

Electrochemical Hydrogen Production from Carbon Monoxide and Steam with a Cell Employing CsH₂PO₄/SiP₂O₇ Composite Electrolyte

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Electrochemical hydrogen pumping was investigated with a cell consisting of a CsH_2PO_4/SiP_2O_7 composite electrolyte at 200°C. When humidified hydrogen was fed to the anode, the evolution rate of hydrogen at the cathode obeyed Faraday's law up to a current density of 1000 mA cm⁻². In this system, the water–gas shift reaction (WGSR) was promoted electrochemically at the anode during polarization with a feed of humidified carbon monoxide. The overpotential was much higher in humidified carbon monoxide than in humidified hydrogen. With the reactor for the catalytic WGSR located upstream of the anode gas, the overpotential significantly depended on the temperature and space velocity of the reactor. The bilayered electrode composed of a Cu spinel oxide and a Pt catalyst exhibited a low overpotential at low current densities due to the formation of hydrogen over the Cu spinel catalyst.

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Hydrogen has attracted much attention as a new energy carrier for the near future and is generally produced by partial oxidation, steam reforming, and autothermal reforming of hydrocarbons. Because the production of hydrogen from fossil fuels is accompanied with the formation of carbon monoxide and carbon dioxide, the purification of hydrogen is important for the effective use of hydrogen. The separation of hydrogen from synthesis gases is conducted with pressure swing adsorption, cryogenic distillation, or membrane separation.

Electrochemical hydrogen pumping is one of the effective methods for the purification of hydrogen from the reformed gases. In this system, proton conductors are employed as electrolytes. Hydrogen and proton are oxidized and reduced at the anode and cathode, respectively, with the current supplied from an external power source

Anode:
$$H_2 \rightarrow 2H^+ + 2e^-$$
 [1]

Cathode: $2H^+ + 2e^- \rightarrow H_2$ [2]

The electrochemical pumping cells with proton exchange membranes were demonstrated.¹⁻³ Purification of hydrogen from the reformed gas, however, is unfavorable at low temperatures because of the deactivation of the platinum electrocatalyst ascribable to poisoning by carbon monoxide, as in polymer electrolyte fuel cells. Iwahara et al.,^{4,5} and Matsumoto et al.,⁶⁻⁹ reported the electrochemical hydrogen extraction from various gases, with the cell consisting of proton-conductive ceramics based on cerates and zirconates as electrolytes at 650–900°C.⁴⁻⁹ In cerate electrolytes, the hydrogen evolution rate did not attain the theoretical value expected from Faraday's law above a specific current density. This low current efficiency resulted from partial electron or hole conduction in the electrolyte under a reducing or oxidative atmosphere. Water management in feeding gas to both electrodes was required for suitable oxygen partial pressure. Furthermore, the inclusion of oxide-ionic conduction in the electrolyte led to a decrease in the current efficiency of hydrogen pumping from anode to cathode. The cerate-based ceramics are decomposed by carbon dioxide, which is contained in the reformed gases. Meanwhile, the zirconates with superior chemical and mechanical stability exhibited a lower conductivity than cerates. Accordingly, there are few stable electrochemical cells available to the electrochemical hydrogen pumping in the presence of carbon monoxide and carbon dioxide.

We have recently reported the proton-conductive CsH₂PO₄/SiP₂O₇ composite at 110-280°C. The composite with a CsH_2PO_4/SiP_2O_7 molar ratio of 1/2 achieved 44 mS cm⁻¹ at 266°C under 30% H₂O/Ar atmosphere.¹⁰⁻¹² In this composite, the chemical reaction at the contacting interface between the two components resulted in the formation of $CsH_5(PO_4)_2$, which served as a proton-conductive phase. This electrolyte was stable in the solid state under fuel cell operating conditions. The fuel cell composed of this composite was operated successfully at around 200 $^\circ \text{C}.^{13}$ In this study, electrochemical hydrogen pumping employing the CsH₂PO₄/SiP₂O₇ composite was investigated at 200°C. Initially, the fundamental property of the electrochemical cell was examined by supplying hydrogen to the anode. Furthermore, we evaluated the feasibility of this system for the production and separation of hydrogen from the carbon monoxide and steam mixture. The water-gas shift reaction (WGSR) of carbon monoxide and steam to form carbon dioxide and hydrogen (Reaction 3) was conducted with the use of catalysts at ca. 200°C

