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Investigation of hydrogen production method using sulfur dioxide

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Hybrid Sulfur (HyS) Process

- HyS process is a type of thermochemical hydrogen production.
- Sulfur compounds (SO_2) are circulated within the system to generate hydrogen.
- Unlike halide-based processes, hydrogen can be produced without halogen reactants.
- Hydrogen production is possible at about 1/7 of the theoretical water electrolysis voltage (1.23 V).[1]

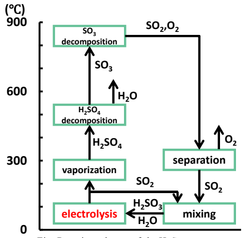

Fig. Reaction scheme of the HyS process.

HyS Process – SO_2 depolarized electrolysis (SDE reaction)

- By separating the electrodes with a cation exchange membrane, the reaction can proceed efficiently.[2]
- Since ~90% of the total process energy is consumed in this electrochemical step,[2] reducing overvoltage is crucial for improving overall efficiency.

$$\text{Cathode}: 2H^+ + 2e^- \rightarrow H_2$$
$$\text{Anode}: H_2SO_3 + H_2O \rightarrow 2H^+ + H_2SO_4 + 2e^-$$
$$\text{Net reaction}: H_2SO_3 + H_2O \rightarrow H_2 + H_2SO_4$$

Theoretical cell voltage：**0.157 V**

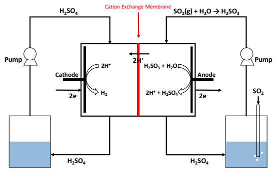

Fig. Experimental setup.

Table. Experimental conditions

Anolyte	1.5 M H_2SO_4, N_2 gas
N_2 gas flow rate	300 mL/min
Catholyte	1.5 M H_2SO_4
Pump flow rate	6000 mL/h

Problem

➢ **Together with H_2O, SO_2 permeates to the cathode side.**
-Sulfur deposition occurs on the cathode electrode.
-Leads to decreased electrolysis efficiency.

Objective

➢ **Reduction of overvoltage in the electrochemical oxidation reaction of the HyS process.**

-Fabrication of cation exchange membranes

Previous studies[3]

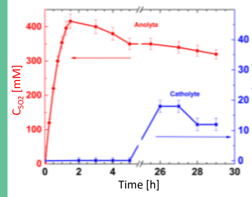

Fig. Time variation of SO_2 concentration in anolyte and catholyte.

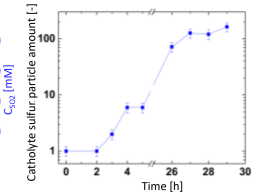

Fig. Time variation of sulfur particle content in catholyte.

- Transfer of SO_2-containing species together with H_2O from the anolyte to the catholyte has been reported.
- Deposition of sulfur (S) and hydrogen sulfide (H_2S) on the cathode surface has also been reported.

Membrane fabrication procedure

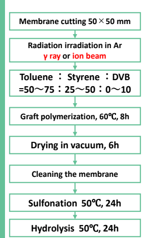

Fig. Membrane fabrication.

Substrate

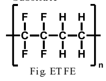

Fig. ETFE

Monomer / Crosslinker

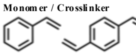

Fig. (left) Styrene (right) Divinylbenzene (DVB)

Fig. ETFE膜 (left) asmade (right) Crosslinked membrane

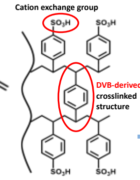

Fig. Structure of the cation exchange membrane (CEM)

Radiation-induced graft polymerization[4]

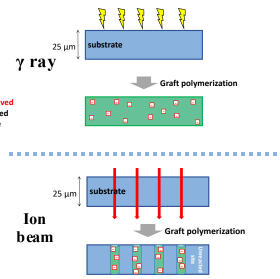

Fig. Schematic illustration of radiation-induced graft polymerization.

- Crosslinking can suppress the permeation of H_2O and SO_2.
- Ion exchange group density can be controlled over a wide range.

Items Investigated

- Effect of cation exchange membrane on ohmic overvoltage
- Influence of electrode catalyst and temperature on electrochemical oxidation

Ion exchange capacity：IEC

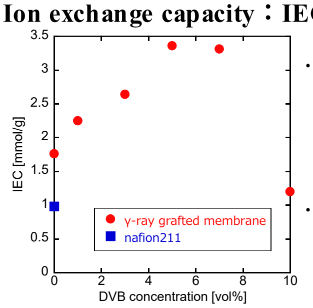

Fig. Relationship between membrane IEC and DVB concentration in the monomer solution.

