A CO-Tolerant Electrocatalyst Based on Platinum and Organic Metal Clusters for Reformate Fuel Cells

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CO–tolerant anode catalysts for reformate-type polymer electrolyte fuel cells are proposed and evaluated in comparison with Pt–Ru alloy catalysts. Composite catalysts were fabricated by mixing platinum precursor and organic metal clusters on carbon and then heat-treating in Ar atmosphere at 400–500°C. CO tolerance tests were conducted in the electrochemical cell using a rotating disk electrode. Also, the anode half-cell and the single fuel cell performances were measured at 70°C with H_2 containing various levels of CO. Compared with commercial Pt–Ru/C catalysts, this class of anode catalysts proved to be promising as CO-tolerant anode catalysts.
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Polymer electrolyte fuel cells (PEFCs) are considered as promising power sources for stationary and residential applications.[1] For such systems, the city gas and methane is reformed into hydrogen and CO_2 and then fed to PEFC. During the reforming process, CO emerges as an impurity and comes into the anode gas chamber. CO blocks the active sites of Pt electrocatalysts and causes serious degradation in the electrode performance of the fuel cell anode.[2] It is thus necessary to develop CO-tolerant catalyst materials which can endure CO poisoning at a level of 100 ppm. CO-tolerant electrocatalysts have been prepared by combinations of Pt with less noble elements, such as ruthenium, tin, molybdenum, and other transition metals.[3,4] Pt–Ru supported on carbon (Pt–Ru/C) has been developed as one of the most promising electrocatalysts for applications as CO-tolerant anode materials in PEFCs.[5,6] However, the cell voltage with 100 ppm CO compared to pure hydrogen obtained with Pt–Ru/C anode is still too far from that acceptable for practical applications. Dissolution of alloy elements during PEFC operation is another problem when degradation of PEFC becomes an issue.[7]

Okada et al. have reported that Pt–VO(salen)/C and Pt–Ni(mqph)/C revealed high CO tolerance compared with Pt/C and PtRu/C alloy catalysts.[8-11] It is considered that anode catalysts consisting of Pt and organic metal complexes are expected to be good candidates as the CO-tolerant anode catalysts of PEFCs.

In this paper, composite electrocatalysts based on Pt and organic metal clusters are prepared and their CO tolerance in hydrogen oxidation reaction (HOR) is studied with a rotating disk electrode in a glass electrochemical cell. The gas-phase tests are performed using a membrane electrode assembly in a half-cell and a single fuel cell system. The metal complex used in this work is a hexanuclear cluster $[Ln_2Cu_4(fsaaep)_4(NO_3)_6]$, which has a unique structure in that the lanthanoid element Ln bridges two CuN_2O_2 chelate units, and two Lns are located on both sides of the double layer containing the four Cu chelates (Fig. 1).[12] Because the structure contains four CuN_2O_2 units, it is strongly expected that OH (and CO) species will interact with these metal chelates and show CO eliminating action when used as a co-catalyst with Pt. The interatomic distances between four Cu chelates is manipulated by selecting the lanthanoid elements.

Experimental

The compound $[Ln_2Cu_4(fsaaep)_4(NO_3)_6]$, abbreviated as $[Ln_2Cu_4(fsaaep)_4]$, where fsaaep=Schiff's base compound between 3-formilsalicylic acid and 2-(2-aminoethyl)pyridine, was synthesized following the procedure reported by Kahn et al.[12] As lanthanoid elements, lutetium (Lu), praseodymium (Pr), and gadolinium (Gd) were incorporated by reacting the precursor compound $Cu(fsaaep)_2·5H_2O$ with $Lu(CH_3COO)_3·4H_2O$ and $Ln(NO_3)_3$ (Ln = Pr,Gd) in acetonitrile at room temperature.[12] Resulting green precipitates were collected and dried in a vacuum oven at 60°C.

