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Improvement of the Thermal Efficiency of Hydrogen Iodine Concentration in I-S Process by Using Radiation-grafted Membrane in Electrolysis System

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Presentation Outline

1. Efficiency problem of I-S process

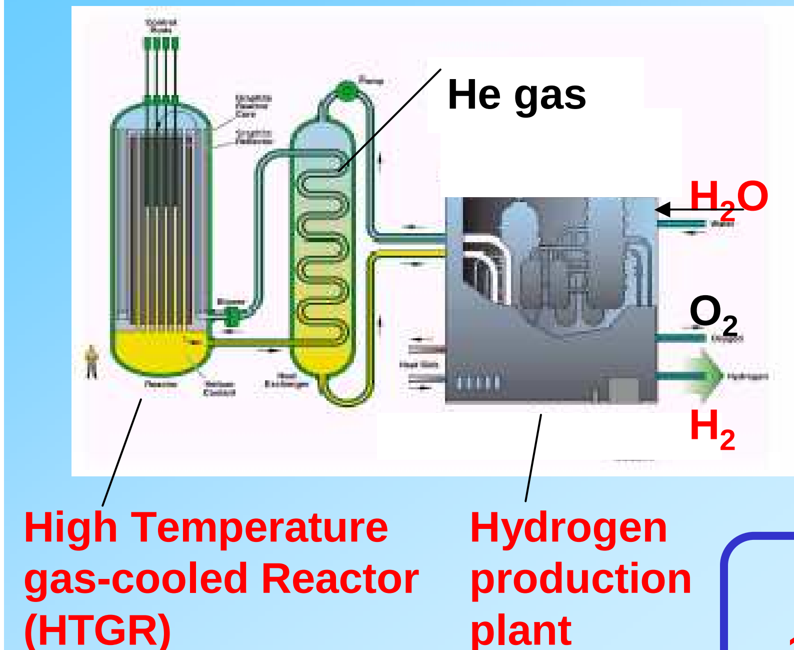
2. Concept of Iodine electrolysis

3. Application of Radiation-grafted membrane

4. Experiment of HI concentration

5. Summary

Thermochemical water-splitting I-S process



Thermochemical water-splitting I-S process has been studied as the next generation large-scale hydrogen production method using nuclear reactor.

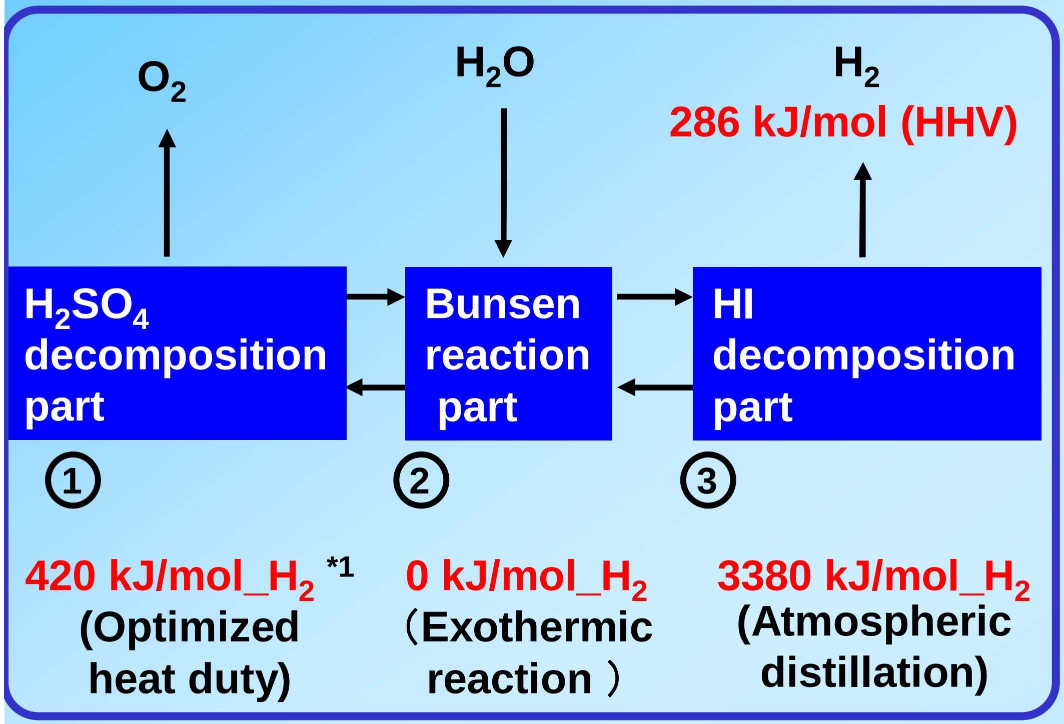
Research issue of I-S process

1. Process efficiency
→ in this presentation

2. Material problem
We have to develop the acid resistant material, because I-S process uses H_2SO_4 and HI at high temperature.
→we are developing glass lining or ceramic component such as SiC.

