6–4 Investigation of the Process Conditions of Inhibition Reactions for Thermal-Efficiency Improvement

— Effects of Impurity Contamination in an HI Concentrator —

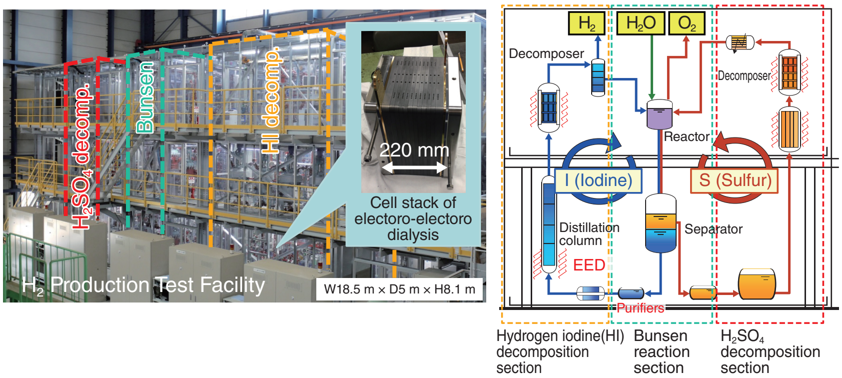


Fig.6-7 External view of the hydrogen-production test facility
We constructed a hydrogen-production test facility with all process components composed of industrial structural material in order to verify the integrity of the components and demonstrate continuous hydrogen-production ability. An electoro-electoro dialysis device (EED) was employed to concentrate the HI solution.

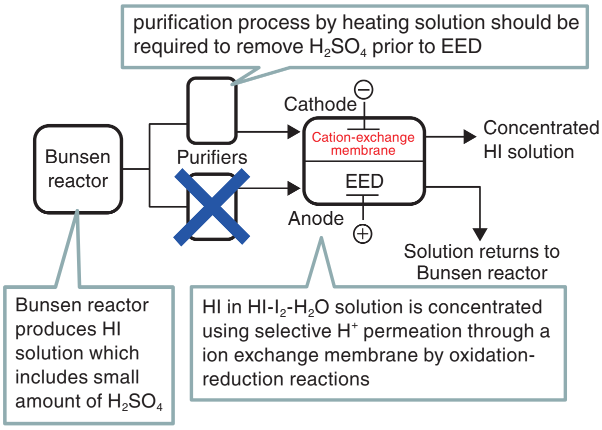


Fig.6-8 Production and concentration of HI Solution
The HI solution produced by the Bunsen reaction is purified to prevent harmful side reactions in HI concentration using the EED device. The purification process for the one-sided EED channel can be eliminated by adapting the proposed method.

Effect of sulfuric acid on electro-electro dialysis of HIx solution

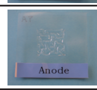
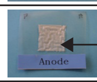
	Exp. conditions	Exp. results : transport number of protons	Visual inspection	
Case A (Purification of both sides)	Catholyte: no H_2SO_4 Anolyte: no H_2SO_4	1.0		(No change)
Case B (Purification catholyte)	Catholyte: no H_2SO_4 Anolyte: with H_2SO_4	1.0		(No change)
Case C (No purification)	Catholyte: with H_2SO_4 Anolyte: with H_2SO_4	0.7		Sulfur deposition

Fig.6-9 View of cation-exchange membrane after HI-concentration experiments using the EED device
No contamination by H_2SO_4 in the bath sides (Case A); one-sided contamination by H_2SO_4 in anolyte (Case B); no sulfur is evidenced. Contamination by H_2SO_4 in catholyte; sulfur is produced (Case C).

We have pursued R&D on a thermochemical hydrogen-production iodine–sulfur process as a heat-utilization application for the high-temperature gas-cooled reactor. This chemical process uses chemical compounds of iodine and sulfur to split water to produce hydrogen by combining three chemical reactions. This process, which can harness heat for nuclear or renewable energy, is a promising next-generation hydrogen-production method that is independent of fossil fuels and that can provide energy security. One important task is to improve the thermal efficiency of hydrogen production.

Reduction of the heat for driving processes is an effective method of improving thermal efficiency. We focused on a purification operation for processing the Bunsen-reaction solution. Bunsen reaction, which is core chemical reaction in the iodine–sulfur process, produces two types of acids in HI- and H_2SO_4-rich solutions from H_2O, I_2, and SO_2; the two acids separate into upper and lower phases with a clear boundary set by the liquid–liquid phase-separation phenomenon. The lower phase, which is rich in HI and I_2, includes an impurity of H_2SO_4; this contamination probably causes HI concentration (an EED with a cation-exchange membrane, Fig.6-7) and HI distillation to occur as a harmful side reaction with the production of solid sulfur. Because of mutual solubility between the two phases, a certain amount of H_2SO_4 is solved into the lower phase; a purification process by heating of the solution is necessary to remove H_2SO_4. This purification causes an increase of heat input because of the heating requirement for solution vaporization.

While optimizations of the operating temperature for the purification process have been studied, we proposed a flow-rate-reduction method of the processed solution itself to reduce the required heat (Fig.6-8), based on the fact that H_2SO_4 turns into sulfur in the reduction environment. The solution after the purification should be concentrated by EED; the solution is fed to both channels of the EED device in the previous flowsheet; H_2SO_4 in the anolyte of the oxidation environment is therefore probably stable. If the method is workable, the required heat can be reduced by reducing the processing solution for the purification; moreover, the flowsheet can be simplified.

To validate the proposed method, we conducted concentration experiments of the HI solution including H_2SO_4 using an EED device. Results met our expectations; the sulfur was not produced in the anolyte; moreover, the contamination in the anolyte was not affected by the cell voltage or the membrane selectivity (Fig.6-9). We revealed that our proposal can save the input heat required for purification. An increase of the hydrogen-production thermal efficiency is approximately 10% of that of the previous method.

Reference
Tanaka, N., Kubo, S. et al., Effect of Sulfuric Acid on Electro-Electrodialysis of HIx Solution, International Journal of Hydrogen Energy, vol.39, issue 1, 2014, p.86-89.