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$
 [3]

The present investigation aimed at the coupling of electrochemical pumping and WGSR because either of the reactions is operative at similar temperature ranges (ca. 200°C). Although CO tolerance of the Pt electrocatalyst was significantly improved at elevated temperatures, the catalyst was inactive for WGSR at 200°C.¹⁴⁻¹⁷ In contrast, Cu-based mixed oxides are excellent catalysts for WGSR. Tanaka et al. reported the relatively high CO conversion of the spinel-type oxides such as CuMn₂O₄ and CuFe₂O₄ at 200°C.^{18,19} Then, the series of hydrogen production processes consisting of the catalytic reaction and the electrochemical separation was demonstrated by locating a Cu-based mixed oxide catalyst at the upstream part of the gas flow.

Experimental

A commercial Pt/C supported on carbon paper (BASF Fuel Cell, Inc., phosphoric acid fuel cell, Pt loading 1.0 mg cm⁻²) was used as an electrode to examine the property of the cell by feeding hydrogen to the anode. With a supply of carbon monoxide and steam, some catalysts were applied on carbon paper for the anode. A commercial Pt catalyst supported on carbon black (40 wt % Pt/C, Alfa Aesar) was employed. The copper-based spinel oxide CuFe_{1.5}Mn_{0.5}O₄ was prepared by the citric acid complex method and was calcined at 900°C for 10 h.¹⁹ This spinel catalyst was mixed with carbon black (Vulcan XC-72) to be a 40 wt % spinel catalyst/C (hereafter abbreviated as Cu spinel/C). The anode was

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Table I. Pt and CuFe _{1.5} Mn _{0.5} O ₄ loading in anode.			
Anode	Pt loading (mg cm ⁻²)	CuFe _{1.5} Mn _{0.5} O ₄ loading (mg cm ⁻²)	
Pt/C Pt/C + Cu spinel/C	1.0, 8.1, 10.6 1.5	12.1	

fabricated with these resultant powders. The catalyst was ultrasonically dispersed in a mixture of deionized water and ethanol (Wako Pure Chemical Industries). The mixture was applied on a Tefloncoated carbon paper (Toray) and dried at ca. 100°C. With the Cu spinel/C catalyst, the carbon paper was initially coated with the Cu-based catalyst, followed by the Pt catalyst to be a bilayered electrode. The Pt and $CuFe_{1.5}Mn_{0.5}O_4$ loadings in these electrodes are summarized in Table I. For the cathode and reference electrode, the commercial Pt/C supported on carbon paper was used.

Cesium dihydrogen phosphate, CsH₂PO₄, was synthesized by drying an aqueous solution of Cs₂CO₃ (Aldrich) and H₃PO₄ (Wako Pure Chemical Industries) overnight at ca. 100°C. The X-ray diffraction pattern of the resultant powder was identical to that of CsH_2PO_4 in the literature.²⁰ The silicon pyrophosphate, SiP_2O_7 , was obtained from SiO₂ (Nippon Silica) and H₃PO₄, which consisted of forms II (monoclinic) and III (pseudotetragonal).^{21,22} The composite electrolyte of CsH₂PO₄/SiP₂O₇ was prepared by mixing the resultant powders in a molar ratio of 1:2. The membrane electrode assembly (MEA) was fabricated by uniaxial pressing of the composite powder with electrodes (13 mm diameter, ca. 1.3 mm thickness, and 0.283 cm² electrode area). The reference electrode was set on the cathode side. Then, the resulting MEA was heat-treated at 220°C for 1 h and placed in the apparatus, as shown in Fig. 1. The shift reactor was located at the upstream part of the gas flow to evaluate the combined system of WGSR and electrochemical hydrogen pumping. A physically mixed catalyst of CuFe_{1.5}Mn_{0.5}O₄ spinel-type oxide and γ -alumina (JRC-ALO-8, The Catalysis Society of Japan) with a weight ratio of 2:1 was used. Before the measurement, a catalyst of 1.0 g in the reactor was reduced at 250 °C for 1 h in 30% H₂O/H₂.