Hydrogen production efficiency by I-S process

The I-S process has **three separate parts**.



Three parts of I-S process and **the required heat duty** by each part (1mol per production Hydrogen)

HI-H_2O azeotrope forbids the separation of pure HI.

In the case of atmospheric distillation, heat duty may reach 3380 kJ/mol to evaporate H_2O.

Hydrogen production efficiency

$$\eta = \frac{\text{(The heating value of } H_2\text{)}}{\text{(Total consumed heat)}}$$

=286 / (420+0+3380) = **7.5 %**

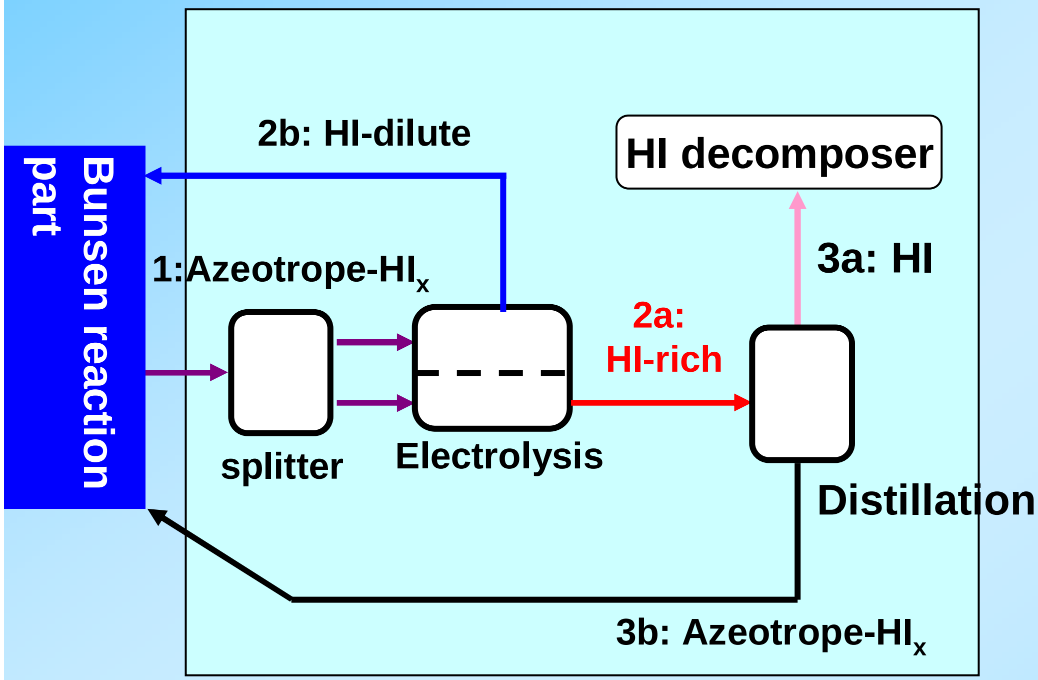
reduce ↓ 295 ～ (380) ↓ **40%(Our target value)** ～ (35%)

We must reduce the heat duty on HI decomposition part from 3380 to 300 ～400 kJ/mol.

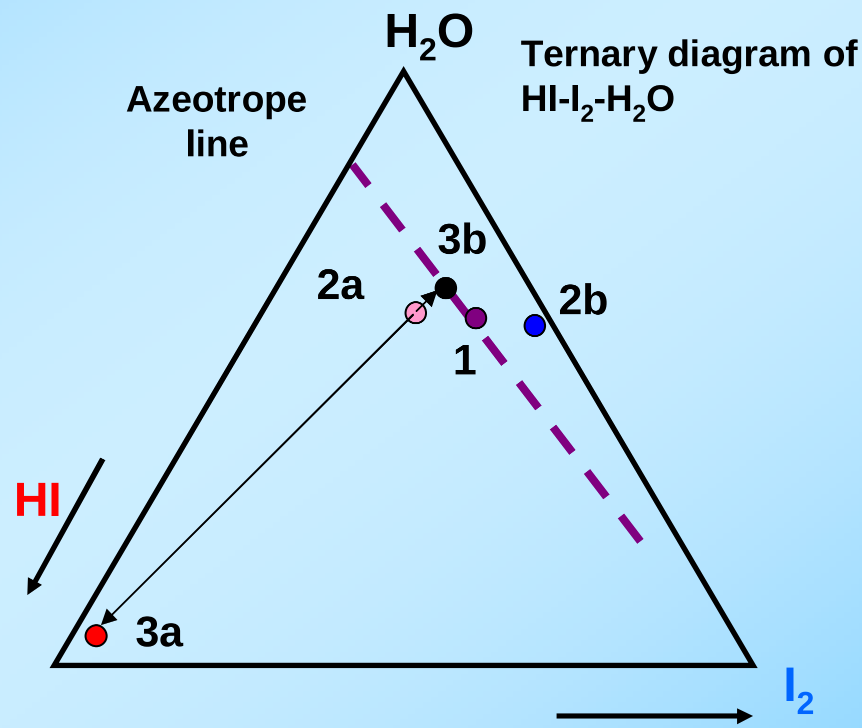
*1 S. Goldstein et al., I. J. Hydrogen Energy 619-626 30 (2005)

