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Energy-saving seawater electrolysis for hydrogen production

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Abstract The change in the polarization potentials of
anode and cathode due to pH change on electrode surfaces
during galvanostatic polarization was examined in 0.5 M
NaCl solutions of different pH. On the basis of these
results, feeding of the anolyte after oxygen evolution to the
cathode compartment for hydrogen production was exam-
ined for energy-saving seawater electrolysis. This was
assumed to prevent the occurrence of a large pH difference
on cathode and anode in electrolysis of neutral solution if
sufficient H^+ is permeated through the membrane. The cell
performance was examined using Nafion 115 or Selemion
HSF membranes for separation of anode and cathode
compartments. The permeation fraction of H^+ with Nafion
115 was 45–65% in 0.5 M NaCl and was about 90% in
0.25 M Na_2SO_4. These values were smaller than 97%
necessary for prevention of the occurrence of pH difference
on cathode and anode. The permeation fraction of H^+ with
Selemion HSF became more than 97% during electrolysis
of 0.025 M Na_2SO_4, and the cell voltage was kept at low
values. These results indicate the effectiveness of our
seawater feeding system if the 97% H^+ permeation fraction
through the membrane is attained.

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Introduction

To supply abundant renewable energy and to avoid global
warming, the authors are proposing global CO_2 recycling
[1–4]. For global CO_2 recycling, Hashimoto et al. have
succeeded to tailor the necessary key materials, that is, the
anodes and cathodes for seawater electrolysis and catalysts
for CO_2 methanation. The most difficult in tailoring the key
materials was the anode for seawater electrolysis. In seawater
electrolysis for energy production a huge amount of chlorine
emissions are not allowed, and hence the anode should
evolve only oxygen even in seawater electrolysis. Hashimoto
and his coworkers succeeded to tailor efficient anodes for
oxygen evolution in seawater electrolysis [5–13]. Anodically
deposited γ-MnO_2-type Mn-Mo oxide anodes showed the
100% oxygen evolution efficiency in the electrolysis of
0.5 M NaCl at 1,000 A m^{-2} and 303 K [8].

For the achievement of this system, the energy-saving
electrolysis with small power consumption is necessary. In
the electrolytic cell, the anode and cathode are separated by a
cation exchange membrane. Figure 1 shows changes in
potentials of oxygen electrode reaction and hydrogen
electrode reaction with solution pH. The theoretical potential
for seawater electrolysis is 1.229 V. However, the pH of the
anode compartment will decrease to about 2 due to oxygen
formation because the permeation fraction of hydrogen ion is
not 100%, and also the pH of the cathode compartment will
increase to about 12 due to hydrogen formation. As a result,
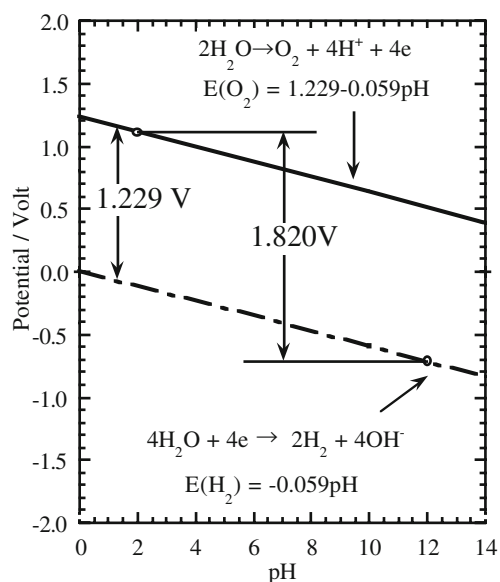the electrolysis voltage will exceed 1.8 V. For the energy

Fig. 1 Changes in potentials of oxygen electrode reaction and hydrogen electrode reaction with bulk solution pH

saving electrolysis it is desirable to avoid the pH difference between solutions on anode and cathode.

