Supporting Information for

A NiRhS Fuel Cell Catalyst -Lessons from Hydrogenase

Seiji Ogo,* Tatsuya Ando, Le Tu Thi Minh, Yuki Mori, Takahiro Matsumoto, Takeshi Yatabe, Ki-Seok Yoon, Yukio Sato, Takashi Hibino and Kenji Kaneko

> *To whom correspondence should be addressed. E-mail: ogo.seiji.872@m.kyushu-u.ac.jp

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Experimental Section

Materials and Methods. All experiments were carried out under an N₂ atmosphere using standard Schlenk techniques and a glovebox. H₂ (99.9999%), D₂ (99.5%), and O₂ gas (99.9999%) were purchased from Sumitomo Seika Chemical Co., Ltd. ¹⁸O₂ (98 atm%) was purchased from Shoko Co., Ltd. H₂¹⁸O (98 atm%) was purchased from Taiyo Nippon Sanso Co., Ltd. D₂O (99.9%) was purchased from Cambridge Isotope Laboratories, Inc. Distilled water and NaOH were purchased from Wako Pure Chemical Industries, Inc. 2,6-Dichlorobenzeneindophenol (DCIP) was purchased from Sigma-Aldrich. Methylene blue trihydrate {3,7-bis(dimethylamino)-5-phenothiazinium chloride trihydrate, [MB](Cl)·3H₂O} was purchased from FUJIFILM Wako Pure Chemical Corporation. Carbon black MSC-30 was purchased from Kansai Coke and Chemicals Company, Limited. Platinum carbon (Pt/C, Pt : C = 46.1 : 53.9%) was purchased from Tanaka Kikinzoku Kogyo K.K. Waterproof carbon cloth (EC-CC1-060T) was purchased from TOYO corporation. Proton-conducting polymer electrolyte (Nafion NRE212) and Nafion 5wt% dispersion solution were purchased from Aldrich. These were used without further purification except Nafion NRE212, which is purified as described below. $[Rh^{III}(\eta^5-C_5Me_5)Cl_2]_2$ and $[Ni^{II}(X)]$ (X = N,N-dimethyl-3,7-diazanonane-1,9-dithiolato) were prepared by the previous method.^{1,2}

¹H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer at 25 °C. ¹H NMR experiments in D₂O were measured using 3-(trimethylsilyl)-propionic-2,2,3,3-*d*₄ acid sodium salt (TSP) as an internal standard. Electrospray ionization mass spectrometry (ESI-MS) data were obtained by a JEOL JMS-T100LC AccuTOF. IR spectra were recorded on a Thermo Nicolet NEXUS 8700 FT-IR instrument (as a KBr disk) and PerkinElmer Spectrum Two (as a solid state). UV-vis spectra were recorded on a JASCO V-670 UV-Visible-NIR Spectrophotometer (light pass length: 0.10 cm). Elemental analysis data were obtained by a Yanaco CHN-coder MT-5 and a PerkinElmer 2400II series CHNS/O analyzer using He as a carrier gas. Gas chromatography mass spectrometry (GC-MS) data were recorded on a SHIMADZU GCMS-QP 2010. Thermal properties of [Ni^{II}Cl(χ)Rh^{III}Cl(η ⁵–C₅Me₅)] (1) were analyzed under an N₂ atmosphere by thermogravimetry-differential scanning calorimetry (TG-DSC) using a NETZSCH STA 449 F3 Jupiter. N₂ flow rate is 100 mL min⁻¹. The mixture of complex **1** (5.0 mg) and carbon black (5.0 mg) is loaded in alumina ceramic crucibles. The measurements were done with a heating temperature rate of 10 °C min⁻¹. X-ray photoelectron (XP)

spectra were recorded on an ULVAC PHI 5000 VersaProbe II system with an Al anode X-ray source. Binding energies were calibrated by the Au $4f_{7/2}$ peak of Au atoms of gold powder, which is mixed with samples, at 84.0 eV.³ X–ray diffraction (XRD) patterns were measured using an X–ray diffractometer (Rigaku SmartLab) with Cu–K α radiation generated at 45 kV and 200 mA {scan speed: 0.02° min⁻¹ ($2\theta = 20-90^{\circ}$)}. In addition to the acquisition of bright-field (BF) images by transmission electron microscope (TEM), both annular dark field (ADF) images and energy-dispersive X-ray spectroscopy (EDS) mappings were performed with an aberration-corrected scanning transmission electron microscope (STEM) using a JEOL JEM-ARM 200F equipped with a JEOL silicon drift detector (SDD) and a JEOL JED-2300T system. Polarization and power density curves and impedance spectra were recorded on a TOYO Corporation Fuel Cell Test System APM-09 and a Solartron Model 1287A Potentiostat/Galvanostat and 1255B Frequency Response Analyzer.