Breaking azeotrope

Traditional approach to break azeotrope
1. Extractive distillation
2. Reactive distillation
3. Electrolysis method ← our proposal



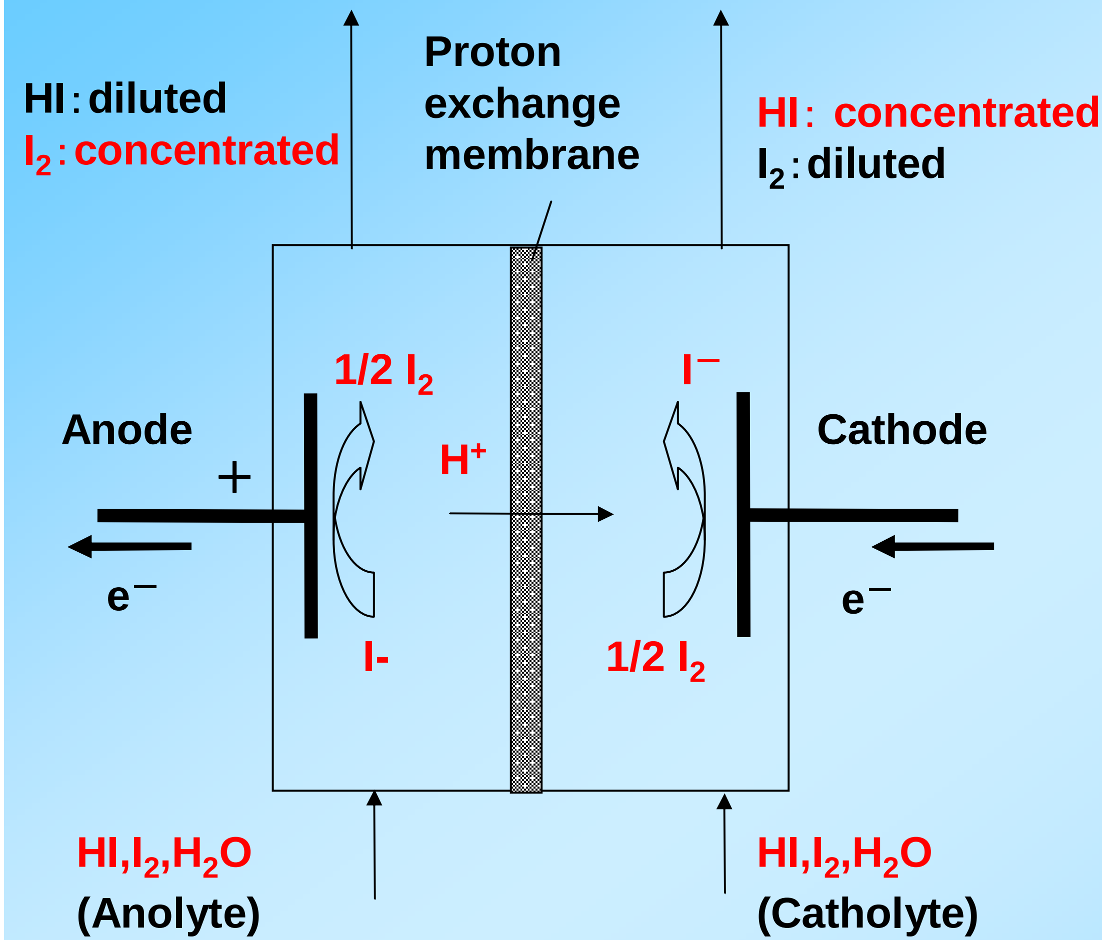
- Put electrolysis in front of HI distillation.
- The HI-I_2-H_2O solution (HIx solution) from the Bunsen reaction part is divided into two flows.
- HI is concentrated in one flow and diluted in the other.
- The HI rich solution is fed to the distillation column.
- We can obtain pure HI at the top.
- Azeotropic HIx solution is separated at the bottom.