In the present work, the authors examined the anodic polarization behavior for the oxygen evolution electrode and the cathodic polarization behavior for the Pt electrode to clarify the relation between the bulk solution pH and the change in the polarization potential due to the pH change on the electrode surface. Based on these data we examined the possibility of energy saving electrolysis using the new seawater feeding system.

Experimental

Punched titanium metal nets of $8 \times 16 \times 1$ or $50 \times 100 \times 1$ mm in dimension were used as the substrate of anode. The titanium substrates were first immersed to remove the air-formed oxide film in 0.5 M HF solution for 5 min, rinsed with de-ionized water and dried in air. The substrates were immersed in 11.5 M H_2SO_4 at 353 K to increase the anchor effect for the electrocatalytically active oxides by surface roughening.

To prevent the formation of insulating titanium oxide during anodic deposition and electrolysis at high current density, IrO_2 was coated on the titanium substrate. The IrO_2 coating was carried out as follows: chloroiridic acid butanol solution was coated on the titanium substrate with a brush, dried at 353 K for 10 min in air, and then baked at 723 K for 10 min in air. This procedure was repeated three times on the titanium substrate, but the final baking of the specimen was continued for 60 min at 723 K in air for calcination. The IrO_2-coated Ti substrate was thus prepared.

The IrO_2-coated Ti substrate was degreased by anodic polarization at 1,000 A m^{-2} for 5 min in 1 M NaOH and then electrolytically rinsed at 1,000 A m^{-2} for 5 min in 1 M H_2SO_4 solution at room temperature. Electrocatalytically active Mn-Mo oxide was anodically deposited on the IrO_2-coated Ti substrate at a constant current density of 600 A m^{-2} in 0.2 M $MnSO_4$ and 0.003 M Na_2MoO_4 solution at pH 0.4 and 353 K for 30 min [8].

A Pt electrode used as a cathode was prepared as follows: a punched titanium metal net was etched in concentrated H_2SO_4 and then was coated with Pt by electroless plating.

Galvanostatic anodic polarization curves for the Mn-Mo oxide electrode of $8 \times 16 \times 1$ mm and cathodic polarization curves for the platinum electrode were separately measured using platinum and Ag/AgCl electrodes as the counter and reference electrodes in 0.5 M NaCl solutions with pH 1.03, 1.34, 1.98, and 5.70. Correction for iR drop was made with a current-interruption technique.

A test cell of the 1/10 size for the real electrolytic cell was prepared to examine our seawater feeding system. The configuration of the cell is shown in Fig. 2. The test cell prepared was composed of an anode, a cathode, and a membrane to separate these electrodes. Anodic and cathodic compartments are 13.8 ml in volume and $50 \times 100 \times 3$ mm in dimension. The Mn-Mo oxide electrode was used as the anode, and the Pt electrode as the cathode. Nafion 115 (Dupont) or Selemion HFS (Asahi Glass) was used as the membrane. As-prepared neutral NaCl and Na_2SO_4 solutions were used as the electrolytes. The neutral solution was fed to the inlet of the anode compartment, and the pH of the solution decreased to about pH 1 due to oxygen evolution in the anode compartment. The pH 1 solution was flowed in the cathode compartment. The pH was measured at the outlet of the cathode compartment. The cell voltage was also measured between anode and cathode during electrol-
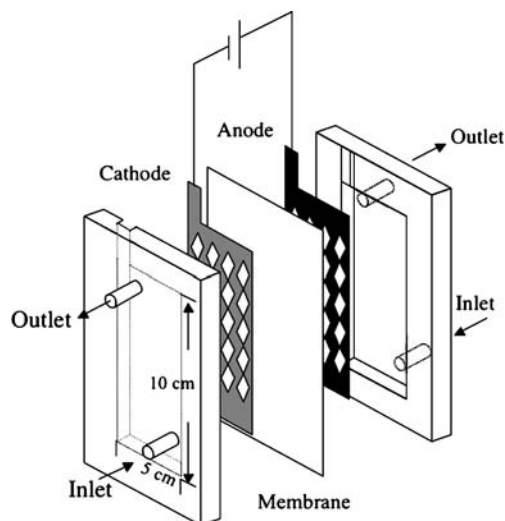

