-prepared membrane can for example then be employed in a highly miniaturized flow reactor, using the cracking of ammonia for example, as a modelreaction to incorporate the membranes to supply high-density hydrogen to the PEMFC as shown in Figure 1.

MATERIALS AND METHODS

We present new electroless palladium plating materials and methods including reactions, which can be applied to complex-shaped substrates leading to homogeneous, dense, and conformal palladium films consisting of small nanoparticles. Notably, autocatalytic, and surface-selective metal deposition could be achieved on a very wide range of materials with sensitization and activation pre-treatments

Substrates

Commercially available ceramic supports purchased from Ceramiques Techniques et Industrielles (CTISA) France were used for the study. These supports are tubular in shape and are made majorly of alumina material with a wash-coat of titania. Their actual composition is 77% alumina and 23% TiO_2. and are 45% porosity and have a pore size of 15nm. All chemicals used in the electroless plating werepurchased from Sigma-Aldrich, UK.

Electroless plating

Electroless plating is an autocatalytic nucleation and growth process, so a seed is needed to initiate thereaction. The reactions proceed at mild conditions and are based on easily accessible chemicals (reducing agent: hydrazine; metal source: $PdCl_2$; ligands: ethylenediaminetetraacetic acid (EDTA). Theuniformity of the deposition is improved by a pre-treatment of the porous surface followed by a sensitization and an activation step [**1,2**]. The sensitization of the surface is achieved by immersing theporous samples in a solution containing tin chloride ($SnCl_2$). Tin ions show a big affinity for oxide layersand are easily absorbed to form Sn^{2+} clusters. The Sn^{2+} clusters act as seeds for the formation of Pd nuclei, which initiates the deposition of larger structures. The technique of electroless plating employed here consists in consecutive immersions in three different solutions (Figure 2): (1) a sensitization solution; (b) an activation solution; and (c) a plating solution respectively. The plating solution is composed of $PdCl_2$ (2.1g), $AgNO_3$ (0.7g), NaEDTA (200ml) and 1M N_2H_4 (10ml) as shown in Table 1. The solution was heated up to 60 °C. Hydrazine was used as reducing agent for the electroless experiments because it has the benefits of being suited to palladium deposition, is active in both acidic and alkaline solutions, and does not leave any traces [**3**]. The solution was stirred for 30 min after mixingthe reagents. The substrates were immersed in the plating solution for times varying from 10, 30, 60, 120 and 300 s at 60 °C and immediately after immersion in the activation solution, the samples were then quickly rinsed in DI water to stop the electroless reaction, and dried with nitrogen. Figures 3 and 4show the uncoated and subsequently metallic coated membrane.

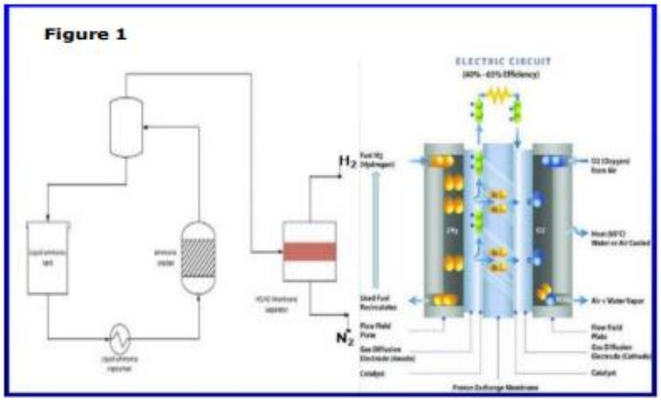


Figure 1

Figure 2: Electroless plating

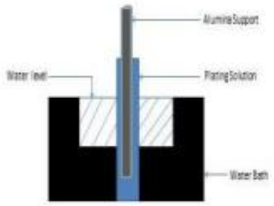
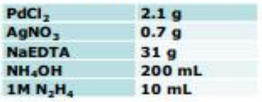