Composite catalysts of 20 wt % Pt amount on carbon was prepared from a mixture of platinum precursor $Pt(NH_3)_4Cl_2·xH_2O$, organic metal complex $[Ln_2Cu_4(fsaaep)_4]$, and the carbon black powder (Vulcan XC-72R) in 1:1:1.3 mass ratio. The powder was dispersed in ethanol, dried in air at 40°C for 60 min, and then subjected to heat-treatment in Ar stream at 400–500°C for 2 h in a furnace.

HOR of electrocatalysts was tested using a rotating disk electrode (RDE) equipped with a three-electrode glass cell in 0.1 mol dm^{-3} $HClO_4$ at 25°C under the bubbling of pure hydrogen or a mixture of 1% CO with H_2. Catalysts were loaded on a glassy carbon disk electrode with a Pt amount of 2.5×10^{-2} mg(Pt) cm^{-2} (apparent area) with diluted (1:50) 5% Nafion solution (Aldrich). The working electrode was the catalyst-supported glassy carbon disk, the counter electrode was the platinum plate, and reversible hydrogen electrode (RHE) was used as the reference electrode. Polarization curves were recorded at the scan rate of 5 mV s^{-1}, and the current at 0.1 V vs RHE was sampled for evaluation of HOR current.

CO tolerance tests for anode catalysts in a gas phase were conducted with a homemade Teflon half-cell equipped with a platinum mesh counter electrode, RHE, and the working electrode in 1 mol dm^{-3} $HClO_4$.[9] The catalyst powder (30 mg) was mixed with 5 wt % Nafion solution (Aldrich) (500 mg) and ethanol (30 mg) to make a catalyst ink. This ink was pasted on a carbon paper (Toray TGP-H-090) that was wet-proof treated with poly(tetrafluoroethylene) (3.3×10^{-3} g cm^{-2}) to prepare the anode electrode.[11] The amount of Pt in the mixed catalyst was 0.3–0.5 mg(Pt) cm^{-2} for the apparent electrode area. The membrane electrode assemblies (MEAs) were prepared by hot-pressing the electrode on one side of a cleansed Nafion 115 membrane at 135°C and 10 MPa for 3 min, and this half-MEA served as the working electrode. The PEFC polarization experiment was carried out using a potentiostat (ALS model 701A), with the cell at 70°C under the flow of pure hydrogen or a mixture of H_2 with 10, 50, or 100 ppm CO in the anode.

Catalyst samples were also evaluated with a single fuel cell mode with 4 cm^2 MEA. The anode was loaded with 20%Pt–$[Ln_2Cu_4(fsaaep)_4]$/C or 20%Pt–10%Ru/C (Johnson Matthey) catalysts on wet-proofed carbon paper (Toray TGP-H-090), with a Pt amount of 3×10^{-4} g(Pt) cm^{-2}, and the cathode was loaded with 20% Pt/C on carbon paper [1×10^{-3} g(Pt) cm^2, ElectroChem]. MEA was prepared by hot-pressing the anode and the cathode
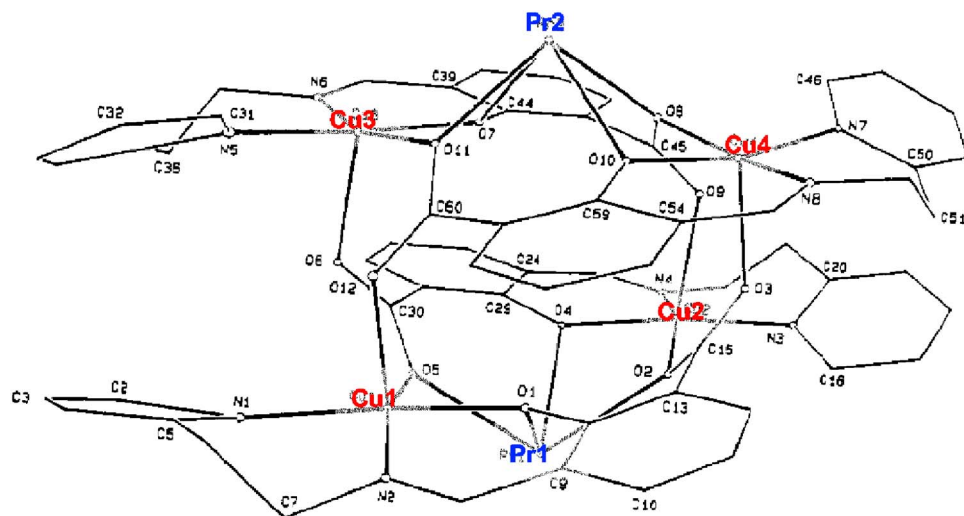
Figure 1. (Color online) View of hexa-nuclear cluster $Ln_2Cu_4(fsaaep)_4(NO_3)_6$.[12]