Fig. 2 Configuration of the electrolytic cell

ysis at the current density of 1,000 A m^{-2}. The pH and potential measured at the same amount of charge for electrolysis at unit time and unit volume of electrolyte as that for the real electrolyzer were regarded as those at the outlet of the cathode compartment, that is, the top of the cell, and the pH and potential of lower parts of the cell were estimated by increasing the flow rate. For instance, the pH and potential measured at the flow rate ten times as high as that of the real electrolyzer were regarded as those at the 10-cm height of the cathode compartment of the real electrolyzer of 100 cm in height.

Results and discussion

Figure 3 shows cathodic polarization curves of Pt electrode for hydrogen evolution and anodic polarization curves of the Mn-Mo oxide anode for oxygen evolution measured in 0.5 M NaCl of different pH at 303 K. The anodic polarization curves of Mn-Mo oxide electrode are not different with the initial pH of the solution because oxygen evolution immediately decreased the pH to about 1 just above the anode surface. On the other hand, in the solution of pH 1.03, the cathodic curve shows the straight Tafel relation. By contrast, the cathodic polarization curves at pH 1.34 and 1.98 shift to lower potentials at about 300 and 20 A m^{-2}, respectively, showing the Tafel relation observed in the solution of higher pH such as pH 10.2. This result suggests that the pH just above the cathode surface increased to about 10.2 due to hydrogen generation. From the result at pH 1.03 we can say that if the hydrogen evolution is carried out in the solution of pH 1 hydrogen evolution does not lead to change in the local pH on the cathode surface, and we do not need to care about cell
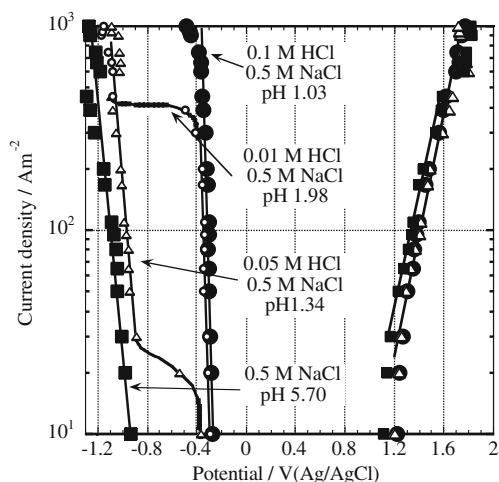
voltage increase. Therefore, the cell voltage at 1,000 A m^{-2} without the membrane will be about 2.0 V if the solution whose pH is decreased to 1 by anodic oxygen evolution is supplied to the cathode compartment.

For the test cell experiment, we used the cation exchange membrane through which both hydrogen and sodium ions competitively permeate. Figure 4 shows models of an ordinary seawater feeding system (a) and our seawater feeding system (b). In the ordinary flow system, simultaneous feeding of seawater to both cathode and anode compartments is carried out. The permeation of sodium ion leaving hydrogen ion leads to acidification of the anode compartment and alkalization of the cathode compartment in the ordinary feeding system. Instead of the ordinary system, as shown in Fig. 4b, if we feed seawater first to the anode compartment and then feed the low pH solution from the outlet of the anode compartment to the cathode compartment, complete neutralization will take place just before seawater passes the outlet of cathode compartment. In such a seawater feeding system, we can expect to electrolyze seawater mostly in acidic solution, and as shown in Fig. 3 if the pH of solution fed to the cathode compartment is 1, we can avoid the pH increase on the cathode surface and hence we can avoid the increase of the cell voltage.