Table 1: Plating bath composition



$PdCl_2$	2.1 g
$AgNO_3$	0.7 g
NaEDTA	31 g
NH_4OH	200 mL
1M N_2H_4	10 mL

Figure 3: Uncoated support

Figure 4: Palladium-coated membrane

RESULTS AND DISCUSSION

He leaks test was carried out after the fabrication of the Pd membrane and the results shown in Figure5 Helium was used to check for any defects or leaks because helium should not permeate a dense palladium membrane. Hence if it is detected in the permeate stream, then it means either the membrane is porous or there is a leak in the seals. The maximum He permeance after deposition of the Pd layer was lower than the 3.13×10^{-6} mol m^{-2} s^{-1} Pa^{-1} which was the maximum permeance for the fresh unmodified alumina support before deposition of the Pd layer. The lower He permeance for the composite Pd membrane indicates that the deposition of the metallic Pd layer was successful. Albeit for a defect free and dense Pd membrane, only H_2 should permeate through when it is dense asconfirmed by adherence of Sievert's Law in Figure 6 and suggests an Arrhenius type dependence of the permeability with temperature against the reciprocal of the absolute temperature and from the slope it can be observed that the temperature dependence on hydrogen permeation follows the Arrhenius- vant Hoff behaviour with a correlation coefficient of 0.9989. The activation energy was calculated fromthe slope as 10.77 kJ/mol and represents the effect of temperature on hydrogen permeation through the membrane. Our observed value agrees with values reported by several authors [**4,5**]. These resultssuggest a solution-diffusion transport of hydrogen in the palladium membrane in which mmolecular hydrogen dissociates at the membrane surface and dissolves into palladium followed by transport through the metallic matrix and then emerges as molecular hydrogen upon re-association. A modifiedmethod for electroless plating was developed which skips the sensitization step during support modification. The maximum hydrogen flux achieved was slightly above 40 cm^3 cm^{-2} s^{-1} using the method compared to the conventional method which involves the 2-step sensitization and activation. In the single-gas hydrogen permeation investigation for the Pd1 membrane, prepared using the conventional electroless plating method, the value of the exponential factor n = 0.5 in accordance withSievert's Law. However, for the mixed-gas hydrogen separation investigation n = 0.62 at 573 K, whichdecreased to 0.55 when the membrane was annealed at 873 K. For the Pd2 membrane, prepared using the modified electroless plating method, n = 1 at 573 K - but the value decreased to 0.76 for themixed-gas hydrogen separation investigation at the same temperature, which depicts a deviation fromSievert's

Law. The susceptibility of the membrane to hydrogen embrittlement when cold hydrogen is allowed to contact its surface is currently being studied. Work is also ongoing to optimize the preparation of the membrane avoiding Tin impurities arising from seeding, reducing the overall time duration of the electroless plating process and preparing palladium membranes of better quality with greater adhesion of the palladium film on the substrate for enhanced hydrogen permeation and durability,

Figure 5: Helium permeance against inlet pressure root of the difference for the Pd1 membrane

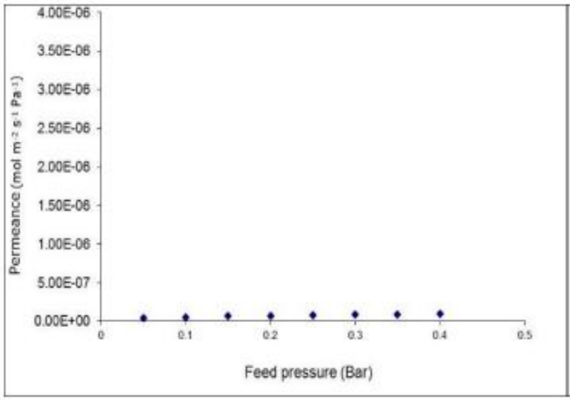
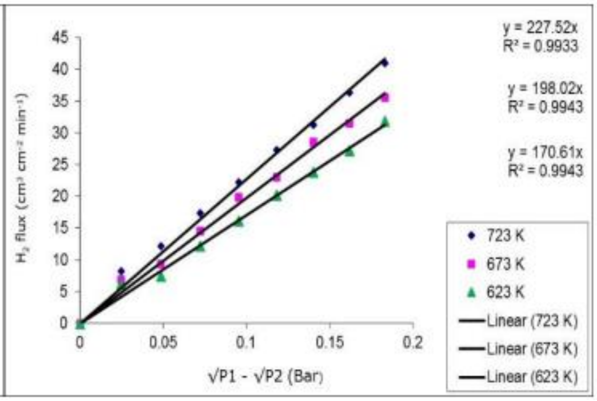


Figure 6: Hydrogen flux against square partial difference of hydrogen across the Pd1 membrane



CONCLUSIONS AND FURTHERWORK

Electroless plating resulted in the deposition of Pd nanoparticles. Under scanning electron microscopicevaluation, the nanoparticles are evenly distributed on the pore walls and on the surface to create a dense layer. As for the thickness of the layer it was around 6 microns. The application of a membrane process for the purification of hydrogen resulting from the cracking of ammonia has been investigated.Mathematical simulations are being conducted for an experimental reactor combining cracking and separation in a single unit to achieve process intensification and further reduce the reactor volume. By shifting the cracking reaction to completion, it is possible to operate at significantly reduced temperatures and pressures and yet attain complete conversion of ammonia.

ACKNOWLEDGEMENTS

The Corresponding Author expresses his profound gratitude to the EPSRC (Grant EP154398) throughthe Network-H2 Program.

REFERENCES

[1] Sard R (1970) The nucleation, growth, and structure of electroless copper deposits J. Electrochem. Soc. 117864–70

[2] Marton J P and Schlesinger M (1968) The nucleation, growth, and structure of thin Ni-P films J. Electrochem. Soc. 115 16

[3] Volpe M, Inguanta R, Piazza S and Sunseri C (2006) Optimized bath for electroless deposition of palladium onamorphous alumina membranes Surf. Coat. Technol. 200 5800–5806

[4] Ilias, S., Su, N., Udo, U.I. & King, F.G. (1997). Application of electroless deposited thin-film palladium compositemembrane in hydrogen separation. *Separation science and technology*. 32, 1-4: 487-504.