

High CO Tolerance of *N,N*-Ethylenebis(salicylideneaminato)oxovanadium(IV) as a Cocatalyst to Pt for the Anode of Reformate Fuel Cells

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Received April 6, 2006. Revised Manuscript Received June 11, 2006

In reformate-type polymer electrolyte fuel cells (PEFCs), CO tolerance of the anode catalysts is a central issue because CO inevitably comes out of the reformer and poisons very seriously the platinum-based catalysts. In this work, long desired novel-type CO-tolerant electrocatalysts have been developed from Pt and organic metal complexes (*N,N*-ethylenebis(salicylideneaminato)oxovanadium(IV) [abbreviated as VO(salen)]) that are potentially superior to Pt–Ru and practically usable as such anode catalysts. These anode catalysts were tested for their CO tolerance using a half and a single fuel cell, at a cell temperature of 70 °C in the presence of 10, 50, and 100 ppm CO. The original metal complexes were mixed with the platinum precursor, platinum tetra-ammine chloride, and supported on the carbon black supporting material and heat-treated at various temperatures. The mixed catalysts Pt–VO(salen)/C revealed only little deterioration for less than 100 ppm CO, which was never attained by the state of the art alloy catalysts. The function of organic metal complex may originate during the heat treatment of catalyst preparation, and this suggests that the valence states of vanadium in Pt–VO(salen)/C play a role in manipulating the oxidation states of platinum. The catalysts were characterized using XRD, TEM, XPS, and XAFS techniques.

Introduction

In reformate-type polymer electrolyte fuel cells (PEFCs), the design of the anode electrocatalysts is still an issue because the catalytic activity of Pt significantly deteriorates in the presence of the small amount of carbon monoxide.^{1,2} Mitigating such a poisoning effect has been an ongoing task for scientists and engineers challenging in the field.³ Electrocatalysts insensitive to CO poisoning can realize a high conversion efficiency of PEFC, as well as simple auxiliary systems. In this sense Pt–Ru alloy has attracted attention for more than 20–30 years as a promising candidate for the anode catalyst of PEFC.^{4–6} The function of Ru is ascribed

to its being the source of oxygen-containing species,⁷ or its ability to weaken CO bonding on Pt due to d-electron deficiency,^{8,9} thus catalyzing the oxidation of CO at potentials much lower than that observed for Pt. However, due to its inadequacy when the CO concentration is higher, and the limited availability of Ru as a natural resource, better substitutes for the Pt–Ru catalyst as the anode electrocatalysts have been sought for more than a decade.

Several such candidates include platinum-based alloy catalyst,^{10,11} ternary platinum alloy catalyst,¹² and oxide-based catalysts.^{13,14} Carbon-supported transition-metal porphyrin catalysts,¹⁵ metal–phthalocyanines, and metal–tetramethylcyclames as cocatalysts¹⁶ have been studied in view of their activity as oxygen reduction catalysts or methanol and CO

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oxidation catalysts. Their performance can be greatly enhanced by heat treatment in an inert atmosphere. Despite this progress, very few catalysts showing a real advantage over Pt–Ru had been reported so far.

In this investigation, a new class of anode catalysts consisting of Pt and organic metal complexes were prepared and tested.¹⁷ These new components can provide wider possibility in manipulating the molecular design and new innovative functions compared to metal alloy catalysts.