We will assume the following seawater feeding cell design instead of parallel seawater feeding to both the anode and cathode compartments: During electrolysis at a constant current density of 1,000 A m^{-2}, neutral seawater is supplied to the bottom of the anode compartment of 100 cm and 600 ml in height and volume, respectively, spending 60 min for passing through the anode compartment. After separation of oxygen and water the seawater coming out
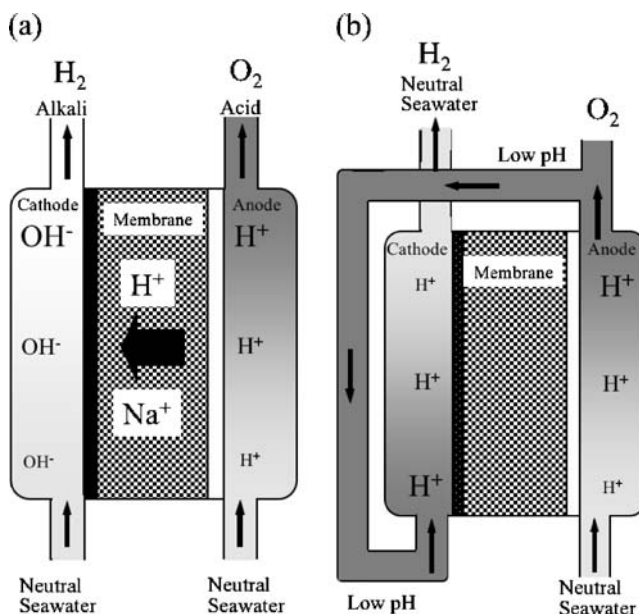

Fig. 3 Galvanostatic cathodic polarization curves of Pt electrode for hydrogen evolution and anodic polarization curves of the Mn-Mo oxide anode for oxygen evolution measured in 0.5 M NaCl of different pH at 303 K

Fig. 4 Models of an ordinary seawater feeding system (**a**) and our seawater feeding system (**b**)

from the anode compartment is fed to the bottom of the cathode compartment. If the cations permeated through the membrane are composed of 98% hydrogen ions and 2% sodium ions, and if the voltage increase due to the membrane resistance at 1,000 A m^{-2} is 0.5 V, the pH on the anode, the pH on the cathode, and the cell voltage during electrolysis will be changed as a function of the cell height as shown in Fig. 5. The pH will become about 0.6 at the outlet of the anode compartment. The pH of the cathode compartment will be kept at the low values just before the outlet of the cathode compartment and the solution will be neutralized at the top of the cathode compartment. In this setup, the cell voltage will be kept almost at the theoretical one in the most parts of the cell.

We constructed a test cell of 1/10 height of the practical electrolyzer in which seawater flow is from the bottom of the anode compartment to the top of the cathode compartment as mentioned above.

Figure 6 shows the pH on the cathode and the cell voltage during electrolysis of 0.5 M NaCl as a function of the cell height in addition to the permeation fraction of hydrogen ion. In this experiment, Nafion115 was used as the ion exchange membrane. Although the height of the electrolyzer used was 10 cm, the abscissa of Fig. 6 and the following figures is written in numerical values ten times as high as those observed, supposing the real electrolyzer of 100 cm in height. The pH increases and exceeds 1.3 immediately after the solution is fed to the bottom of cathode compartment. Therefore the cell voltage increases. The permeation of hydrogen ion was about 50%. Figure 7 shows the change in the pH, the cell voltage, and the permeation fraction for Nafion115 in 0.25 M Na$_2$SO$_4$. The cell voltage is kept at 2.5 V up to 15 cm of the cell height. Over 15 cm, the cell voltage increases due to pH increase.

Fig. 6 Changes in the pH on the cathode, the cell voltage, and the permeation fraction of hydrogen ion through Nafion115 membrane during electrolysis of 0.5 M NaCl as a function of the cell height

The permeation of hydrogen ion was about 90%. Because the hydrogen ion permeation fraction is much smaller than 98%, pH increases at the vicinity of the inlet of the cathode compartment. The difference between sodium chloride and sodium sulfate is due to the difference in concentration of free sodium ion based on difference in dissociation.