The hydrogen pumping capacity was examined by applying the dc to the cell at 200°C. Hydrogen or carbon monoxide was fed to the anode. The gas supplied to the cathode consisted of argon and a small amount of hydrogen so as to decrease the concentration overpotential of hydrogen.³ The feeding gas was humidified at 30% by passing through water at ca. 70°C. The total flow rate for both electrodes was maintained at 150 mL min⁻¹, unless otherwise noted. The concentrations of hydrogen and carbon dioxide in the outlet gas after the water trap were analyzed by a thermal conductivity detector (Varian, CP-4900). The evolution rate was estimated by measuring the increase in concentration with passing currents. For the evaluation of the overpotential, the reactant gas and humidified hydrogen were supplied to the anode and cathode sides, respectively. The potential and ohmic resistances of the anode were measured against the reference electrode by galvanostatic steady state



Figure 2. Evolution rates of hydrogen gas at the cathode as a function of current density with a supply of $30\% H_2O/H_2$ to the anode at $200^{\circ}C$.

polarization and ac impedance spectroscopy techniques, respectively (Solartron 1287 potentiostat and Solartron 1260 frequency response analyzer). The overpotential at the anode was calculated from the ohmic loss and potentials under an open-circuit condition and polarization.⁸

Results and Discussion

Hydrogen pumping from humidified hydrogen fed to anode.-The evolution rates of hydrogen gas at the cathode as a function of current density are shown in Fig. 2. The broken line represents the theoretical evolution rates calculated from Faraday's law. The obtained results of two consecutive measurements obeyed Faraday's law and were highly reproducible. At 1000 mA cm⁻², the difference in voltage between the anode and cathode increased by ca. 5 V in 30 min. The impedance spectra of a cell with a two-electrode system measured under an open-circuit condition before and after the hydrogen pumping tests are shown in Fig. 3. The ohmic resistance remained unchanged during the first measurement. In contrast, the impedance spectrum after the second measurement exhibited a remarkable increase in ohmic and polarization resistances. This impedance increase indicated that the large reaction overpotential at 1000 mA cm^{-2} should give rise to the partial decomposition of the electrolyte accompanied with a decrease in its conductivity. This degradation, however, did not affect the current efficiency of hydrogen pumping, judging from the hydrogen evolution rate. Consequently, this system was sufficiently operable as a hydrogen pump.



Figure 1. Schematic drawing of cell configuration.



Figure 3. Impedance spectra of a single cell at 200° C before and after the hydrogen pumping tests.



Figure 4. Schematic drawing of the electrochemical hydrogen extraction from a gas mixture of carbon monoxide and steam.

Hydrogen extraction from humidified carbon monoxide fed to anode.— The electrochemical production and separation of hydrogen from carbon monoxide and steam were examined. The fabricated Pt/C electrode (Pt loading 1.0 mg cm⁻²) was used for the anode. When carbon monoxide and steam were fed to the anode under an open-circuit condition, hydrogen was hardly detected at the anode. Thus, the catalytic activity against WGSR for the Pt/C catalyst was negligibly small at 200°C. With the passing current, two reactions have to be considered: electrochemically-promoted WGSR (Fig. 4a) and electrolysis of water (Fig. 4b).

Electrochemically-promoted WGSR

Anode:
$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$
 [4]
Cathode: See Reaction 2.