- 1: Bunsen outlet
- 2a: HI-rich → Feed of distillation
- 2b: HI-dilute → Bunsen part
- 3a: Top of distillation
- 3b: Bottom of distillation → Bunsen part

HI solution can go across azeotrope line by "Electric power" and main separation is assumed distillation.

Concept of HI concentration by iodine electrolysis



Concept of HI concentration by iodine electrolysis

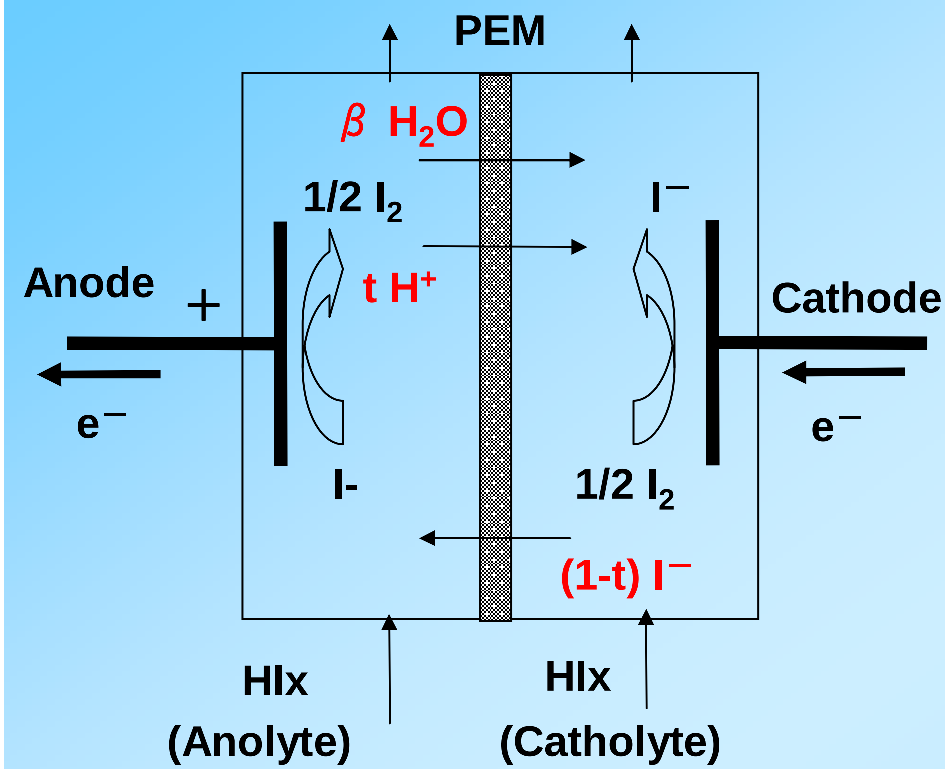
- The HIx solutions are separated by PEM.
- On the anode, I^- is oxidized to I_2
  $I^- + H^+ \rightarrow 1/2\ I_2 + e^-$
- On the cathode, I_2 is reduced to I^-
  $1/2\ I_2 + e^- \rightarrow I^- + H^+$
- Proton (H^+) permeates through the membrane.

↓

HI is concentrated and I_2 is diluted at the catholyte.

While reverse change occurs at the anolyte.

Proton transport number and water permeation coefficient



Concept of HI concentration when considering (t, β).

At the anode

$I^- + tH^+ + \beta H_2O \rightarrow 1/2\, I_2 + e^- + (1-t)I^-$

$tI^- + tH^+ + \beta H_2O \rightarrow 1/2\, I_2 + e^-$

$t(HI) + \beta H_2O \rightarrow 1/2\, I_2 + e^-$

At the cathode

$1/2\, I_2 + e^- + (1-t)I^- \rightarrow I^- + tH^+ + \beta H_2O$

$1/2\, I_2 + e^- \rightarrow tI^- + tH^+ + \beta H_2O$

$1/2\, I_2 + e^- \rightarrow t(HI) + \beta H_2O$

Practically, two important parameters must be taken into account.

1. Proton transport number

I^- permeate through the membrane.

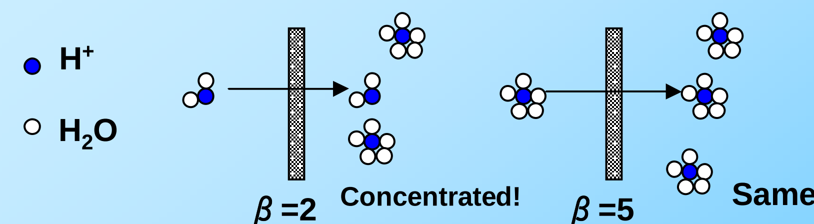
$$t = \frac{H^+}{H^+ + I^-}$$

2. Water permeation coefficient

Water permeates through the membrane together with H^+ .