Figure 8 shows the pH on the cathode the cell voltage and the permeation fraction of hydrogen ion during electrolysis of 0.5 M NaCl solution as a function of the cell height for the use of Selemion HSF membrane known as hydrogen ion selective exchange membrane. The cell voltage is kept below 3 V up to 10 cm of the cell height. Over 10 cm, the cell voltage increases up to about 3.3 V with pH increase. The hydrogen permeation fraction is not sufficiently high even if we used the hydrogen ion selective
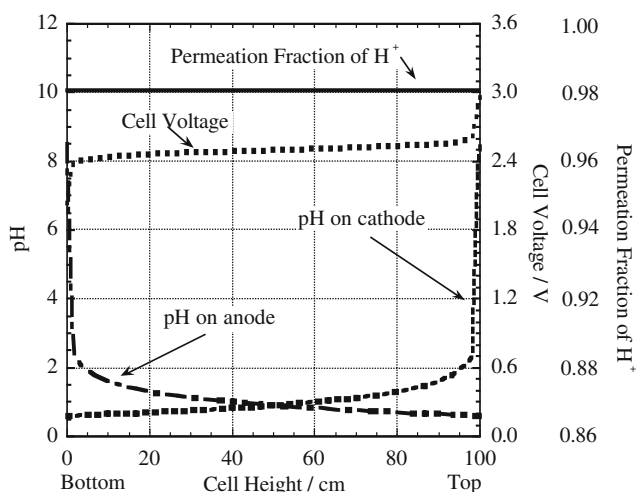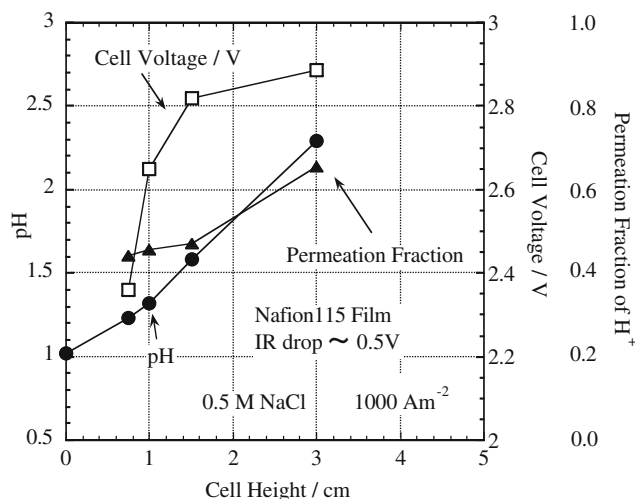

Fig. 5 Assumed changes in the pH on cathode and anode and the cell voltage during electrolysis as a function of the cell height at the permeation rate of hydrogen ion of 98%
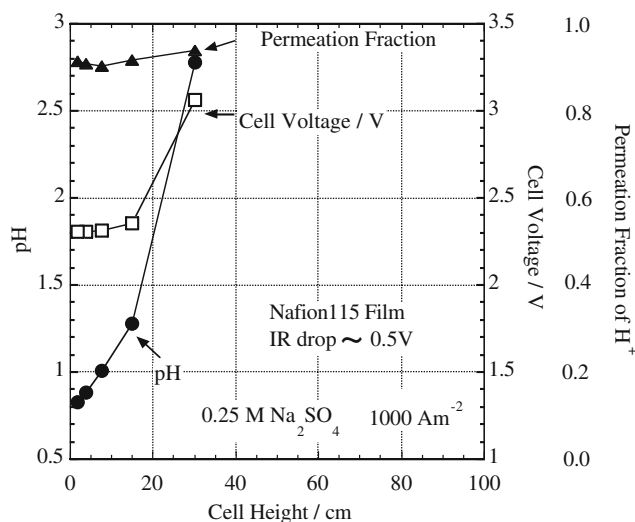