[Ni^{II}Cl(X)Rh^{III}Cl(η^5 –C₅Me₅)] (1). A methanol solution (5 mL) of [Ni^{II}(X)] (27.9 mg, 0.10 mmol) was added to a solution of [Rh^{III}(η^5 –C₅Me₅)Cl₂]₂ (30.9 mg, 0.05 mmol) in a mixed solution of methanol (5.0 mL) and acetonitrile (3.0 mL). The resulting solution was stirred for 1 h at room temperature. The solvents were removed by evaporation to yield a brown solid, which was purified by recrystallization from acetone/diethyl ether solution {yield: 51% based on [Rh^{III}(η^5 –C₅Me₅)Cl₂]₂}. Diffusion of diethyl ether into acetone solution of **1** gave its single crystal suitable for X-ray analysis. ¹H NMR (300 MHz, in D₂O, referenced to TSP, 25 °C): δ 1.70 {s, 15H, C₅(CH₃)₅}, 1.60–3.68 (m, 14H, –CH₂–), 2.70 (s, 6H, N–CH₃). IR (cm⁻¹, solid state): 2987 (w, aliphatic C–H), 2960 (w, aliphatic C–H), 2915 (m, aliphatic C–H), 2852 (m, aliphatic C–H), 2811 (w, aliphatic C–H), 1493 (w, aromatic C=C), 1460 (s, aromatic C=C), 1446 (s, aromatic C=C), 1372 (s, aromatic C=C). ESI-MS (in methanol): *m/z* 551.1 {[**1** – Cl]⁺, relative intensity (*I*) = 100% in the range *m/z* 200–2000}. Anal. Calcd for **1** (C₁₉H₃₅N₂Cl₂S₂NiRh): C, 38.80; H, 6.00; N, 4.76%. Found: C, 38.79; H, 5.98; N, 4.74%.

[Ni^{II}Cl(X)(μ -H)Rh^{III}(η^5 -C₅Me₅)] (2). [Ni^{II}Cl(X)Rh^{III}Cl(η^5 -C₅Me₅)] (1) (29.5 mg, 0.50 mmol) was dissolved in water (5.0 mL) at pH 7.0 (20 mM phosphate buffer) and stirred for 24 h under an H₂ atmosphere (0.1–0.8 MPa) at room temperature. The solvent was evaporated, and acetone was added into the residue. The acetone solution was collected by decantation (4 × 1.0 mL). The solvent was removed by evaporation to provide 2, which was dried in vacuo (yield: 89% based on 1). A single crystal

suitable for X-ray analysis was obtained from acetone/acetonitrile solution at 25 °C. FT-IR (cm⁻¹, KBr disk): 2982 (m, aliphatic C–H), 2955 (m, aliphatic C–H), 2919 (s, aliphatic C–H), 2878 (aliphatic C–H), 2850 (s, aliphatic C–H), 1801 (s, Ni–H–Rh), 1633 (m, aromatic C=C), 1469 (s, aromatic C=C), 1460 (s, aromatic C=C), 1449 (s, aromatic C=C), 1427 (s, aromatic C=C), 1378 (s, aromatic C=C). ESI-MS (in acetonitrile): m/z 517.1 ([**2** – Cl]⁺, I = 100% in the range m/z 200–2000). Anal. Calcd for **2** (C₁₉H₃₆N₂ClS₂NiRh): C, 41.22; H, 6.55; N, 5.06%. Found: C, 41.37; H, 6.49; N, 4.86%.

[Ni^{II}Cl(X)(μ –D)Rh^{III}(η^5 –C₅Me₅)] (D-labelled 2). D-labelled 2 was prepared by the same method for the synthesis of 2 except the use of D₂ instead of H₂. FT-IR (cm⁻¹, KBr disk): 1292 (Ni–D–Rh). ESI-MS (in acetonitrile): *m/z* 518.1 ([D-labelled 2]⁺, *I* = 100% in the range *m/z* 200–2000).

Preparation of Dry-Distilled Catalysts (DDCs). Mixtures of $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (5.0 mg) and carbon black (5.0 mg) were put on apparatus. The apparatus was vacuumed until the pressure was around 15–20 Pa and heated at 100–800 °C under reduced pressure (ca. 15–20 Pa) for 1 h to generate dry-distilled catalysts (DDCs). After heat treatment, the apparatus was cooled to room temperature.

Stoichiometric Reduction of 2,6-Dichlorobenzeneindophenol (DCIP) with 2 in the Absence of H₂. An aqueous solution of DCIP (0.102 µmol) and $[Ni^{II}Cl(X)(\mu-H)Rh^{III}(\eta^5-C_5Me_5)]$ (2) (0.102 µmol) was stirred in water (0.60 mL) at pH 7.0 (25 mM phosphate buffer) at room temperature for 35 min under an N₂ atmosphere. The solution was filtrated and analyzed by UV-vis spectroscopy and ESI-MS spectrometry. The yield of two-electron reduced-form of DCIP (DCIPH₂) was determined as 78% based on 2 by UV-vis spectroscopy. It was confirmed that no reduction of DCIP occurred in the absence of 2 (as blank experiments).

