

**DEVELOPMENT OF A SENSOR FOR MONITORING HYDROGEN
IN HUMID CHLORINE GAS:
SELECTION OF SHEATHING MATERIALS**

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ABSTRACT

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The monitoring of hydrogen in the electrolysis cell gas is important in a chlor-alkali plant. An increase in hydrogen concentration in the chlorine gas indicates a lower efficiency in operation of the electrolytic cell. The explosion limit for hydrogen is 6% which can occur in the chlorine liquefaction section of the plant. It is undesirable to permit access of the chlorine to the sensor that catalyzes the reaction between hydrogen and chlorine. Such a reaction would clearly alter the detection of hydrogen and nullify the principle of the sensor. Thus, an acceptable sheathing material is required. Various materials have been tested at 80°C with a 5% hydrogen gas mixture in dry chlorine gas to determine the permeability coefficients of hydrogen and chlorine. One of the criteria of the acceptable sheathing material is expected to have the ratio of the hydrogen to chlorine permeability coefficients of more than 10 000. In the present study, epoxy vinyl ester resin is currently a most acceptable sheathing material since it has no Breakthrough Time of chlorine in 160 hours.

บทคัดย่อ

กิตติมา จำสอางค์: การศึกษาหาวัสดุที่มีคุณสมบัติที่เหมาะสมที่จะนำไปเคลือบลงบนเครื่องมือที่ใช้วัดความเข้มข้นของก๊าซไฮโดรเจนในก๊าซคลอรีนอย่างชื้น (Development of a Sensor for Monitoring Hydrogen in Humid Chlorine Gas: Selection of Sheathing Materials) อ. ที่ปรึกษา : ศ.ดร. แฟรงค์ อาร์ สจิวรด และ ผศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ 82 หน้า ISBN 974-13-0687-3

โรงงานคลอรีนอัลคาไลมีความจำเป็นที่จะต้องทำการตรวจวัดปริมาณความเข้มข้นของก๊าซไฮโดรเจน เนื่องจากอัตราการเพิ่มขึ้นของไฮโดรเจนในก๊าซที่เป็นส่วนผสมระหว่างไฮโดรเจนและคลอรีน บ่งชี้ถึงประสิทธิภาพการทำงานที่ลดต่ำลงของอิเล็กโทรไลซิสเซลล์ ซึ่งมีผลต่อความปลอดภัยของโรงงาน ทั้งนี้หากความเข้มข้นของไฮโดรเจนเพิ่มขึ้นเกินกว่า 6% ซึ่งเป็นค่าความเข้มข้นที่ต่ำที่สุดของไฮโดรเจนในคลอรีน อาจก่อให้เกิดการระเบิดขึ้นในโรงงานได้ นอกจากนี้ก่อนทำการตรวจวัดความเข้มข้นของไฮโดรเจน จะต้องทำการแยกก๊าซไฮโดรเจนออกจากคลอรีน เนื่องจากก๊าซคลอรีนจะทำปฏิกิริยากับก๊าซไฮโดรเจนในเครื่องวัด ซึ่งส่งผลให้เครื่องวัดแสดงค่าที่ผิดพลาดของค่าความเข้มข้นของไฮโดรเจน จึงมีการศึกษาเพื่อค้นหาวัสดุเพื่อนำมาเคลือบลงบนเครื่องวัดที่จะทำให้ไฮโดรเจนแทรกผ่านแต่ในขณะเดียวกันก็สามารถป้องกันคลอรีนไม่ให้ผ่านเข้าไปยังเครื่องวัดได้ โดยมีเกณฑ์ว่าวัสดุประเภทนี้จะต้องมีอัตราการให้ไฮโดรเจนแทรกผ่านสูงกว่าคลอรีนประมาณ 10 000 เท่า ในการศึกษานี้ได้ทำการทดลองวัสดุประเภทต่างๆ ได้แก่ สารละลายฟลูออโรดิน ฟลูออโรดินคอลลอยด์ อีพอกซีไวนิลเอสเทอร์เรซินและแผ่นฟลูออโรดินสำเร็จรูปซึ่งมีความหนา 0.7 มิลลิเมตร โดยวัสดุสามชนิดแรกจะต้องทำการเคลือบลงบนแผ่นเทฟลอนหนา 0.15 มิลลิเมตร ก่อนที่จะนำวัสดุทั้งหมดไปทำการทดลองหาอัตราการแทรกผ่านของไฮโดรเจนและคลอรีนที่อุณหภูมิ 80 องศาเซลเซียส โดยใช้ก๊าซที่ประกอบด้วยไฮโดรเจน 5% และก๊าซคลอรีนบริสุทธิ์ตามลำดับ จากผลการทดลอง สามารถสรุปได้ว่าวัสดุประเภทอีพอกซีไวนิลเอสเทอร์เรซินเป็นวัสดุที่มีคุณสมบัติเหมาะสมที่จะนำไปเคลือบลงบนเครื่องตรวจวัดค่าความเข้มข้นของไฮโดรเจนมากที่สุด เนื่องจากสามารถสกัดกั้นคลอรีนไม่ให้แทรกผ่านเนื้อวัสดุไว้ได้ภายในระยะเวลา 160 ชั่วโมง