catalyst-loaded carbon paper (2×2 cm^2) to each side of the Nafion 115 membrane at the pressure of 10 MPa at 135°C for 3 min.

Results and Discussion

Figure 2 shows polarization curves of HOR in 0.1 mol dm^{-3} HClO$_4$ at 25°C, measured for RDE loaded with various catalysts. In a H$_2$ saturated condition, HOR currents were around 1 mA cm^{-2} but

declined when 1% CO was added to H$_2$. When N$_2$ gas was bubbled in the solution, the current was almost zero, confirming that the observed polarization current was due to H$_2$ oxidation. Comparing the HOR behavior without and with CO, Pt–[Lu$_2$Cu$_4$(fsaaep)$_4$]/C appears to show a good CO tolerance as Pt–Ru/C.

Table I summarizes the result of hydrogen oxidation current for various electrocatalysts at the same Pt amount. The mass activities
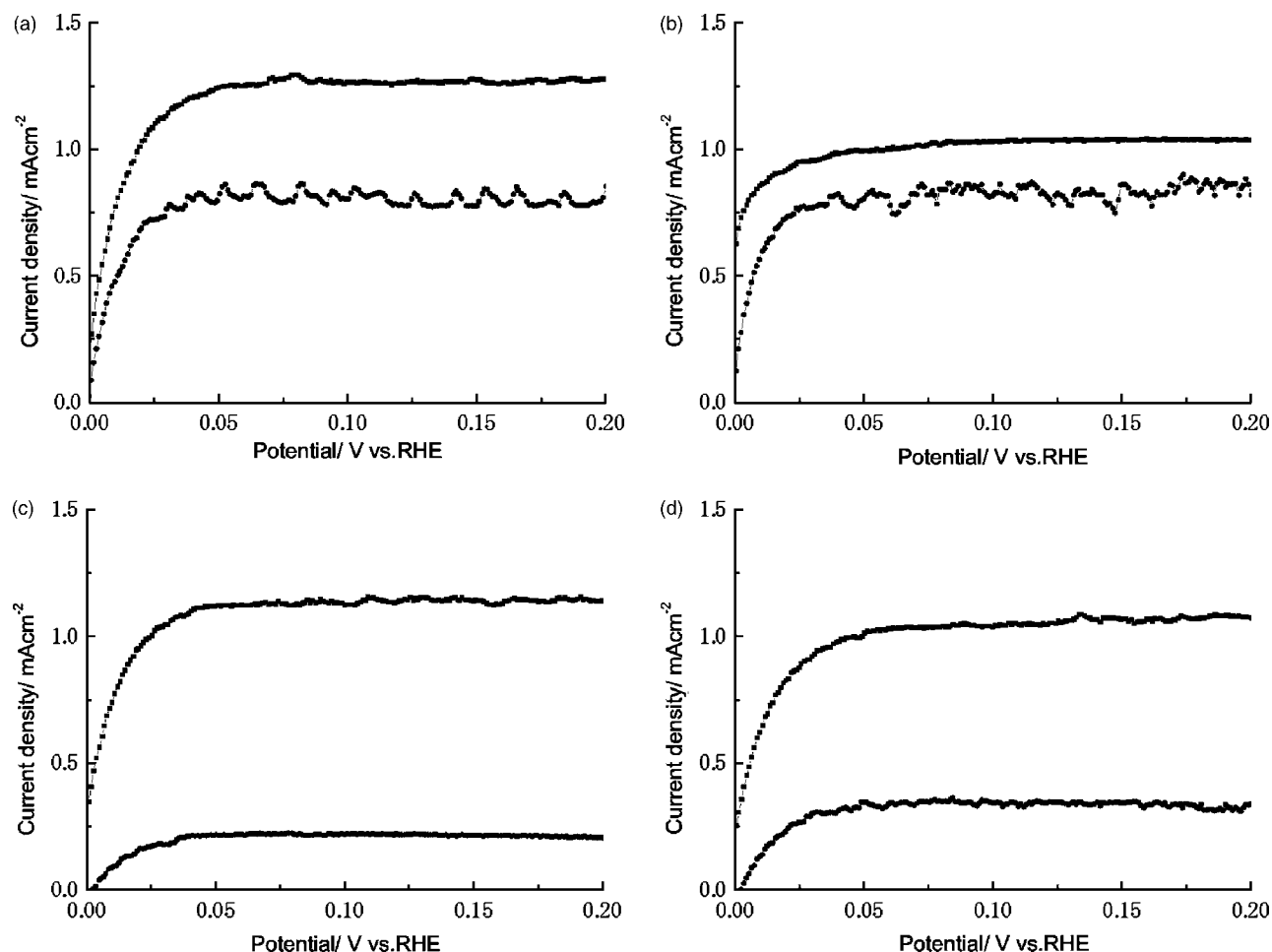