Catalytic Reduction of DCIP with 1 in the Presence of H₂. An aqueous solution of DCIP (0.92 μ mol) and [Ni^{II}Cl(X)Rh^{III}Cl(η^5 -C₅Me₅)] (1) (0.034 μ mol) was stirred in water (0.60 mL) at pH 3.0–9.0 (25 mM buffer solution) at 25 °C for 2 h under an H₂ atmosphere (0.1 MPa). The pH of resulting solution was adjusted to pH 10 by addition of 1.0 M NaOH/H₂O. The turnover number (TON, mol of DCIPH₂/mol of 1) of two-electron reduced-form of DCIP (DCIPH₂) based on 1 was determined by UV-vis spectroscopy. It was confirmed that no reduction of DCIP occurred in the

absence of 1 and/or H₂ (as blank experiments).

Catalytic Reduction of Methylene Blue ([MB]⁺) with 1 in the Presence of H₂. An aqueous solution of [MB]⁺ (4.25 μ mol) and [Ni^{II}Cl(X)Rh^{III}Cl(η^5 -C₅Me₅)] (1) (0.14 μ mol) was stirred in water (2.5 mL) at pH 5.0 (25 mM acetate buffer) at 30 °C for 6 h under an H₂ atmosphere (0.1 MPa). The resulting solution was filtrated and a 40 μ L portion of it was diluted with water at pH 5.0 (25 mM acetate buffer) to 400 μ L. The turnover number {TON, mol of MBH/mol of 1} of two-electron reduced-form of [MB]⁺ (leucomethylene blue, MBH) based on 1 was determined by UV-vis spectroscopy. It was confirmed that no reduction of [MB]⁺ occurred in the absence of 1 and/or H₂ (as blank experiments).

Reaction of 2 with O₂ in the Absence of H₂. O₂ (2 mL) was injected into an aqueous solution (0.50 mL) of $[Ni^{II}Cl(X)(\mu-H)Rh^{III}(\eta^5-C_5Me_5)]$ (2) (1.41 mg, 2.55 μ mol) at pH 8.0 (25 mM phosphate buffer) and stirred at 40 °C for 45 min under an N₂ atmosphere. A portion (0.1 mL) of the resulting solution was diluted with water at pH 8.0 (25 mM phosphate buffer) up to 0.5 mL and analyzed by ESI-MS. As a result, 1-derived complex was observed, which should be formed from the reduction of O₂ by the hydride ligand of **2**.

Stoichiometric Reduction of ¹⁸O₂ to H₂¹⁸O with 2 in the Absence of H₂. ¹⁸O₂ (2 mL) was injected into an aqueous solution (0.50 mL) of $[Ni^{II}Cl(X)(\mu-H)Rh^{III}(\eta^5-C_5Me_5)]$ (2) (2.85 mg, 5.1 µmol) at pH 7.0 (25 mM phosphate buffer) and stirred at 25 °C for 5 h under an N₂ atmosphere. The resulting solution was passed through a short silica column to remove complex(es). H₂¹⁸O was detected by GC-MS.

Reduction of ¹⁸O₂ to H₂¹⁸O with 1 in the Presence of H₂ in Water. H₂ was bubbled through an aqueous solution (0.50 mL) of [Ni^{II}Cl(X)Rh^{III}Cl(η^5 -C₅Me₅)] (1) (1.5 mg, 2.55 µmol, 5.1 mM) at pH 7.0 (25 mM phosphate buffer) for 20 min. ¹⁸O₂ (2 mL) was injected into the resulting solution, and the resulting solution was stirred at 25 °C for 5 h. The resulting solution was passed through a short silica column to remove complex(es). The amount of H₂¹⁸O in the resulting solution was quantified by GC-MS. The TON [{(mol of H₂¹⁸O)/(mol of 1)}/2] was determined as 0.5 based on 1. Four-electron reduction of one molecule of O₂ to two molecules of H₂O corresponds to TON = 1.

Catalytic Reduction of $[MB]^+$ with the DDC Prepared at 600 °C in the Presence of H₂. An aqueous suspension of $[MB]^+$ (4.25 µmol) and the DDC prepared at 600 °C (0.11 mg, 0.14 µmol, mol of the DDC means mole of 1 before dry distillation

because it is valid to compare the NiRh-based catalytic activities, where the NiRh metals should remain after dry distillation) was stirred in water (2.5 mL) at pH 5.0 (25 mM acetate buffer) at 30 °C for 6 h under an H₂ atmosphere (0.1 MPa). The resulting suspension was filtrated and a 40 μ L portion of it was diluted with water at pH 5.0 (25 mM acetate buffer) to 400 μ L. The turnover number {TON, mol of MBH/mol of DDC} of two-electron reduced-form of [MB]⁺ (leucomethylene blue, MBH) based on the DDC was determined by UV-vis spectroscopy. It was confirmed that no reduction of [MB]⁺ occurred in the absence of the DDC (as blank experiments).

