DEVELOPMENT OF A DEVICE TO MEASURE HYDROGEN CONCENTRATION IN THE PRESENCE OF MOIST CHLORINE: INFLUENCE OF A NOVEL MEMBRANE

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ABSTRACT

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Recently, an amperometric sensor attached with a hydrogen-selective membrane made of epoxy vinyl ester based resin, Derakane® 470-300, coated on a Teflon® sheet, has been proposed to measure hydrogen concentration in the presence of moist chlorine. The response of the sensor is not satisfactory. The Derakane® layer gives a slow response time, and the brittleness of the resin makes the thin membrane easy to crack. The cracking allows Cl_2 to get into the sensor and nullifies the principle of the sensor. As a result, a sandwich membrane having an active layer less than 0.10 mm thick between two sheets of Teflon® was introduced in this study. It was believed that the sandwich technique would enhance transmembrane flux and physical strength of the membrane. However, no research has been carried out on the ability of the thin-active-layer membrane to withstand chlorine. Thus, sandwich membranes of two types of Derakane® resin; 470-300 and 8084 were prepared. The H_2 and Cl_2 permeability coefficients of the membranes in H_2-Ar atmosphere and Cl_2 atmosphere at 25, 50 and 80°C were determined. Mixed gas experiments were carried out at 80°C to determine the effect of the presence of chlorine on the permeation of hydrogen through the membrane. The selectivity was calculated by the permeability ratio of hydrogen and chlorine. From the experimental results, both types of membrane allow chlorine to pass through but Derakane® 8084 showed higher selectivity for hydrogen than Derakane® 470-300 in the range of temperature studied. A decrease in hydrogen and chlorine permeability coefficients was found in the experiment of 5% H_2 and 95% Cl_2 mixed gas system. The permeability coefficient of hydrogen is lower in 5%H_2/Cl_2 than in the mixed gas containing 1% H_2 whereas the chlorine permeability coefficient is higher.

บทคัดย่อ

สุชาดา ภัสสรารัตน์ : การศึกษาเยื่อเลือกผ่านสำหรับอุปกรณ์ในการวัดความเข้มข้นของก๊าซไฮโดรเจนในก๊าซคลอรีนชื้น (Development of A Device to Measure Hydrogen Concentration in The Presence of Moist Chlorine : Influence of A Novel Membrane) อ.ที่ปรึกษา : ศ. ดร. แฟรงค์ อาร์ สจ๊วร์ต (Prof. Dr. Frank R. Steward) และ ผศ. ดร. ธีรศักดิ์ ฤกษ์สมบูรณ์ 62 หน้า ISBN 974-03-1590-9

เยื่อเลือกผ่านทำด้วย เดราเคนเคลือบบนแผ่นเทฟลอน ได้นำมาติดตั้งในอุปกรณ์ในการวัดปริมาณก๊าซไฮโดรเจนในก๊าซคลอรีนชื้น แต่การตอบสนองของอุปกรณ์ไม่เป็นที่น่าพอใจ เนื่องจากเดราเคนชะลอการตอบสนองของอุปกรณ์ และยังแตกง่ายทำให้ก๊าซคลอรีนแพร่เข้าไปภายในเซนเซอร์ได้ ทำความเสียหายให้แก่กระบวนการวัดปริมาณก๊าซไฮโดรเจน ดังนั้นโครงการนี้จึงได้เลือกศึกษา เยื่อเลือกผ่านที่มีลักษณะเป็นแซนด์วิชมีเดราเคนความหนาน้อยกว่า 0.10 มม. อยู่ระหว่างแผ่นเทฟลอน 2 แผ่น ปริมาณก๊าซไฮโดรเจนที่ผ่านเยื่อเลือกผ่านชนิดนี้จะมากกว่าชนิดเคลือบ อย่างไรก็ตามยังไม่มีการศึกษาความสามารถในการต้านทานก๊าซคลอรีนของเยื่อเลือกผ่านชนิดนี้