Figure 2. Polarization curves of HOR on RDE loaded with various catalysts, measured in 0.1 mol dm^{-3} HClO$_4$ at 25°C, where H$_2$ gas is bubbled without and with 1% CO: (a) Pt–Ru/C, (b) Pt–[Lu$_2$Cu$_4$(fsaaep)$_4$]/C, (c) Pt–[Pr$_2$Cu$_4$(fsaaep)$_4$]/C, and (d) Pt–[Gd$_2$Cu$_4$(fsaaep)$_4$]/C. Rotation speed 300 rpm, potential scan rate 5 mV s^{-1}.

Table I. Comparison of H_2 oxidation current at 0.1 V vs RHE in 0.1 mol dm^{-3} $HClO_4$ saturated with H_2 gas containing 1% CO, measured on RDE loaded with various electrocatalysts.

	Mass activity $[mA\ mg(Pt^{-1})]$/ current ratio (%)	
	Pure H_2	1% CO/H_2
20 wt %Pt–10 wt %Ru/C	50.7 (100)	32.4 (64)
20 wt %Pt–$[Lu_2Cu_4(fsaaep)_4]$/C	41.1 (100)	32.5 (79)
20 wt %Pt–$[Pr_2Cu_4(fsaaep)_4]$/C	45.1 (100)	8.5 (19)
20 wt % Pt–$[Gd_2Cu_4(fsaaep)_4]$/C	40.8 (100)	14.1 (35)

in H_2 gas were 50.7, 41.1, 45.1, and 40.8 mA $mg(Pt)^{-1}$ for Pt–Ru/C, Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C, respectively. Seeing the current ratio for 1% CO/H_2 as compared to H_2, the catalyst Pt–$[Lu_2Cu_4(fsaaep)_4]$/C showed a high CO tolerance under 1% level of CO in H_2 saturated in 0.1 mol dm^{-3} $HClO_4$. The catalytic activity of a commercial Pt–Ru/C (Johnson Matthey) used for comparison was also maintained under 1% CO/H_2. However, the catalytic activity of Pt–$[Pr_2Cu_4(fsaaep)_4]$/C and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C decreased below 35% under 1% CO/H_2.