$H^+:H_2O = 1:\beta$

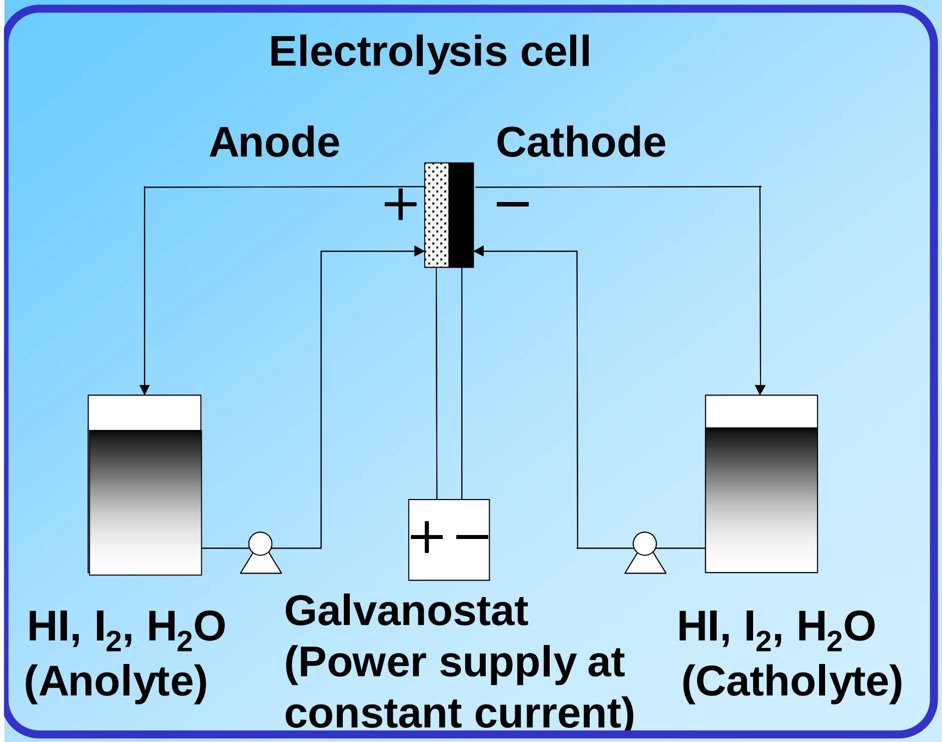
($H^+:H_2O = 1:5$ at azeotrope composition)



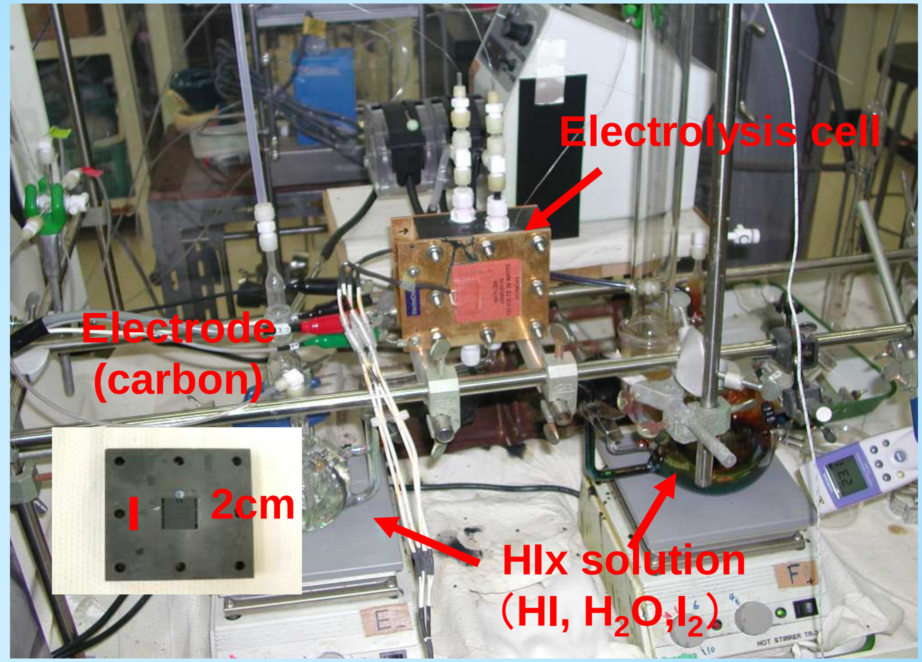
The less I^- and H_2O permeate, the more HI concentrate.