Fig. 7 Changes in the pH on the cathode, the cell voltage, and the permeation fraction of hydrogen ion through Nafion115 membrane during electrolysis of 0.25 M Na$_2$SO$_4$ as a function of the cell height
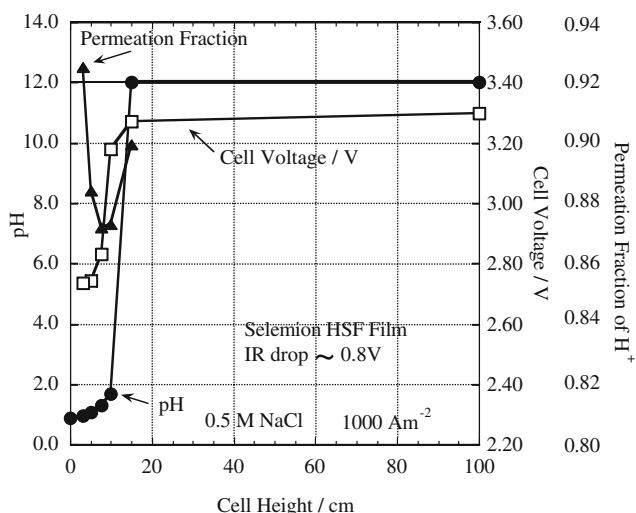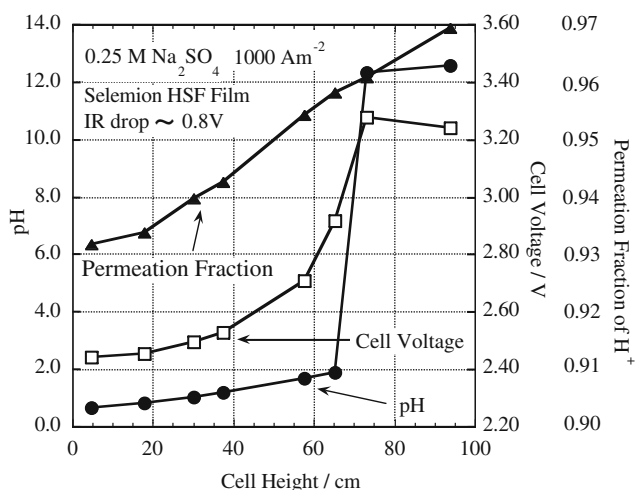
Fig. 8 Changes in the pH on the cathode, the cell voltage, and the permeation fraction of hydrogen ion through Selemion HSF membrane during electrolysis of 0.5 M NaCl as a function of the cell height

membrane. We expected the hydrogen permeation of 98% but in this experiment it was about 90%. The high dissociation of sodium chloride is responsible for higher amount of permeation of sodium ion with a consequent lower permeation of hydrogen ion. To confirm this fact, we tried to electrolyze Na_2SO_4 solution, because the dissociation of sodium sulfate is lower than sodium chloride.

Figure 9 shows the result of electrolysis of 0.25 M Na_2SO_4 solution with Selemion membrane. As was expected, the cell voltage is lower than 2.8 V up to 60 cm of the cell height. However, the pH increases and exceeds 1.3 more than 60 cm, and the cell voltage increases to about 3.3 V. The amount of hydrogen ion permeated though the membrane is not enough to neutralize the catholyte because the permeation of hydrogen ion is smaller than 97% in this concentration of sodium ion. If the permeation of Na^+ is

sufficiently lower, the permeation of hydrogen ion should be sufficiently higher to keep low pH in the cathode compartment. Thus, we tried to decrease the concentration of free sodium ion by diluting the sodium sulfate solution.

Figure 10 shows the result of electrolysis of 0.025 M Na_2SO_4 with the Selemion membrane. If we decrease the concentration of free sodium ion, we can keep low pH in the cathode compartment and hence we can electrolyze at a nearly constant voltage of 2.5 V. The permeation of hydrogen became about 97%.