Figure 3 depicts the variation of the hydrogen oxidation current with time, which was conducted to evaluate CO tolerance with time. The current was measured at 1% CO in H_2 with RDE at 0.1 V vs RHE for a period of 600 s, after keeping the potential at 0.8 V vs RHE for 60 s. The hydrogen oxidation currents of Pt–$[Lu_2Cu_4(fsaaep)_4]$/C and Pt–Ru/C were maintained after duration for 600 s. In constant, the hydrogen oxidation currents of Pt–$[Pr_2Cu_4(fsaaep)_4]$/C and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C declined immediately after 1% CO/H_2 inlet. From these behaviors, Pt–$[Lu_2Cu_4(fsaaep)_4]$/C was expected to be a good anode catalyst for PEFC because of high CO tolerance. The dependence of CO tolerance on lanthanoid metals suggests that the metal site would work for CO adsorption, and this tendency is strongly affected by the metal element.

Figure 4 shows the CO oxidation peaks observed during the anodic potential sweep of the stripping tests in 0.1 mol dm^{-3} $HClO_4$. CO stripping was performed after the linear sweep voltammetry experiment for CO tolerance, switching the gas from 1% CO/H_2 to N_2. Preadsorbed CO is oxidized during the first anode potential sweep, and repeated scanning did not reveal any more peaks.
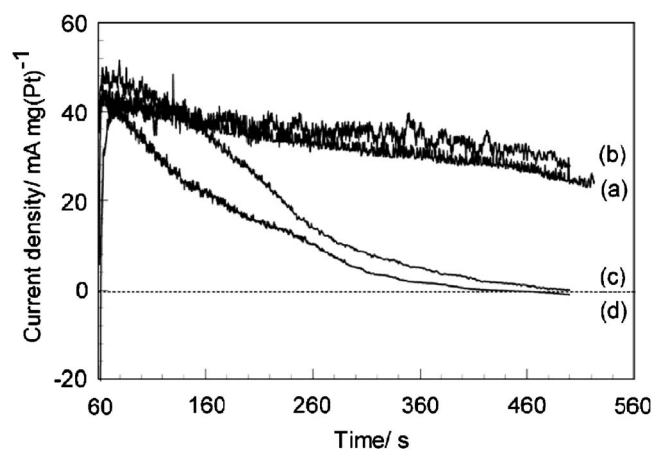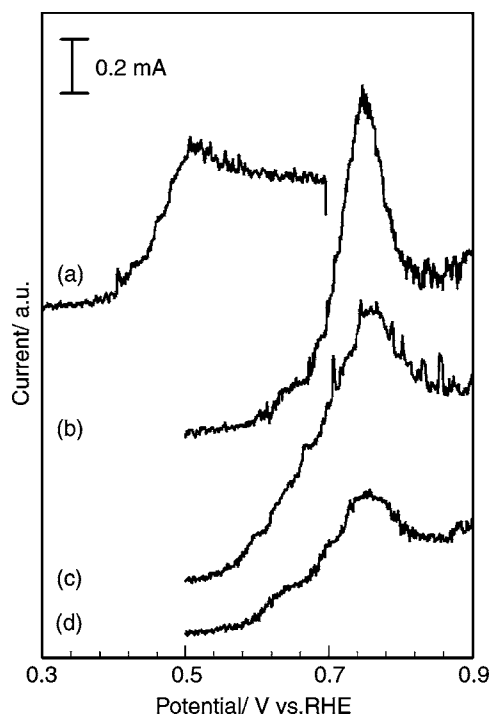

Figure 4. CO stripping voltammetry after keeping the potential at 0.1 V RHE for 10 min in hydrogen gas containing 1%CO: (a) Pt–Ru/C, (b) Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, (c) Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and (d) Pt–$[Gd_2Cu_4(fsaaep)_4]$/C.

The CO oxidation peaks of Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C appeared at 0.76 V vs RHE, which agreed with the CO oxidation peak of Pt/C.[13] The CO oxidation peak of Pt–Ru/C was observed at a much lower potential (0.49 V vs RHE), indicating that organic-metal-complex-based catalysts may exhibit different behavior during H_2 (CO) oxidation in comparison with traditional Pt–Ru catalysts. Against the expectation, the height of CO oxidation peaks was in the order: Pt–$[Lu_2Cu_4(fsaaep)_4]$/C > Pt–$[Pr_2Cu_4(fsaaep)_4]$/C > Pt–$[Gd_2Cu_4(fsaaep)_4]$/C, which indicates that the amount (and ease) of CO adsorption on the catalysts is in this order. Seeing the CO stripping potential, Pt would work as the site of CO adsorption, but the lanthanoid metal site would also participate in CO adsorption.