Electrolysis of water

Anode:
$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$$
 [5]
Cathode: See Reaction 2

To clarify the reaction at the anode, the evolution rate of carbon dioxide in the outlet gas with passing current was evaluated, as summarized in Table II. The calculated values are based on the assumption that the passed current is completely consumed for the electrochemically-promoted WGSR, in conformity with Faraday's law. The measured value agreed well with the calculated one. Thus, it can be concluded that hydrogen was extracted to the cathode via the electrochemically-promoted WGSR under current loading. Furthermore, the anodic overpotential was remarkably lower for the

(Fig. 5). In this condition, the hydrogen production was confirmed at the cathode during polarization, as shown in Fig. 6. Then, considering the low activity against catalytic WGSR for the Pt/C catalyst at 200°C, the operation of the cell gave rise to the formation of hydrogen from a gas mixture of carbon monoxide and steam. In Fig. 6, the electrochemically-promoted WGSR (Fig. 4a) is regarded as a faradaic reaction to calculate theoretical values. Hydrogen was extracted in the theoretically estimated amount, as in humidified hydrogen (Fig. 2). Accordingly, the electrochemical extraction and separation of hydrogen from humidified carbon monoxide were successfully verified at 200°C.

supply of humidified carbon monoxide than for humidified argon

The anodic overpotential of Pt/C electrodes with various Pt loadings was evaluated in a gas mixture of carbon monoxide and steam, as shown in Fig. 7. These electrodes exhibited extremely higher overpotential in humidified carbon monoxide than in humidified hydrogen (cf. 1-2 mV at 2-10 mA cm⁻² in 30% H₂O/H₂). The an-

Table II. Evolution rate of carbon dioxide in the outlet gas of anode with passing current.

Current density (mA cm ⁻²)	Evolution (µmol mi	Evolution rate of CO_2 (µmol min ⁻¹ cm ⁻²)	
	Measured value	Calculated value	
5	1.28	1.55	
10	2.98	3.11	



Figure 5. Anodic overpotential as a function of current density with a supply of $30\% H_2O/CO$ or $30\% H_2O/Ar$ at 200°C.

odic overpotential of Pt/C electrodes decreased with an increase in the Pt loading. The slope of overpotential vs logarithm of current density was almost the same for different Pt loadings in the range of $1.0-10.6 \text{ mg cm}^{-2}$, suggesting that the reaction process was unchanged for Pt/C electrodes in this range of Pt loading.

The electrochemically-promoted WGSR over Pt/C electrode did not readily proceed, while this electrode was significantly active for hydrogen oxidation (Reaction 1). It is expected that the reduction in overpotential for hydrogen extraction and separation from carbon monoxide and steam is achieved by the combination of catalytic WGSR (Reaction 3) and the subsequently electrochemical separation of hydrogen from the post-WGSR gas (Reactions 1 and 2). Then, the shift reactor with a mixed catalyst of CuFe_{1.5}Mn_{0.5}O₄



Figure 6. Evolution rates of hydrogen gas at the cathode as a function of current density with a supply of $30\% H_2O/CO$ to the anode at 200 °C.



Figure 7. Overpotential of the anode with various Pt loadings as a function of current density with a supply of 30% H₂O/CO at 200° C.

spinel-type oxide and γ -alumina was located at the upstream part of the gas flow, as shown in Fig. 8. This spinel-type oxide was reported to be active for the catalytic WGSR above 175°C in the hydrogenrich gas. The influence of the space velocity (SV) in the shift reactor on the anodic overpotential of the Pt/C electrode (Pt loading 1.0 mg cm⁻²) was analyzed at 200°C by changing the flow rate of the supply gas. Figure 9 shows the anodic overpotential as a function of current density with a supply of post-WGSR gas. Clearly, the formation of hydrogen over the mixed catalyst in the reactor reduced the overpotential of the electrode at a current density of 2-10 mA cm⁻². As the SV in the reactor increased, the drastic increase in the overpotential was confirmed at a lower current density. This indicated that the hydrogen formed by the catalytic reaction is preferentially pumped into the cathode. Moreover, the anodic overpotential of the Pt/C electrode (Pt loading 1.0 mg cm^{-2}) also depended on the temperature of the shift reactor, as shown in Fig. 10. At 100 and 200°C, the overpotential in the low current density region was substantially higher than that at 250°C. The conversion of carbon monoxide over the mixed catalyst was low, and hydrogen was deficient below 200°C. At 250°C, the overpotential significantly increased with the current density, though hydrogen was rapidly pumped into the cathode at a low current density. As the current density increases, the supplied current should initiate electrochemically-promoted WGSR as well as oxidation of hydrogen from the catalytic WGSR because of the limited hydrogen pro-



Figure 8. Schematic drawing of the apparatus for electrochemical hydrogen pumping with the shift reactor.