Summary

The ordinary three electrode cell experiments consisting of working, counter, and reference electrodes in 0.5 M NaCl solutions with different pH revealed the following potential change of the electrode as a result of pH change on the electrode. The galvanostatic cathodic polarization curve of Pt electrode showed the straight Tafel relation in the solution of pH 1.03. By contrast, the polarization curves at pH 1.34 and 1.98 shifted to lower potentials at about 300 and 20 A m^{-2}, respectively, showing the Tafel relation observed in the solution of higher pH such as pH 10.2 as a result of hydrogen evolution. On the other hand, the pH on the anode surface almost immediately changed to about pH 1 as a result of oxygen evolution.

Based on the above-mentioned results, we examined the possibility of the energy-saving seawater electrolysis by avoiding the cell voltage increase. Instead of simultaneous parallel feeding of sodium chloride solution to both anode and cathode compartments, neutral sodium chloride solution was supplied first to the anode compartment and the low pH solution from the outlet of the anode compartment

Fig. 9 Changes in the pH on the cathode, the cell voltage, and the permeation fraction of hydrogen ion through Selemion HSF membrane during electrolysis of 0.25 M Na_2SO_4 as a function of the cell height
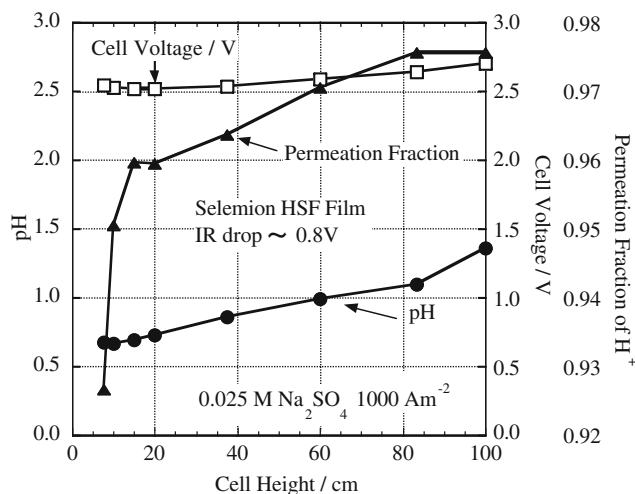

Fig. 10 Changes in the pH on the cathode, the cell voltage, and the permeation fraction of hydrogen ion through Selemion HSF membrane during electrolysis of 0.025 M Na_2SO_4 as a function of the cell height

was supplied to the cathode compartment. In such seawater feeding, if the permeation of hydrogen ion from the anolyte to the catholyte through the cation exchange membrane is 98% of total amounts of cations permeated, the cell voltage increase is assumed to be avoided. The following conclusions were drawn.

With a Nafion membrane, the permeation of hydrogen ion was 45–65 and about 90% in 0.5 M NaCl and 0.25 M Na_2SO_4 solutions, respectively. The pH increased near the inlet of the cathode and the cell voltage could not be kept to 2.5 V.

Even if a hydrogen ion selective exchange membrane Selemion was used, the permeation of hydrogen ion was lower than 90% in 0.5 M NaCl solution. The increase of pH was avoided until 10 cm of the cell height, where the cell voltage was about 2.7 V.

With the Selemion membrane, the permeation of hydrogen ion was 93–95% in 0.25 M Na_2SO_4 solution. The increase of pH was avoided until 60 cm of the cell height, where the cell voltage was lower than 2.8 V.

In the electrolysis of 0.025 M Na_2SO_4 solution using Selemion, the permeation of hydrogen ion was 97–98%. The cell voltage ranged from 2.5 to 2.7 V in all parts of the cell.

In conclusion, the energy-saving electrolysis by avoiding the influence of pH change on the electrode surfaces can be realized by feeding neutral seawater first to the anode compartment and then feeding the seawater coming out from the anode compartment to the cathode compartment, if the permeation of hydrogen ion through the membrane is higher than about 97% in the electrolysis of 0.5 M NaCl at the current density of 1,000 A m^{-2}.

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