CO tolerance tests for the anode catalysts were carried out in a half-cell at 70°C, consisting of a half-MEA with a Nafion 115 membrane in H_2 gas and in H_2 with various concentrations of CO at the same Pt amount. Figure 5 shows the polarization curves of hydrogen oxidation for Pt–Ru/C and Pt–$[Lu_2Cu_4(fsaaep)_4]$/C in H_2 with various concentrations of CO. In pure H_2, the catalytic activities of both electrode catalysts were not much different. The catalytic activity of Pt–$[Lu_2Cu_4(fsaaep)_4]$/C was maintained above 50% under 100 ppm level CO. In content, the catalytic activity of Pt–Ru/C decreased with increasing CO concentration.

Table II summarizes the hydrogen oxidation currents in a half-cell, measured on various electrocatalysts in H_2 gas and in H_2 with various concentrations of CO at the same Pt amount. The mass activities in H_2 gas were 3.78, 3.38, 2.98, and 3.61 A $mg(Pt)^{-1}$ for Pt–Ru/C, Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C, respectively. For 10 and 100 ppm CO, the retention of the current from the pure H_2 to CO-containing H_2 was 84 and 20, 77 and 46, 88 and 32, and 86 and 32% for Pt–Ru/C, Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and Pt–$[Gd_2Cu_4(fsaaep)_4]$/C, respectively. Comparing Table II with Table I, it is roughly seen that the CO tolerance performance accords

Figure 3. Time variation of HOR current density on RDE with various catalysts measured in 0.1 mol dm^{-3} $HClO_4$, after keeping the potential for 60 s at 0.8 V vs RHE and then at 0.1 V vs RHE for 600 s: (a) Pt–Ru/C, (b) Pt–$[Lu_2Cu_4(fsaaep)_4]$/C, (c) Pt–$[Pr_2Cu_4(fsaaep)_4]$/C, and (d) Pt–$[Gd_2Cu_4(fsaaep)_4]$/C.
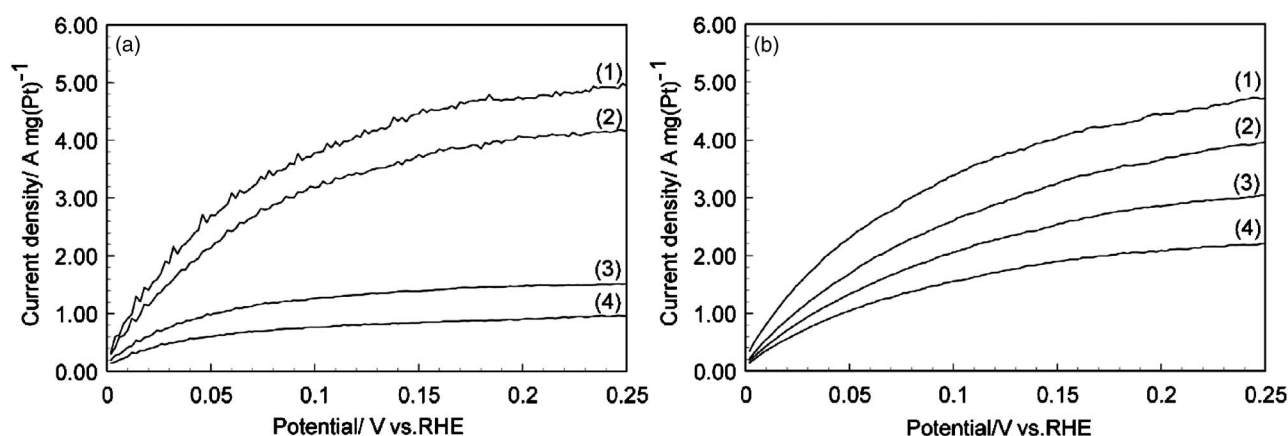
Figure 5. Current–potential curves under various amounts of CO for (a) Pt–Ru/C and (b) Pt–[Lu$_2$Cu$_4$(fsaaep)$_4$]/C: (1) pure H$_2$, (2) 10 ppm CO/H$_2$, (3) 50 ppm CO/H$_2$, and (4) 100 ppm CO/H$_2$.