Reduction of ¹⁸O₂ to H₂¹⁸O in the Presence of H₂ in Water with the DDC Prepared at 450 °C. H₂ was bubbled through an aqueous suspension (0.50 mL) of the DDC prepared at 450 °C (2.0 mg, 2.55 µmol, mol of the DDC means mole of **1** before dry distillation because it is valid to compare the NiRh-based catalytic activities, where the NiRh metals should remain after dry distillation) at pH 7.0 (25 mM phosphate buffer) for 20 min. ¹⁸O₂ (2 mL) was injected into the suspended solution. The resulting suspension was stirred at 25 °C for 5 h and then it was passed through a short silica column to remove catalyst(s). The amount of H₂¹⁸O in the resulting solution was quantified by GC-MS. The TON [{(mol of H₂¹⁸O)/(mol of DDC)}/2] was determined as 1.7 based on the DDC. Four-electron reduction of one molecule of O₂ to two molecules of H₂O corresponds to TON = 1.

pH Adjustment. The pH of the solution was adjusted by using glycine– hydrochloric acid buffer (pH 3.0), acetate buffer (pH 4.0–5.0), phosphate buffer (pH 6.0–8.0) and carbonate buffer (pH 9.0). In a pH range of 3.0–9.0, the pH values of the solutions were determined by a pH meter (IQ Scientific Instruments, Inc., IQ200) equipped with a stainless steel micro pH probe (IQ Scientific Instruments, Inc., PH15-SS).

Preparation of NiRh Anode with 1. $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (5.0 mg) and carbon black (5.0 mg) were mixed, and the mixture was loaded on a waterproof carbon cloth (5 cm²) to make a gas diffusion electrode.

Preparation of DDC Anodes. DDCs, which were prepared from mixture of $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (5.0 mg) and carbon black (5.0 mg) at 100–800 °C, were loaded on a waterproof carbon cloth (5 cm²) to make a gas diffusion electrode.

Preparation of NiRh Cathode with 1. $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (5.0 mg) and carbon black (5.0 mg) were mixed, and the mixture was loaded on a waterproof carbon cloth (5 cm²) to make a gas diffusion electrode.

Preparation of DDC Cathodes. DDCs, which were prepared from mixture of $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (5.0 mg) and carbon black (5.0 mg) at 100–800 °C, were loaded on a waterproof carbon cloth (5 cm²) to make a gas diffusion electrode.

Preparation of Pt/C Anode and Cathode. To a Nafion solution (59 mg) was added Pt/C (11 mg), in which a Nafion-to-carbon ratio is 2, and the resulting suspension was sonicated for 1 h. The suspension was loaded on a waterproof carbon cloth (5 cm²) to make a gas diffusion electrode. The loading of Pt is 1.0 mg cm⁻².

Membrane Electrode Assembly (MEA) and Fuel Cell Assembly. The Nafion membrane NRE212 was boiled in 3% H_2O_2/H_2O for 1 h, 1.0 M H_2SO_4/H_2O for 1 h, and distilled water for 1 h. A piece of the pretreated Nafion NRE212 was sandwiched between two gas diffusion electrodes that are prepared by the above procedure to obtain MEA and the MEA was assembled in 5 cm² fuel cell hardware.

Polarization Measurement. Fuel cell polarization curves were measured on the 2-electrode setup by connecting RE1 and CE to anode and connecting RE2 and WE to cathode, where the current and voltage values were recorded using linear sweep voltammetry.

Electron Microscopic Analysis. TEM and STEM observations were carried out using a JEOL JEM-ARM200F electron microscope equipped with a CEOS spherical aberration corrector for an electron probe. EDS mappings were measured using a JEOL JED-2300T system that is attached to the JEM-ARM200F. TEM and STEM observations were conducted at an acceleration voltage of 200 kV. TEM images were acquired with a Gatan Orius 200D charge-coupled-device camera. STEM images were recorded using an annular dark-field detector, a Gatan DigiscanII system, and Gatan DigitalMicrograph software.

X-ray Crystallographic Analysis. A single crystal of 1 was obtained from an acetone solution diffused by diethyl ether under an N₂ atmosphere. A single crystal of 2 was obtained from a mixture of acetonitrile and acetone solution under an N₂ atmosphere. Measurements were made on a Rigaku/MSC Saturn CCD diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71070$ Å). Data were collected and processed using the CrystalClear program. All calculations were performed using

the teXsan crystallographic software package of Molecular Structure Corp. or the CrystalStructure crystallographic software package except for refinement, which was performed using SHELXL-97. Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre under reference numbers CCDC-1996959 and 1996960, respectively.