The value of (t, β) is essential to evaluate the efficiency of electrolysis.

HI concentration Experiment



Schematic diagram of HI concentration experiment

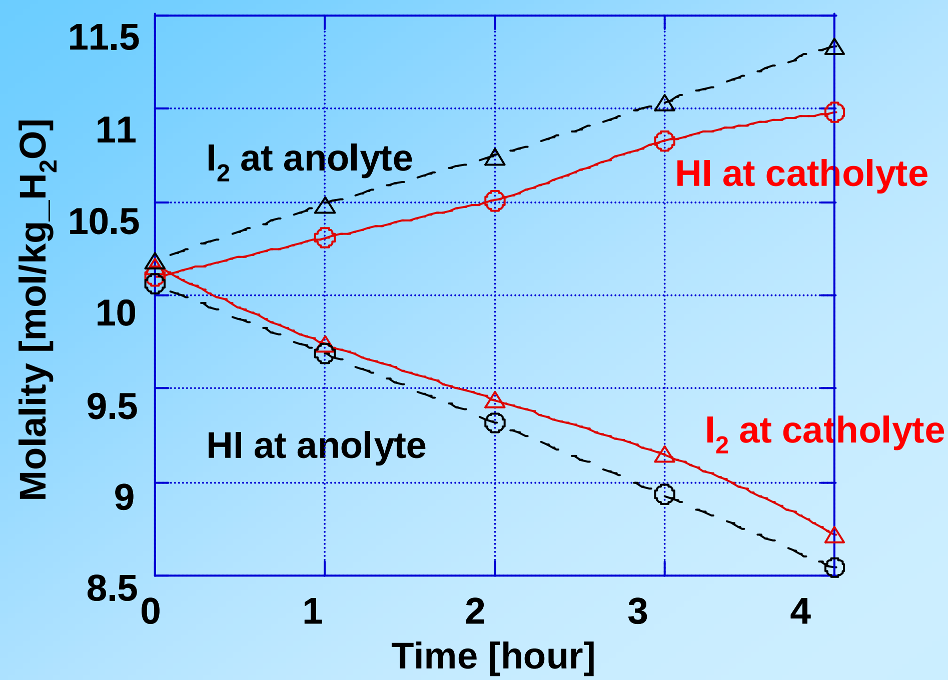


Photograph of experimental apparatus

Electrolysis cell	PEMFC-EFC05-01 (ElectroChem Inc.)
Effective membrane area	5.0 cm^2
Pressure	1 atm (abs.)
Temperature	40℃
Current density	200 mA/cm^2

Experimental conditions

Result of HI concentration experiment



The molality change of HI and I_2 using **Nafion117**.

Conditions

Initial molality of catholyte and anolyte
HI : 10.1 mol/kg_H_2O
I_2 : 10.1 mol/kg_H_2O
(HI: I2 = 1 : 1)
Total amount of HIx: 420 g

The molality was analyzed by **titration** at every hour.

Molality in 4 hours

Catholyte (HI rich side)
HI : 11.0 mol/kg_H_2O
I_2 : 8.7 mol/kg_H_2O

Anolyte (HI dilute side)
HI: 8.5 mol/kg_H_2O
I_2: 11.3 mol/kg_H_2O

HI concentration is possible.

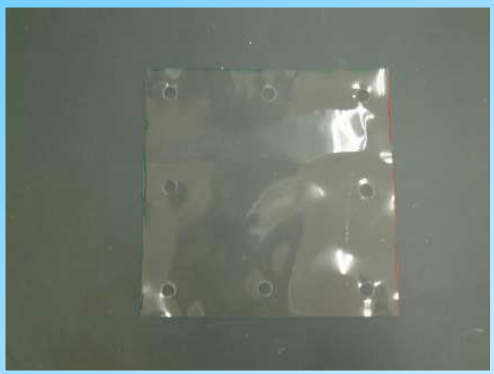
(t, β) could be calculated from the molality change.

↓

t=0.9 β=2 in the case of **Nafion117**

Radiation-grafted membrane

We aim to acquire value (t, β) for another proton exchange membrane.



Nafion 117

Radiation-grafted membrane (RGM)

Beam Science group of JAEA (former JAERI) is also under study on the preparation of cation exchange membranes by use of a radiation-induced graft polymerization method [*2].

↓

This method allows us to adjust easily the membrane properties such as ion exchange capacity and proton conductivity.

The intensive research on RGM has carried out for the purpose of fuel cell applications.