Table II. Comparison of H$_2$ oxidation current at 0.1 V vs RHE on various electrocatalysts, measured in a half-cell at 70°C with H$_2$ anode gas containing various amounts of CO.

	Mass activity [A mg(Pt^{-1})]/current ratio (%)			
Catalysts	H$_2$	10 ppm CO/H$_2$	50 ppm CO/H$_2$	100 ppm CO/H$_2$
20 wt% Pt–10 wt %Ru/C	3.78 (100)	3.18 (84)	1.27 (34)	0.77 (20)
20 wt % Pt–[Lu$_2$Cu$_4$(fsaaep)$_4$]/C	3.38 (100)	2.60 (77)	2.06 (64)	1.55 (46)
20 wt % Pt–[Pr$_2$Cu$_4$(fsaaep)$_4$]/C	2.98 (100)	2.61 (88)	1.47 (49)	0.94 (32)
20 wt % Pt–[Gd$_2$Cu$_4$(fsaaep)$_4$]/C	3.61 (100)	3.10 (86)	2.27 (63)	1.17 (32)

Figure 6. Polarization curves and power density–current density curves of (a) Pt–Ru/C, (b) Pt–[Lu$_2$Cu$_4$(fsaaep)$_4$]/C, (c) Pt–[Pr$_2$Cu$_4$(fsaaep)$_4$]/C, and (d) Pt–[Gd$_2$Cu$_4$(fsaaep)$_4$]/C measured with a PEFC single cell. Anode gas: H$_2$(○), H$_2$ + 10 ppm CO (△), H$_2$ + 50 ppm CO(□), and H$_2$ + 100 ppm CO(◇).

well between two kinds of HOR experiments, and 1% CO/H$_2$ in 0.1 mol dm^{-3} HClO$_4$ for RDE corresponds with CO in the H$_2$ gas phase of a half-cell somewhere between 10 and 50 ppm. It is re-

markable that the performance of electrocatalysts based on Pt and the organic metal complex revealed high activity for H$_2$ oxidation in the presence of CO as compared to Pt–Ru/C.

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Polarization curves measured in single fuel cells are illustrated in Fig. 6. In single-cell measurements, the best polarization behavior and CO tolerance were observed on Pt–Ru/C, and the performances for Pt–[Ln_2Cu_4(fsaaep)$_4$]/C declined especially with Ln = Pr and Gd, although Pt–[Lu_2Cu_4(fsaaep)$_4$]/C showed good CO tolerance. The failure of good polarization performance in pure H_2 indicates the problems of the catalyst ink and MEA fabrication for the complex catalysts, as experienced with other organic metal complex catalysts.[10,11] This weak point is being further addressed now, and researches are in progress to improve the contact of the catalyst–membrane interface.

Conclusions

A unique structure of Pt–[Ln_2Cu_4(fsaaep)$_4$]/C (Ln = Lu,Pr,Gd) (Fig. 1) proved to make a good CO adsorption site in the metal center, and this resulted in good CO tolerance when co-catalyzed with Pt. The concept of composite catalysts that contains organic metal complexes as co-catalysts with Pt, with a working hypothesis where the co-catalyst mitigates CO poisoning on Pt, appears to be successful.

Future work needs to improve the performance of these complex catalysts by overcoming the weak point that such composites made from the metal (Pt) and organic substances (metal complex) deteriorate the mixing capability of the catalyst ink solutions.

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