- IEC is an indicator of the number of ions that a membrane can adsorb, determined by titration.

$$\mathrm{IEC}\,[\mathrm{mmol\,g^{-1}}] = \frac{0.01 \times V_{NaOH}}{W_d}$$

W_d: Membrane weight after sulfonation [g]

- Grafting time: 8 h, total monomer concentration (St + DVB) = 50%At a DVB concentration of 10%, IEC decreased significantly. →This is attributed to DVB reacting with radicals more rapidly than St, leading to polymerization and crosslinking structures that suppressed St polymerization.

IEC varied from 1.0 to 3.3 mmol/g depending on the DVB concentration in the monomer solution, with the grafting time fixed at 8 h and the total monomer concentration at 50%.

SDE reaction – ohmic overvoltage (without catalyst)

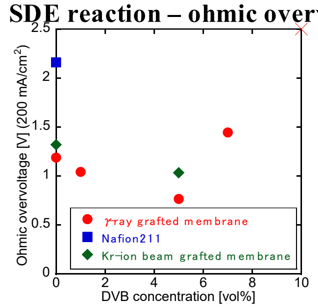

Fig. Relationship between DVB concentration and ohmic overvoltage

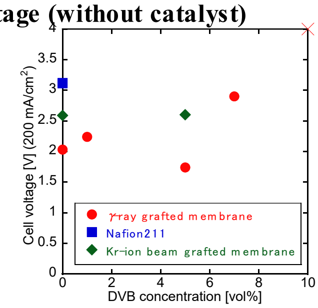

Fig. Relationship between DVB concentration and cell voltage

The lowest ohmic overvoltage was observed at a DVB concentration of 5 vol% (200 mA/cm²: 0.76 V, 1.03 V).Cell voltage ranged from 1.74 to 5.38 V regardless of IEC.

SDE reaction – Effect of temperature

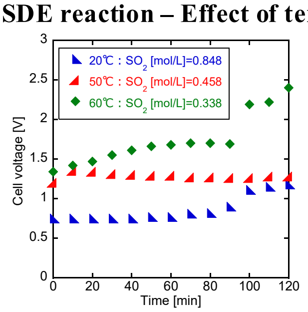

Fig. Relationship between cell voltage and time at 100 mA/cm²

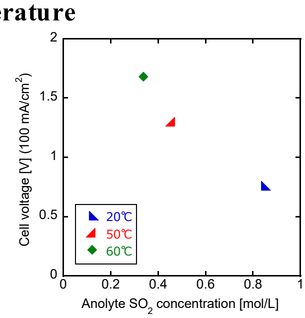

Fig. Relationship between SO_2 solubility and cell voltage at different temperatures

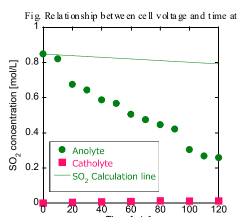

Fig. Relationship between solution concentration and electrolysis time at 20℃

Increasing the solution temperature led to higher cell voltages after 60 min: 20°C : 0.76 V, 50°C : 1.30 V, 60°C : 1.68 V.

SDE reaction – Effect of Pt/C catalyst

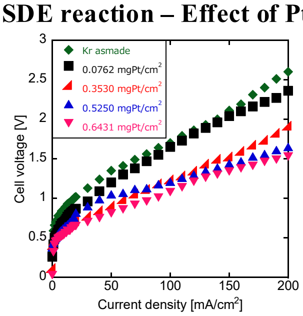

Fig. Relationship between current density and cell voltage

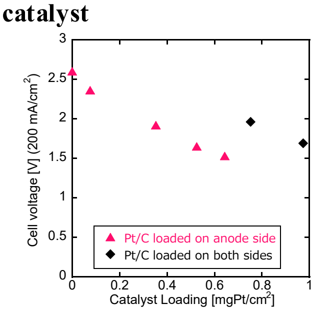

Fig. Relationship between catalyst loading and cell voltage

When a Kr-beam-grafted membrane was loaded with 0.6431 mgPt/cm² of Pt/C on one side, the lowest cell voltage of 1.57 V was observed at 200 mA/cm².

Conclusion

1) L.E. Brecher et al., Int. J. Hydrogen Energy, 2, 1, (1977), 7-15
2) 河村ら, "硫黄サイクルハイブリッド法による水素製造", 75, (2007)
3) Tulskiy, G., et al. (2016). Electrochemical Energy Technology, 2(1). 13-16
4) Shin-ichi Sawada et al., International Journal of Hydrogen Energy, 45, (2020), 13814-13820

- With grafting time fixed at 8 h and total monomer concentration at 50%, IEC varied from 1.0 to 3.3 mmol/g depending on DVB concentration.
- Increasing the solution temperature led to higher cell voltages at 100 mA/cm² and 60 min: 20°C : 0.76 V, 50°C : 1.30 V, 60°C : 1.68 V.
- Using a Kr-beam-grafted membrane loaded with Pt/C catalyst resulted in a cell voltage of 1.57 V at 200 mA/cm².