Experimental Section

N,N-Ethylenebis(salicylideneaminato)oxovanadium(IV)¹⁸ [abbreviated as VO(salen)] was synthesized as reported in earlier works. The details about the mixed catalysts prepared have been described elsewhere.¹⁹ Mixed catalysts were prepared from the platinum precursor, i.e., platinum tetra-amine chloride Pt(NH₃)₄Cl₂·xH₂O, and VO(salen) in a 50:50 mass % ratio. Sixty milligrams of the mixed catalysts and 40 mg of carbon black (Vulcan XC-72R) were mixed in ethanol in a mortar, dried in air at 80 °C for 60 min, and then heat-treated in an Ar atmosphere at 300–600 °C for 2 h in a furnace. After the heat treatment, 30 mg of the catalyst-supported carbon powder (abbreviated as Pt–VO(salen)/C) was mixed with 500 mg of 5 wt % Nafion solution (Aldrich) together with 30 mg of ethanol and stirred, to get an ink of the mixture. This mixture was then transferred to the carbon paper disk (TORAY TGP-H-090, 0.3 mm in thickness, 8 mm in diameter) that was pretreated to a wet-proof condition with poly(tetrafluoroethylene) (PTFE, 3.3 × 10⁻³ g cm⁻²). The amount of Pt in the mixed catalyst was 5.4 × 10⁻⁴ g(Pt) cm⁻², for the apparent electrode area of the disk. Half side membrane electrode assembly (half-MEA) was prepared by hot-pressing the catalyst-loaded carbon paper disk to one side of Nafion 115 membrane at the pressure of 100 kg cm⁻² at 130 °C for 3 min.

The catalyst powder after the heat treatment was characterized by transmission electron microscopy (TEM, Hitachi HF-2210), to determine the particle size distribution. The particles included in carbon were analyzed for metal atomic ratios by an energy-dispersive X-ray analysis (EDX) attached to a scanning transmission electron microscope (STEM). X-ray photoelectron spectroscopy (XPS) was used to determine the surface oxidation states of the metals. XPS spectra were collected using a Perkin-Elmer PHI5600 spectrometer, with an Al K α monochromatic source (15 kV, 20 mA). The binding energy scale was calibrated with respect to the C 1s (284.80) signal. Curve fitting of the spectra was made by a combination of Gaussian and Lorentzian functions on a Shirley-type background. X-ray absorption fine structure (XAFS) spectra of K-edge for vanadium and L-edge for platinum were measured at the BL-7C station of the Photon Factory in the National Laboratory for High Energy Physics (KEK-PE) equipped with a Si(111) monochromator and a total reflection double mirror. The vanadium K-edge and platinum L-edge spectra were recorded in a transmission mode and analyzed by the extended X-ray absorption fine structure (EXAFS) analysis program: Rigaku EXAFS (REX). The catalysts were also examined by X-ray diffraction (XRD) techniques using a Shimadzu XD-D1 spectrometer with Cu K α radiation (40 kV, 40 mA). The X-ray diffractograms were obtained with a scan rate of 1 deg min⁻¹ for 2 θ values between 20° and 70°.

The half cell used was the same as described previously.¹⁹ The electrochemical experiment for CO tolerance tests with anode catalysts was mainly carried out in a half cell consisting of a half-MEA with a Nafion 115 membrane, and an Au mesh electric contact in a Teflon holder with a gas inlet and outlet. H₂ gas containing 0, 10, 50, and 100 ppm CO was supplied to the carbon paper side of the catalyst layer, and the Nafion membrane side was in contact with 1 mol dm⁻³ HClO₄ deaerated with N₂ gas and thermostated at 70 °C. The flow rate of H₂ gas was 20 cm³ min⁻¹. The working electrode was the half-MEA with the catalyst-supported carbon paper disk; the platinum plate and the reversible hydrogen electrode (RHE) in 1 mol dm⁻³ HClO₄ were used as the counter and the reference electrodes, respectively. After a steady rest potential was attained (ca. 1 h), potential was scanned at a scan rate of 5 mV s⁻¹ for the polarization measurement, in a potential range from 0 to 500 mV vs RHE, using a Solartron model SI 1287 potentiostat.

The catalyst performance was further tested in a single fuel cell configuration. Membrane electrode assemblies (MEAs) having active areas of 4 cm² were made to test the catalysts in a fuel cell. Anode was loaded with 20%Pt–VO(salen)/C, 20%Pt/C (ElectroChem), or 20%Pt–10%Ru/C (Johnson Matthey) catalysts on carbon paper (TORAY TGP-H-090), each with 3 × 10⁻⁴ g(Pt) cm⁻², and cathode was loaded with 20%Pt/C on carbon paper (1 × 10⁻³ g(Pt) cm⁻², ElectroChem) for each MEA. MEA was prepared by hot-pressing the anode and the cathode catalyst-loaded carbon paper (2 × 2 cm²) to each side of the Nafion 115 membrane at the pressure of 100 kg cm⁻² at 135 °C for 3 min. The cell temperature was 70 °C and the reactant gas streams were saturated with water vapor at 60 °C. The anode was fed with H₂ gas with or without CO at the flow rate of 0.06 L min⁻¹, and the cathode was fed with air at the flow rate of 0.4 L min⁻¹. Before the polarization experiment, the single cell was conditioned at 600 mV for 3 h either in pure H₂ or in H₂/CO, to reach a steady-state condition. The polarization curves were obtained in the potential range of 1000 mV down to 100 mV with a step scan of 50 mV per 2 min for all the experiments.