Entry	Anode Catalyst	Cathode Catalyst	Current Density of Fuel Cell (mA cm ⁻² at	Current Density of Half Cell (mA cm ⁻² at 0.4 V vs RHE ^[a])		Ref. and [Ref. in manuscript]
			0.4 V)	Anode	Cathode	
0 ^[b]	Pt	Pt	231	330 (at 0.2 V vs RHE)	255	This work
1A	NiRh sulfide	Pt	10	37	_	This work
1B	Pt	NiRh sulfide	53	_	27	This work
2	NiRh sulfide	Carbon	_	0.022 (at 0.2 V vs RHE)	_	4 [6a]
3	Pt	NiRh sulfide	_	_	155	5 [6b]
4	Pt	NiCo sulfide	_	_	4.8	6 [6c]
5 ^[c]	RhPt sulfide	Carbon	105 (at 0.8 V)	_	_	7 [6d]
6 ^[d]	Pt-Ru/C	RhRu sulfide	27	_	_	8 [6e]
7	Pt	FeCo sulfide	_	_	5.5	9 [6f]
8 ^[e]	Microbes	FeCo sulfide	0.31	_	_	10 [6g]
9 ^[e]	Microbes	FeAg sulfide	0.33	_	_	11 [6h]
10 ^[e]	Pt	FeAg sulfide	_	_	3.4	11 [6h]
11	Pt	FeCo sulfide	_	_	5.3	12 [6i]

Table S1 Competitive Analysis of Current Densities of H₂-O₂ Fuel Cells and Half Cells with Heterogeneous Heterometallic Sulfide Catalysts.

[a] RHE: Reversible hydrogen electrode. [b] As a reference under the same conditions as entries 1A and 1B. [c] A H₂-Br₂ fuel cell. [d] A direct methanol fuel cell. [e] A microbial fuel cell.

	Ni ^{II} Rh ^{III} Dichloride Complex 1	Ni ^{II} Rh ^{III} Hydride Complex 2
X-ray	Figure S2	Figure 1
ESI-MS	Figure S3	Figure S7
¹ H NMR	Figure S4	_ [a]
IR	Figure S5	Figure S8
UV-vis	Figure S6	Figure S6
TG-DSC	Figures 3 and S13	_

 Table S2 Characterization of Complexes 1 and 2.

[a] Complex 2 is paramagnetic.

	H ₂ -Oxidation Process		O ₂ -Reduction Process	
	$1 \rightarrow 2$	$2 \rightarrow 1$	$1 \rightarrow 2$	$2 \rightarrow 1$
UV-vis	Figure S6	Figure S9	Figure S6	_
ESI-MS	Figure S7	Figure S10	Figure S7	Figure S12
FT-IR	Figure S8	_	Figure S8	_

Table S3 Analysis of Change from 1 to 2 (or 2 to 1).

Table S4 TONs for Catalytic Reactions in Flask or Maximum Power Density of Fuel Cellwith 1 or the DDC (Dry-Distilled Catalyst).

	1	DDC
TON for H ₂ -Oxidation in Flask Experiments	Figure S11 and Table S7	Table S7
TON for O ₂ -Reduction in Flask Experiments	Table S7	Table S7
Maximum Power Density of H_2 - O ₂ Fuel Cell with the Catalyst as the Anode (mW cm ⁻²)	Figures 5a and S18a Table S8	Figures 5a and S18b Table S8
Maximum Power Density of H_2 - O ₂ Fuel Cell with the Catalyst as the Cathode (mW cm ⁻²)	Figures 5b and S19a Table S8	Figures 5b and S19b Table S8
Maximum Power Density of H_2 - O ₂ Fuel Cell with the Catalyst as both the Anode and the Cathode (mW cm ⁻²)	Figure S22a Table S8	Figure S22b Table S8

	DDC
Elemental Analysis	Figure 3 and Table S6
XPS	Figure S14
XRD	Figure S15
BF-TEM	Figures 4 and S16
ADF-STEM	Figures 4 and S16
STEM-EDS	Figures 4 and S16

 Table S5 Characterization of the DDC (Dry-Distilled Catalyst).

Entry	Dry Distillation	Elemental	Elemental Content (wt%)			
	Temperature (°C)	С	Н	Ν	S	
1	Not Heated	68.02	2.91	2.40	5.36	
2	200	67.38	2.82	2.30	5.40	
3	300	73.31	0.85	0.25	5.52	
4	450	71.72	0.33	0.17	5.53	
5	600	74.20	0.28	0.21	5.24	
6	800	75.10	0.13	0.11	3.88	

Table S6 Elemental Analysis of a Mixture of 1 and Carbon Black in a Weight Ratio of1:1 according to the Heating Temperature.