Figure 9. Anodic overpotential as a function of current density with a supply of post-WGSR gas at 200°C. This measurement was conducted with changing the SV in the shift reactor.

duction in the shift reactor. The high conversion of carbon monoxide was responsible for the low concentration of carbon monoxide and steam in the post-WGSR gas at 250°C. Thus, the electrochemically-promoted WGSR did not readily proceed, leading to a higher overpotential in the high current density region of 7–20 mA cm⁻² at 250°C than at the other reactor temperatures.

The shift catalyst installed upstream of the gas flow was effective for the promotion of hydrogen extraction from humidified carbon monoxide during passing the low current densities. Then, the overpotential of the bilayered electrode composed of Cu spinel/C and



Figure 10. Anodic overpotential as a function of current density with a supply of post-WGSR gas at 200°C. This measurement was conducted with changing the shift reactor temperature.



Figure 11. Overpotential of the anode consisting of Pt/C with and without Cu-based catalyst as a function of current density with a supply of 30% H₂O/CO at 200°C.

Pt/C catalysts was examined to clarify the feasibility of the combined process for hydrogen production of the catalytic reaction and electrochemical separation in the anode chamber. Figure 11 shows the anodic overpotential of the bilayered electrode as a function of current density. The SV for the catalytic reaction over Cu spinel/C attained 2.6 \times 10⁶ 1 kg⁻¹ h⁻¹. The overpotential of this electrode was higher than that of the Pt/C electrode (Pt loading 1.0 mg cm^{-2}) at 5–15 mA cm⁻². The porosity in the layer containing the Cu spinel catalyst may be insufficient for the diffusion of reactant gases. Considering the lower overpotential at 2 mA cm⁻² for this electrode than for every Pt/C electrode investigated, the Cu spinel in the electrode promoted the catalytic WGSR, as in the case with location of the shift reactor at 250 °C. As shown in Fig. 10, the overpotential was 260 mV at 2 mA cm⁻² in the post-WGSR gas formed at 200°C, while this bilayered electrode exhibited an overpotential of 48 mV at the same current density despite the large SV of the catalytic reaction. The Cu spinel catalyst adjacent to the Pt/C catalyst in this electrode raised the hydrogen concentration in the vicinity of the electrocatalyst, resulting in a smooth hydrogen oxidation and low overpotential. Consequently, this electrochemical property indicates that the bilayered electrode should be available for the successive processes of catalytic reaction and electrochemical hydrogen pumping in the anode chamber, and it is important to control the electrode structure for further performance enhancement.

Conclusions

The cell consisting of a CsH_2PO_4/SiP_2O_7 composite electrolyte was investigated for the current efficiency for hydrogen pumping and the anodic overpotential of an electrode with a feed of humidified hydrogen and humidified carbon monoxide at 200°C. The hy-

drogen evolution rate at the cathode agreed well with that calculated from Faraday's law in the whole range of current density investigated regardless of the feeding gas. With the supply of humidified carbon monoxide to this electrochemical cell, the electrochemicallypromoted WGSR proceeded. The electrode in humidified carbon monoxide, however, exhibited higher overpotential by 2 orders of magnitude than that in humidified hydrogen. The reactor with a shift catalyst was installed at the upstream part of the gas flow for the decrease in overpotential. The overpotential of the Pt/C electrode in post-WGSR gas was reduced by hydrogen formed in the shift reactor. The bilayered electrode composed of a Cu spinel and Pt catalysts was evaluated for the series of hydrogen production processes consisting of the catalytic WGSR and the electrochemical pumping in the anode chamber. This electrode was effective for smooth hydrogen extraction from carbon monoxide and steam at low current densities. Consequently, it is important not only to select the suitable catalyst material but also to optimize the location of the shift catalyst and the electrode structure for further investigation of hydrogen production and separation processes.

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