

CHAPTER V

CONCLUSION

The dense palladium membranes on porous stainless steel tubes with average pore size of $0.1\mu\text{m}$ were successfully prepared by the electroless plating technique. The thickness of palladium membrane depended on the plating time required until dense palladium membrane was obtained which was evaluated by helium flux measurement. It was found that hydrogen permeation flux increased with increasing exposure temperature but with lower palladium membrane thickness. The selectivity coefficient of both palladium membranes were very high comparing to the one previously reported by other research group, even exposed at high temperature and high pressure difference. In case of Tube 2 which had palladium thickness $2\mu\text{m}$ lower than Tube 1, however, it showed poor selectivity particularly when it was exposed at 450°C and pressure difference of 3 atm. It can thus be concluded that the effective palladium membrane must have the optimum thickness that will allow high hydrogen permeation with high selectivity.

Dry reforming using the palladium membrane tube reactor obviously gave the higher conversion of methane and carbon dioxide than the one using the conventional tube reactor at the same condition. Other factors influencing the methane and carbon dioxide conversion in palladium membrane tube reactor included the reaction temperature, the feed flow rate in the shell side, and the sweep gas flow rate in the tube side. These reactions were operated at temperature $350\text{-}450^\circ\text{C}$ to prevent the damage of the palladium membrane tube. In a separated experiment using another palladium membrane tube with $18\mu\text{m}$ palladium layer thickness and high selectivity coefficient, its hydrogen permeation flux increased with increasing reaction temperature upto 450°C , then it decrease at 500°C . Such a decrease was attributed to the metal diffusion from porous stainless steel tube to palladium membrane which was evidenced by its SEM micrograph and EDS mapping scans for iron, nickel, and chromium of the tube cross-section. Several kinds of materials for preventing this intermetallic diffusion were attempted unsuccessfully. Finally, it was found that chromium oxide layer, developed by oxidation of chromium layer plated by electroplating technique before palladium plating, could inhibit the intermetallic

diffusion. However, the optimum thickness of chromium layer must be controlled so that all chromium could be oxidized completely to chromium oxide. When chromium layer thickness was more than $3.5\mu\text{m}$, unoxidized chromium would be able to diffuse into palladium layer. In the intermetallic diffusion prevention study, hydrazine hydrate must be used due to the unavailability of dehydrated hydrazine. This caused the thicker palladium layer due to coarser morphology of palladium during deposition. However, the third dense palladium membrane tube with very high selectivity was obtained. Due to the chromium oxide layer and higher palladium layer thickness, lower hydrogen permeation flux was measured comparing to the performance of Tube 1. Interestingly, hydrogen permeation flux kept increasing at higher exposure temperature including at 500°C . This observation, together with the EDS mapping scan study of the palladium membrane disk could possibly be concluded that containing chromium oxide layer, chromium oxide was the suitable intermetallic diffusion barrier.

5.1 Further works

1. Palladium plating using hydrazine hydrate

Since anhydrous hydrazine was not available here, hydrazine hydrate must be used. However, coarser morphology of palladium was obtained which affected the hydrogen permeation. Hydrazine hydrate should be treated before use, for example, with sodium hydroxide. Some factors must be considered for obtaining the proper morphology of palladium.

2. Observing the working life time of palladium membrane containing the Cr_2O_3 layer at 500°C or higher should be observed.