Results and Discussion

Electrochemical CO Tolerance Test with Half-MEA.

Figure 1 shows the effect of the heat treatment temperature on the catalytic activity of Pt–VO(salen)/C derived from polarization curves. The hydrogen oxidation reaction (HOR) current at 100 mV RHE on the Pt–VO(salen)/C catalyst anode in H₂ containing 100 ppm CO is shown in Figure 1a, both as the current retention as compared to pure H₂ and as the mass activity (current per unit mass of Pt contained in the catalysts). In Figure 1b the mass activity is compared against the concentration of CO, with the heat treatment temperature as a parameter. There appears an optimum heat treatment temperature for the activity of the calcined catalysts at around 400 °C. Above and below this heat treatment temperature, the performance declined. It is also observed that the performance of the catalyst increases with increasing the Pt–VO(salen) amount on carbon black Vulcan XC-72R (6%, 12%, and 20% in mass), which clearly demonstrates that VO(salen) effectively works on the CO tolerance.

Comparison of various commercial Pt–Ru/C catalysts, expressed as the mass activity, is shown in Table 1. It is seen that for all the catalysts the normalized HOR currents are very low at the CO level of 100 ppm. For 10 and 50 ppm CO, the retention of the current from the pure H₂ to CO-containing H₂ was 47% and 6.5%, 48% and 7.5%, and

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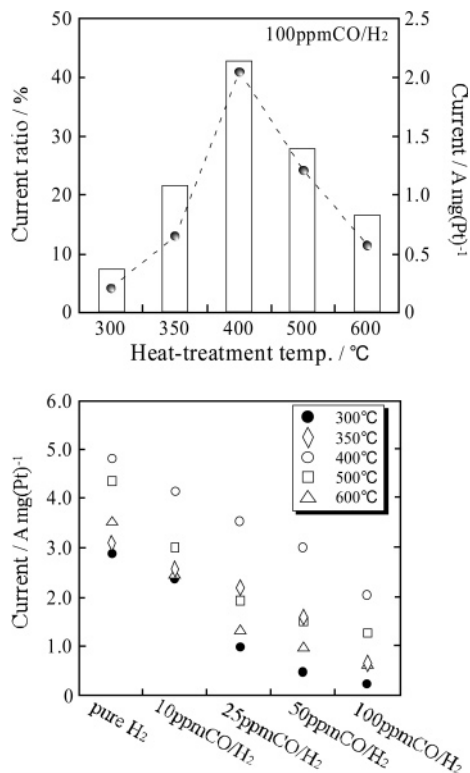


Figure 1. Effect of heat treatment temperature of 20%Pt–VO(salen)/C on the H₂ oxidation current containing various amounts of CO. (a) H₂ oxidation current containing 100 ppm CO, in current ratio as compared to H₂ oxidation current in pure H₂ (bars) and in mass activity (dots). (b) The mass activity for H₂ oxidation containing various amounts of CO.