↓

RGM exhibited high proton conductivity and low water permeation.

↓

We try to apply this RGM for the iodine electrolysis.

*2 T. Yamaki et al., Preparation of Proton Exchange Membranes Based on Crosslinked Polytetrafluoroethylene for Fuel Cell Applications, Polymer, 45 (2004) 6539-6573.

(t, β) of radiation-grafted membrane

Sample No.	Thickness [μ m]	Proton conductivity [mS/cm]
Nafion 117	180	60
RGM	90	76.7

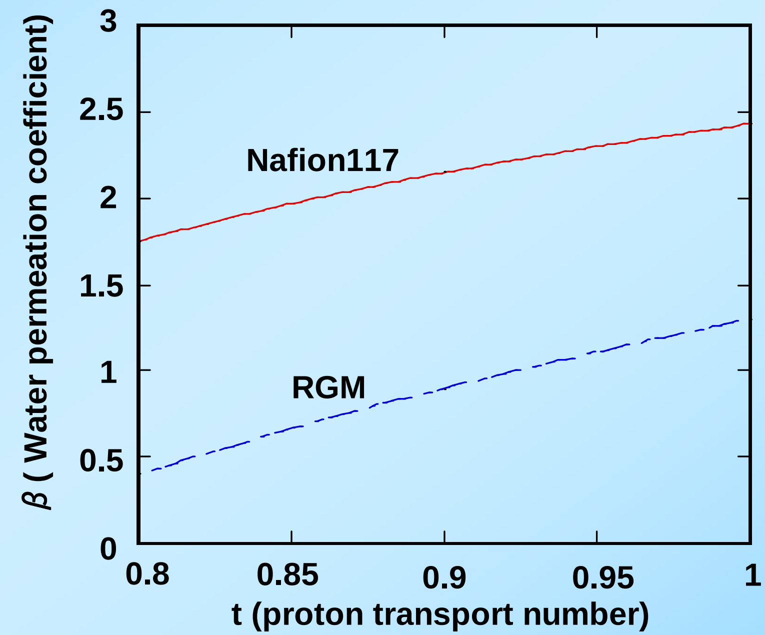
Characteristics of the examined membranes

Concentration experiment was performed for this RGM on the same condition in Nafion.

↓

(t, β) was calculated from the molality change.

Because we couldn't measure weight of permeated H_2O with accuracy, independent determination of (t , β) was not succeeded.



The possible location range of parameter set (t, β) for each membrane.

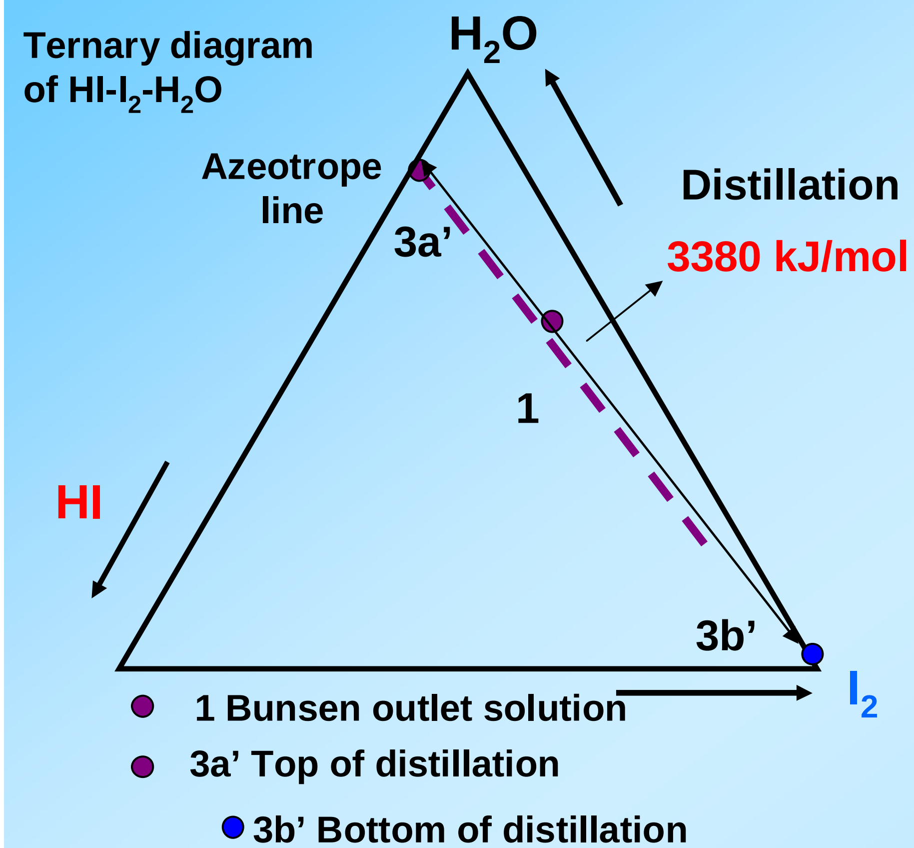
・β of the RGM were in between 0.4 and 1.2, which were far lower than that of Nafion, 1.7-2.4.