Entry	Catalytic	Catalyst	Dry Distillation	pН	TON
	Reaction		Temperature (°C)		
1	H ₂ -oxidation ^[a]	Complex 1	Not Heated	5.0	4.0 ^[b]
2	H ₂ -oxidation ^[a]	DDC	600	5.0	17 ^[b]
3	¹⁸ O ₂ -reduction ^[c]	Complex 1	Not Heated	7.0	0.48 ^[d]
4	¹⁸ O ₂ -reduction ^[c]	DDC	450	7.0	1.7 ^[d]

Table S7 TONs for Catalytic Reactions Depending on Dry Distillation Temperatures inFlask Experiments in Water.

[a] TONs for H₂-oxidation are determined by using methylene blue [MB]⁺ as an electron acceptor.

[b] The turnover numbers {TONs, mol of MBH/mol of catalyst} of two-electron reducedform of [MB]⁺ (leucomethylene blue, MBH) based on 1 or the DDC were determined by UV-vis spectroscopy. The number of moles of DDC was estimated from the number of moles of 1.

[c] The ¹⁸O₂-reduction using **1** or the DDC with H_2 in water were confirmed by an ¹⁸O₂experiment wherein $H_2^{18}O$ was formed as an electron donor, as observed by gas chromatography mass spectrometry (GC-MS).

[d] The turnover numbers (TONs, [(mol of $H_2^{18}O$)/(mol of catalyst)]/2) were determined based on 1 or the DDC. The number of moles of DDC was estimated from the number of moles of 1.

Entry	Anode Catalyst	Cathode Catalyst	OCV	Maximum
			(V)	Power Density
				$(mW cm^{-2})$
1	1	Pt	0.57	0.0296
2	DDC at 100 °C	Pt	0.66	0.0149
3	DDC at 200 °C	Pt	0.60	0.00738
4	DDC at 300 °C	Pt	1.01	1.82
5	DDC at 400 °C	Pt	1.01	3.73
6	DDC at 500 °C	Pt	1.01	3.86
7	DDC at 600 °C	Pt	1.00	4.85
8	DDC at 700 °C	Pt	0.98	4.77
9	DDC at 800 °C	Pt	0.95	4.72
10	Pt	1	0.57	0.188
11	Pt	DDC at 100 °C	0.51	0.157
12	Pt	DDC at 200 °C	0.66	0.154
13	Pt	DDC at 300 °C	0.76	19.8
14	Pt	DDC at 400 °C	0.75	24.1
15	Pt	DDC at 500 °C	0.76	24.0
16	Pt	DDC at 600 °C	0.78	26.1
17	Pt	DDC at 700 °C	0.79	26.0
18	Pt	DDC at 800 °C	0.77	23.8
19	1	1	0.40	0.0101
20	DDC at 600 °C	DDC at 600 °C	0.78	4.53
21	Pt	Pt	0.99	92.5

Table S8 H_2 - O_2 Fuel Cell Performances with 1, the DDC or Pt as Anode and/or Cathode Catalysts.

Entry	Catalytic	Anode	Cathode	Exchange Current	
	Reaction	Catalyst	Catalyst	Density (mA cm ⁻²)	
1	H ₂ -Oxidation	1	Dt	0.0286	
1	(anode)	1	1 t	0.0280	
2	H ₂ -Oxidation	DDC at 600 °C	Dt	12.0	
2	(anode)	DDC at 000 C	FL	13.7	
2	O ₂ -Reduction	Dt	1	0.0161	
3	(cathode)	FL	1	0.0101	
4	O ₂ -Reduction	D+	DDC at 600 °C	10.5	
	(cathode)	FL	DDC at 600°C	10.5	

 Table S9 Exchange Current Densities of Catalytic Reactions with 1 and the DDC.



Fig. S1 Competitive analysis of current densities of H_2 - O_2 fuel cells and half cells with heterogeneous heterometallic sulfide catalysts. The current densities (mA cm⁻²) were obtained at cell voltages of 0.4 V in fuel cells except for entry 5 where the current density was obtained at cell voltages of 0.8 V in fuel cells. The current densities (mA cm⁻²) were obtained at 0.4 V vs RHE (Reversible hydrogen electrode) in half cells except for the HOR (H₂-oxidation reaction) at the anode in entries 0 and 2 where the current densities were obtained at 0.2 V vs RHE. The entry numbers and current densities shown in Fig. S1 are consistent with Table S1. Entry 5 is a H₂-Br₂ fuel cell. Entry 6 is a direct methanol fuel cell. Entries 8, 9 and 10 are microbial fuel cells.



Fig. S2 ORTEP drawing of 1 with ellipsoids set at the 50% probability level. The hydrogen atoms of the ligand X (N,N'-dimethyl-3,7-diazanonane-1,9-dithiolato) and C₅Me₅ are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ni1…Rh1 3.376(1), Ni1–S1–Rh1 90.47(4), Ni1–S2–Rh1 90.45(4).