Table 1. Comparison of H₂ Oxidation Current Containing Various Amounts of CO for Different Pt–Ru Catalysts^a

catalysts	current ratio [%] ^b /(mass activity [A mg(Pt) ⁻¹])			
	pure H ₂	10 ppm CO/H ₂	50 ppm CO/H ₂	100 ppm CO/H ₂
30%Pt–15%Ru/C (Johnson Matthey)	(2.9 ₁)	96 (2.7 ₈)	29 (0.83)	12 (0.34)
20%Pt–10Ru/C (Johnson Matthey)	(2.8 ₁)	68 (1.9 ₂)	20 (0.57)	10 (0.28)
20%Pt–20%Ru/C (E-TEK)	(5.6 ₉)	47 (2.6 ₆)	6.5 (0.37)	3.0 (0.17)
15%Pt–15%Ru/C (E-TEK)	(4.6 ₂)	48 (2.2 ₀)	7.5 (0.35)	3.9 (0.18)
20%Pt–10%Ru/C (Electrochem)	(6.4 ₁)	79 (5.0 ₉)	3.0 (0.19)	1.4 (0.09)

^a The electrolysis performed in a half cell at 70 °C; MEA area: 0.502 cm²; scan rate: 5 mV s⁻¹; potential range: 0–500 mV vs RHE. ^b HOR current at 100 mV vs RHE derived from the polarization curves, normalized by that for pure H₂.

79% and 3.0% for the 20%Pt–20%Ru (E-TEK), 15%Pt–15%Ru/C (E-TEK), and 20%Pt–10%Ru (Electrochem.), respectively. In comparison with these Pt–Ru/C catalysts, deterioration of catalytic activity by CO is successfully suppressed with Pt–VO(salen)/C. The retention of the mass activity of Pt–VO(salen)/C heat-treated at 400 °C was higher than 40%, even at 100 ppm CO level.

In Figure 2, the performances of Pt–VO(salen)/C heat-treated at 400 °C is compared with those of 20% Pt/C (ElectroChem, MA) and 20%Pt–10%Ru/C (Johnson Matthey, Inc, Co.) of the same Pt amount. The mass activity in neat H₂ was 7.6, 4.1, and 4.8 A mg(Pt)⁻¹ for Pt/C, Pt–Ru/C, and Pt–VO(salen)/C, respectively. It should be noticed that the catalytic activity of Pt/C and Pt–Ru/C dramatically

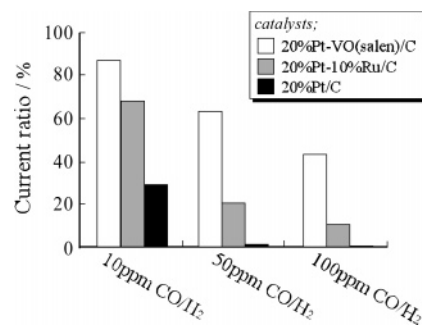


Figure 2. Comparison of CO tolerance of Pt–VO(salen)/C heat-treated in argon at 400 °C with Pt/C and Pt–Ru/C measured in a half cell at 70 °C. The current at 100 mV RHE in each gas containing various amounts of CO in comparison with that in pure H₂ is shown as the bar.

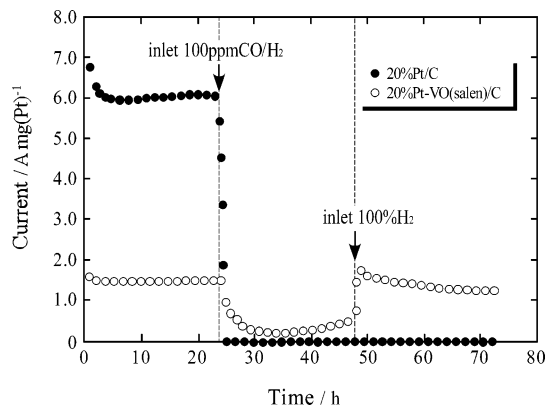


Figure 3. Change of the hydrogen oxidation current at 100 mV vs RHE by the addition of 100 ppm CO gas shown in the time course, measured for Pt–VO(salen)/C and Pt/C catalysts.

decreased with increasing the concentration of CO. On the other hand, Pt–VO(salen)/C revealed very high CO tolerance, maintaining their catalytic ability to more than 50 ppm CO level, which has never been matched by commercial catalysts. It is remarkable that this is the first time where the performance of the organic complex based catalysts revealed high activity for H₂ oxidation in the presence of CO.