ในโครงการศึกษานี้ ได้ทำการทดสอบหาความสามารถในการแพร่ผ่านของก๊าซไฮโดรเจนและคลอรีนผ่านเยื่อเลือกผ่านที่มีลักษณะแบบแซนด์วิชซึ่งทำด้วย เดราเคน 2 ชนิดคือ เดราเคน 470-300 และ เดราเคน 8084 ที่อุณหภูมิ 25, 50 และ 80 องศาเซลเซียส รวมทั้งได้ทดสอบด้วยก๊าซผสมระหว่างไฮโดรเจนและคลอรีนที่มีปริมาณก๊าซไฮโดรเจน 1% และ 5% ที่อุณหภูมิ 80 องศาเซลเซียส เพื่อศึกษาการแทรกผ่านของก๊าซไฮโดรเจนในก๊าซคลอรีน จากการศึกษาพบว่าก๊าซคลอรีนสามารถแพร่ผ่านเยื่อเลือกผ่านแบบแซนด์วิชทั้งสองชนิดได้ โดยเยื่อเลือกผ่านที่ทำด้วยเดราเคน 8084 มีอัตราการเลือกผ่านก๊าซไฮโดรเจนมากกว่า และอุณหภูมิมีผลกระทบต่ออัตราการเลือกผ่านของเยื่อเลือกผ่านเดราเคน 8084 มากกว่าของเดราเคน 470-300 ความสามารถในการแพร่ผ่านของทั้งก๊าซไฮโดรเจนและคลอรีนกับเยื่อเลือกผ่านเดราเคน 8084 น้อยลงเมื่อทดลองกับก๊าซผสม อีกทั้งยังพบว่า ความสามารถในการแพร่ผ่านของก๊าซไฮโดรเจนเมื่อก๊าซผสมมีปริมาณไฮโดรเจน 1% มากกว่าเมื่อใช้ก๊าซผสมมีปริมาณไฮโดรเจน 5% แต่ความสามารถในการแพร่ผ่านของก๊าซคลอรีนจะมากกว่าเมื่อก๊าซผสมมีปริมาณก๊าซไฮโดรเจนมากกว่า

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LIST OF SYMBOLS

α_ι	Selectivity
ρ	Electrical resistivity of the single phase Pd/H solid solution
ρ_H	Resistivity due to hydrogen atoms
ρ_l	Resistivity due to lattice vibration
ΔH_S	Heat of solution of the penetrant in the polymer
Δp	Partial pressure difference of permeant i on either side of membrane
A	Cross sectional area to flow, m^2
A	Area of the contacted test material, m^2
	assumed volume Volume of gas that is used to generate the calibrations, equals to 100 mL for Kitagawa detector tube
c_i	Gas concentrations on interface i, mol m^{-3}
C_i	Concentration of hydrogen at time T_i, $\mu g\ m^{-3}$
D	Diffusion coefficient, $m^2\ s^{-1}$
D_0	Pre-exponential factor
E_D	Activation energy for diffusion, J mol^{-1}
E_P	Activation energy for permeation, J mol^{-1}
F	Faraday's constant
F	Flow rate of fresh argon through the test cell, $m^3\ min^{-1}$
J	Flux of gas transporting through membrane, mol $m^{-2}\ sec^{-1}$
k	Linear function of reciprocal absolute temperature
$K_g(T)$	Equilibrium constant
l	Thickness of material, m.
l_T	Total thickness

Lj	Thickness of material j, m
n	Number of electrons per mole
perm.	Absolute amount of permeant at any one time, mg
P_{H2}	Permeability of hydrogen in membrane material
P_{H2}	Hydrogen pressure (atm)
p_i	Gas partial pressures on interface i, Pa
$P_i(T_i)$	Permeation rate, $\mu g\ m^{-2}\ min^{-1}$
$P_{i,j}$	Permeation rate of permeant i through material j, $\frac{mol}{sec}$
R	Gas constant
$\overline{R}(T, x_H)$	Resistance ratio of a palladium wire
R_i	Resistance to the gas transfer for layer i
S	Solubility constant
S_0	Pre-exponential constant
T	Absolute temperature
T_i	Time at which concentration of hydrogen in collection gas was C_i, min
x_H	Atom ratio of hydrogen in palladium
z	Number of moles of electrons involved in electrochemical reaction