Fig. S3 a) A positive-ion electrospray ionization (ESI) mass spectrum of 1 in methanol. The signal at m/z 551.1 corresponds to $[1 - Cl]^+$. b) Signal at m/z 551.1 for $[1 - Cl]^+$. c) Calculated isotope distribution for $[1 - Cl]^+$.



Fig. S4 A ¹H NMR spectrum of **1** in D₂O. 3-(Trimethylsilyl)-propionic-2,2,3,3- d_4 acid sodium salt (TSP), reference with the methyl proton resonance set at 0.00 ppm. †: water.



Fig. S5 An IR spectrum of 1 as a solid state.



Fig. S6 UV-vis spectra of a) **1** (0.17 mM) and b) **2** (0.17 mM) in water at pH 7.0 (20 mM phosphate buffer) at 25 °C. Light pass length: 0.10 cm.



Fig. S7 a) A positive-ion electrospray ionization (ESI) mass spectrum of **2** in acetonitrile. The signal at m/z 517.1 corresponds to $[\mathbf{2} - \text{Cl}]^+$. b) Signal at m/z 517.1 for $[\mathbf{2} - \text{Cl}]^+$. c) Calculated isotope distribution for $[\mathbf{2} - \text{Cl}]^+$. d) A positive-ion ESI mass spectrum of Dlabelled **2** in acetonitrile. The signal at m/z 518.1 corresponds to [D-labelled $\mathbf{2} - \text{Cl}]^+$.



Fig. S8 IR spectra of a) 2 and b) D-labelled 2 as KBr disks. c) The difference spectrum between a) and b).



Fig. S9 a) A UV-vis spectrum of 2,6-dichlorobenzeneindophenol (DCIP) (0.17 mM) in water at pH 7.0 (25 mM phosphate buffer) as a blank experiment without 2. b) A UV-vis spectrum obtained from the reaction of 2 (0.17 mM) with one equivalent of DCIP (0.17 mM) in water at pH 7.0 (25 mM phosphate buffer) at room temperature for 35 min under an N₂ atmosphere to form DCIPH₂ (two-electron reduced-form of DCIP). Light pass length: 0.10 cm.



Fig. S10 a) A positive-ion electrospray ionization (ESI) mass spectrum obtained from the reaction of 2 (0.17 mM) with one equivalent of DCIP (0.17 mM) in water at pH 7.0 (25 mM phosphate buffer) at room temperature for 35 min under an N₂ atmosphere. Before the ESI-MS measurement, the resulting solution was diluted by acetonitrile. The signal at m/z 551.0 corresponds to $[1 - Cl]^+$. b) Signal at m/z 551.0 for $[1 - Cl]^+$. c) Calculated isotope distribution for $[1 - Cl]^+$.



Fig. S11 pH-dependent TONs for reduction of DCIP (0.92 μ mol) with 1 (0.034 μ mol) under an H₂ atmosphere (0.1 MPa) in water (0.6 mL) at pH 3.0–9.0 (buffer solution) at 25 °C for 2 h.



Fig. S12 a) A positive-ion electrospray ionization (ESI) mass spectrum of 1 in water at pH 8.0 (25 mM phosphate buffer) obtained from the reaction of 2 (5.1 mM) with O₂ (2 mL) in water at pH 8.0 (25 mM phosphate buffer) at 40 °C for 45 min under an N₂ atmosphere. The signal at m/z 551.0 corresponds to $[1 - Cl]^+$. b) Signal at m/z 551.0 for $[1 - Cl]^+$. c) Calculated isotope distribution for $[1 - Cl]^+$.



Fig. S13 Thermogravimetry-differential scanning calorimetry (TG-DSC) curves of mixture of 1 (5 mg) and carbon black (5 mg) under an N_2 atmosphere (flow rate of N_2 gas: 100 mL min⁻¹, heating rate: 10 °C min⁻¹).



Fig. S14 X-ray photoelectron (XP) spectra of the Rh 3d, Ni 2p, S 2p, N1s and Cl 2p regions for **1** and the DDCs prepared at 300 °C, 450 °C, 600 °C and 800 °C.



Fig. S15 XRD patterns of 1, the DDCs prepared at 100–800 °C and carbon black.

		Complex 1	DDC prepared at 200 °C	DDC prepared at 230 °C
		(No Dry Distillation)		
BF-TEM		2 µm	50 nm	200 nm
ADF-S	TEM	200 nm	- 1.0 μm	10 nm
EDS	Rh			
	Ni			
	S			
	Line Profile			

Fig. S16 BF-TEM and ADF-STEM images with EDS elemental mappings of **1** and the DDCs prepared at 200–800 °C.

		DDC prepared at 250 °C	DDC prepared at 280 °C	DDC prepared at 300 °C
BF-TEM		200 nm	200 nm	200 nm
ADF-S	TEM	20 nm	10 nm	25 nm
EDS	Rh			
	Ni			
	S			
	Line Profile	Market and Market		

Fig. S16 (continued) BF-TEM and ADF-STEM images with EDS elemental mappings of **1** and the DDCs prepared at 200–800 °C.