↓

RGM showed low water permeation for iodine electrolysis.

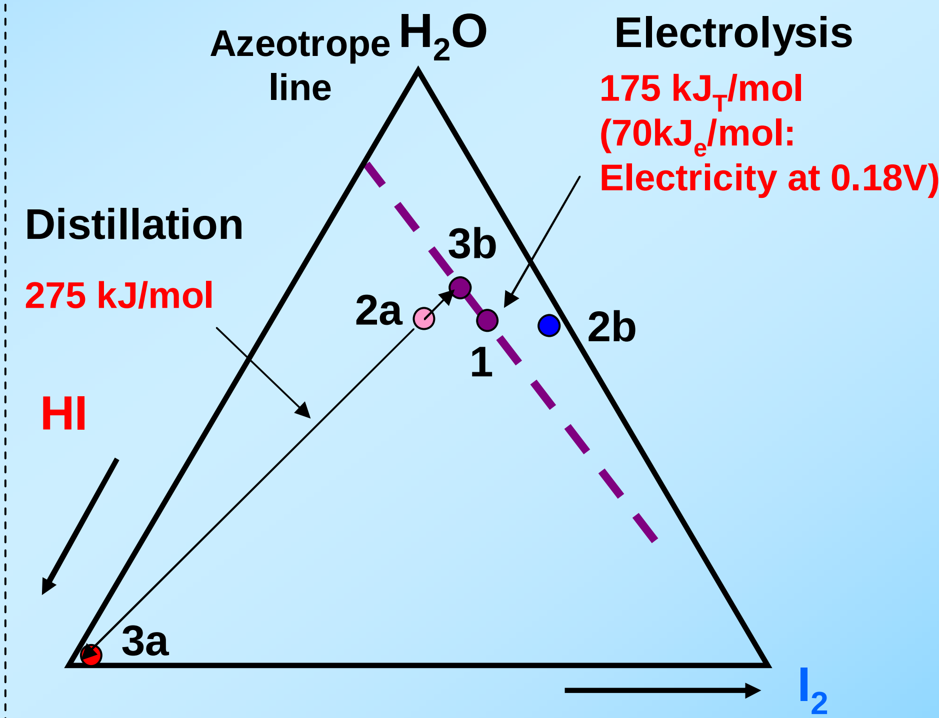
Improvement of the conversion efficiency using Electrolysis

Only distillation



The latent heat of evaporation of H_2O in azeotropic HI solution is necessary.

Application of electrolysis



H_2O evaporation is not necessary.
→Heat duty for the distillation can be greatly decreased.

According to the previous experimental result*3, HI concentration can be carried out by small amount of electricity.

We can reduce heat duty for HI part from 3380 to 450 (=275+175) kJ/mol.

*3 Onuki et al., J. Membr. Sci. 192 (2001) 129-136

Comparison of concentration efficiency

RGM shows low water permeation.
→RGM is expected to reduce electric energy of HI concentration.

	Nafion 117	Radiation-grafted membrane
Electrolysis (Electric energy)	70 kJ_e/mol at 0.18V ↓ ÷40 % 175 kJ_T/mol	49 kJ_e/mol at 0.18V ↓ ÷40 % 122 kJ_T/mol
Distillation	275 kJ/mol	275 kJ/mol
HI decom. part	450 kJ/mol	397 kJ/mol
Total hydrogen production efficiency	32.7 % →	34.8 %

The heat to electricity energy conversion efficiency (electricity production efficiency) is at least 40 % in the HTGR.

We can reduce heat duty for HI decomposition part from 450 to 397 kJ/mol using RGM.

We can improve the total hydrogen production efficiency by 2 % only replacing to the effective membrane.

Summary

1. Electrolysis can reduce heat duty of HI decomposition part.
2. Concentration performance of radiation-grafted membrane is higher than that of Nafion, because RGM had low water permeation coefficient.
3. The total hydrogen production efficiency can be improved by 2 % only replacing to the effective membrane.

Future plan

1. Search other membranes which have high performance for concentration.
2. Durability test for the membranes.
3. Check the influence of metal ion derived from structural material such as Fe.
4. Demonstration experiment in all set of HI part devices. (electrolysis, distillation, and decomposition)