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ABBREVIATIONS

ASTM	American Standard Test Method
B/T	Breakthrough Time
GC	Gas Chromatograph
Gr	Graphite disc
Pd	Palladium
PFSA	Perfluorosulfonic acid
Pt	Platinum black
SS	Stainless steel

LIST OF SYMBOLS

ϕ	Permeability coefficient, $\text{mol m}^{-1} \text{Pa}^{-1} \text{s}^{-1}$
ρ	Electrical resistivity of the single phase Pd/H solid solution
ΔH	Enthalpy change of reaction
α_H	Empirical deviation from ideality as $x_H \rightarrow 0$, $a_H \rightarrow x_H$ according to Sievert's law
ρ_H	Resistivity due to hydrogen atoms
ϕ_{H_2}	Permeability coefficient of hydrogen in membrane material
ϕ_i	Permeability coefficient of permeant i in the material, $\frac{\text{mol}}{\text{m Pa sec}}$
β_{jn}	Eigen value
ρ_l	Resistivity due to lattice vibration
Δp_i	Partial pressure difference of permeant i on either side of
ϕ_T	Total permeability coefficient in multi-layer materials
A	Cross sectional area to flow, m^2
a	Activity of the indicated species
a_H	Activity at the atom ratio x_H in the single phase Pd/H solution
$a_{H_3O^+}$	Activity of water in the polymer electrolyte
a_i	Activity of the indicated species i
A_T	Test cell exposed area
C_1, C_2	Concentrations of hydrogen dissolved in membrane at each side of interfaces
C_{A1}	Hydrogen concentration in Teflon
C_{A2}	Hydrogen concentration in water
C_b	Tube calibration concentrations as scale unit on the tube, ppm
C_{Hi}	Concentration of hydrogen at time t_i , $\mu\text{g m}^{-3}$
C_i	Gas concentrations on interface i, mol m^{-3}
D	Diffusion coefficient, $\text{m}^2 \text{s}^{-1}$

D_0	Pre-exponential factor
D_1	Diffusion coefficient of hydrogen in Teflon at 25°C
D_2	Diffusion coefficient of hydrogen in water at 25°C
E	Theoretical decomposition voltage
E^0	Half-cell potential, given by Nernst equation
E_A	Activation energy
F	Faraday's constant
F_{Ar}	Flow rate of fresh argon through the test cell, $m^3 \text{ min}^{-1}$
$F_j(x)$	Expanded function in an infinite series of eigenfunctions at $t=0$
H	Henry's Constant of hydrogen dissolved in water at 25°C
J	Electrical equivalent of heat
K	Constant equals to S multiplied by H
k	Linear function of reciprocal absolute temperature
$K_g(T)$	Equilibrium constant of chemical reaction involving hydrogen gas and palladium metal
L	Thickness of material, m
L_i	Thickness of layer i in multi-layer materials
L_T	Total thickness of material
M	Net chemical changes
n	Number of equivalents involved
N	Rate of gas diffusion through solids
p_1, p_2	Gas partial pressure on either side of interfaces, Pa
P_{H_2}	Rate of hydrogen permeation
p_{H_2}	Pressure of hydrogen in gas, atm
p_i	Gas partial pressures on interface i , Pa
P_i	Permeation rate of permeant i through material, $\frac{mol}{sec}$
$P_i(t_i)$	Permeation rate, $\mu g \text{ m}^{-2} \text{ min}^{-1}$

P_M	Absolute amount of permeant at any one time, mg
Q	Molar flow rate of permeant, mol s ⁻¹
Q_C	Total charge passed through the electrode during the experiment
R	Gas constant
$\bar{R}(T, x_H)$	Resistance ratio of a palladium wire
R_i	Resistance to the gas transfer for layer i
S	Solubility constant
S_{H_2}	Solubility of H ₂ in Teflon at 25°C
T	Absolute temperature, K
T_C	Critical temperature
t_i	Time at which concentration of hydrogen in collection gas was C_{Hi} , min
V_a	Volume of gas that is used to generate the calibrations
$w(x)$	Sturm-Liouville weighting function for the cartesian co-ordinate system
W_j	Discontinuous-weighting function
x_H	Atom ratio of hydrogen in palladium
X_{jn}	Eigenfunction in cartesian co-ordinate system
z	Number of moles of electrons involved in electrochemical reaction