		DDC prepared at 400 °C	DDC prepared at 450 °C	DDC prepared at 500 °C
BF-TEM		200 nm	200 nm	200m
ADF-STEM		20 nm	20 nm	20 nm
EDS	Rh			
	Ni			
	S			
	Line Profile			

Fig. S16 (continued) BF-TEM and ADF-STEM images with EDS elemental mappings of **1** and DDCs prepared at 200–800 °C.

		DDC prepared at 600 °C	DDC prepared at 700 °C	DDC prepared at 800 °C
BF-TEM		200 nm	200 nm	200 nm
ADF-STEM		20 nm	20 nm	20 nm
EDS	Rh			
	Ni			
	S			
	Line Profile	A CONTRACTOR OF THE REAL OF TH		

Fig. S16 (continued) BF-TEM and ADF-STEM images with EDS elemental mappings of **1** and DDCs prepared at 200–800 °C.



Fig. S17 An abstract depiction of a polymer electrolyte fuel cell. Water-saturated H_2 and O_2 gases flow through conduits in the electrodes. Complex 1 or DDC is immobilized on carbon cloth sandwiched between the electrode and the proton-conducting polymer electrolyte. Protons pass through the polymer electrolyte and electrons flow through an electrical circuit from the anode to the cathode.



Fig. S18 Polarization and power density curves at 60 °C for H₂-O₂ fuel cells. a) Anode: $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (1.0 mg cm⁻²). Cathode: Pt/C (1.0 mg_{Pt} cm⁻²). b) Anode: the DDC prepared at 600 °C. Cathode: Pt/C (1.0 mg_{Pt} cm⁻²). Active area of membrane electrolyte assembly (MEA): 5 cm². Proton-conducting polymer electrolyte: Nafion NRE212. Flow rate of water-saturated H₂ gas: 200 mL min⁻¹. Flow rate of water-saturated O₂ gas: 200 mL min⁻¹. Humidity: 100%. Carbon black: MSC-30 from Kansai Coke and Chemicals Company, Limited. Carbon cloth: TOYO Corporation EC-CC1-060T.



Fig. S19 Polarization and power density curves at 60 °C for H₂-O₂ fuel cells. a) Anode: Pt/C (1.0 mg_{Pt} cm⁻²). Cathode: $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (1.0 mg cm⁻²). b) Anode: Pt/C (1.0 mg_{Pt} cm⁻²). Cathode: the DDC prepared at 600 °C. Active area of membrane electrolyte assembly (MEA): 5 cm². Proton-conducting polymer electrolyte: Nafion NRE212. Flow rate of water-saturated H₂ gas: 200 mL min⁻¹. Flow rate of water-saturated O₂ gas: 200 mL min⁻¹. Humidity: 100%. Carbon black: MSC-30 from Kansai Coke and Chemicals Company, Limited. Carbon cloth: TOYO Corporation EC-CC1-060T.



Fig. S20 Tafel plots of H₂-oxidation with a) **1** and b) the DDC prepared at 600 °C for fuel cells comprising **1** or the DDC as the anode catalyst and Pt as the cathode catalyst (I = current, R = ohmic resistance). Tafel plots of O₂-reduction with c) **1** and d) the DDC prepared at 600 °C for fuel cells comprising Pt as the anode catalyst and **1** or the DDC as the cathode catalyst.



Fig. S21 Impedance spectra of H₂-oxidation with a) 1 and b) the DDC prepared at 600 °C for fuel cells comprising 1 or the DDC as the anode catalyst and Pt as the cathode catalyst. Impedance spectra of O₂-reduction with c) 1 and d) the DDC prepared at 600 °C for fuel cells comprising Pt as the anode catalyst and 1 or the DDC as the cathode catalyst. The spectra were measured under open-circuit conditions by changing the frequency from 0.01 to 10^5 Hz. Ohmic resistances for each measurement are less than 100 m Ω cm².



Fig. S22 Polarization and power density curves at 60 °C for H₂-O₂ fuel cells. a) Anode and cathode: $[Ni^{II}Cl(X)Rh^{III}Cl(\eta^5-C_5Me_5)]$ (1) (1.0 mg cm⁻²). b) Anode and cathode: the DDC prepared at 600 °C. Active area of membrane electrolyte assembly (MEA): 5 cm². Proton-conducting polymer electrolyte: Nafion NRE212. Flow rate of water-saturated H₂ gas: 200 mL min⁻¹. Flow rate of water-saturated O₂ gas: 200 mL min⁻¹. Humidity: 100%. Carbon black: MSC-30 from Kansai Coke and Chemicals Company, Limited. Carbon cloth: TOYO Corporation EC-CC1-060T.

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