In Figure 3, the time course of the hydrogen oxidation currents of the prepared catalysts at 100 ppm CO in H₂ was examined under potentiostatic conditions at 100 mV RHE in the half cell. For a platinum anode catalyst, the hydrogen oxidation current declined immediately after 100 ppm CO inlet, and the current did not recover even if the pure hydrogen was fed again, suggesting a strong CO adsorption on the platinum surface. On the other hand, in the case of Pt–VO(salen)/C anode, after H₂ with 100 ppm CO was switched to pure H₂, the current recovered and remained at the initial level. It is indicated that even after CO was introduced the chemical structure and character of the Pt–VO(salen)/C were sustained at 50 mV potentiostatic conditions, and when new H₂ molecules adsorbed onto the Pt–VO(salen) catalysts, they displaced the adsorbed CO to the gas phase. It can be inferred that VO(salen) mitigated the poisoning of CO on the Pt surface.

CO oxidation peaks observed during the anodic potential sweep of the stripping tests are presented in Figure 4, for the Pt/C (ElectroChem), Pt–Ru/C (Johnson Matthey), and Pt–VO(salen)/C catalysts. CO stripping was performed after

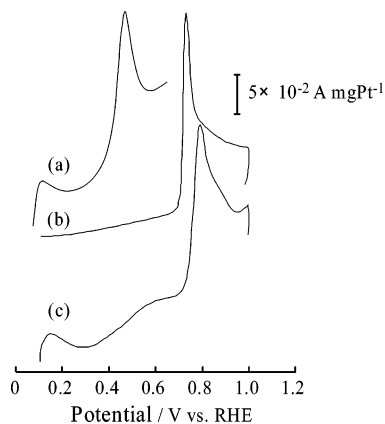


Figure 4. CO stripping voltammetry after keeping the potential at 50 mV RHE for 1 h in hydrogen gas containing 100 ppm CO. Electrode catalysts: (a) 20%Pt–10%Ru/C, (b) 20%Pt/C, and (c) 20%Pt–VO(salen)/C. Sweep rate: 50 mV s⁻¹.

the linear sweep voltammetry experiment for CO tolerance, in the same half cell with N₂ flowing through the cell with potential scanning at a scan rate of 50 mV s⁻¹ between 100 and 1000 mV. Pre-adsorbed CO is oxidized during the first anodic potential sweep, and repeated scanning did not result in these peaks.

An intense single peak of adsorbed CO oxidation for Pt/C appeared at 790 mV (vs RHE) in the positive-going sweep, which agreed with reported results by Schmidt et al.²⁰ The CO oxidation peak for the bimetallic Pt–Ru/C surface was observed at much lower potential (480 mV vs RHE) as compared to Pt/C, with a smaller CO oxidation current, which has been ascribed to the oxidation of CO by oxygen-containing species on Ru sites according to the bifunctional mechanism.⁷ On the other hand, the CO oxidation peak for the Pt–VO(salen)/C appeared at the most positive potential among these, indicating that Pt–VO(salen)/C as a catalyst may exhibit very different behavior during H₂ (CO) oxidation in comparison with traditional Pt–Ru catalysts.

Catalytic Activity of CO-Tolerant Catalysts in a Single Cell. Parts (a), (b), and (c) of Figure 5 depict the polarization curves of Pt/C, Pt–Ru/C, and Pt–VO(salen)/C, corrected for the ohmic drop, for the electro-oxidation of H₂ containing various concentrations of CO gas. The performance of different catalysts in a single PEFC cell almost reproduces the trend found for the oxidation of H₂ containing various concentrations of CO gas in the half-cell experiments, except for the decline of performance of the Pt–VO(salen)/C catalyst in the case of high CO concentration. Some problems were found with this catalyst in making good gas diffusion layer on the carbon paper. The presence of vanadium compounds may change the colloidal chemistry of the ink, and this can alter the porous structure of the diffusion electrodes. This problem should be solved in future works.

As evident from the data, the cell performance is higher for Pt–VO(salen)/C than for Pt–Ru/C especially in the case of 10 and 50 ppm CO, which is in agreement with the results of half-cell experiments. As long as the reformat gas is used containing less than 50 ppm CO, the Pt–VO(salen)/C

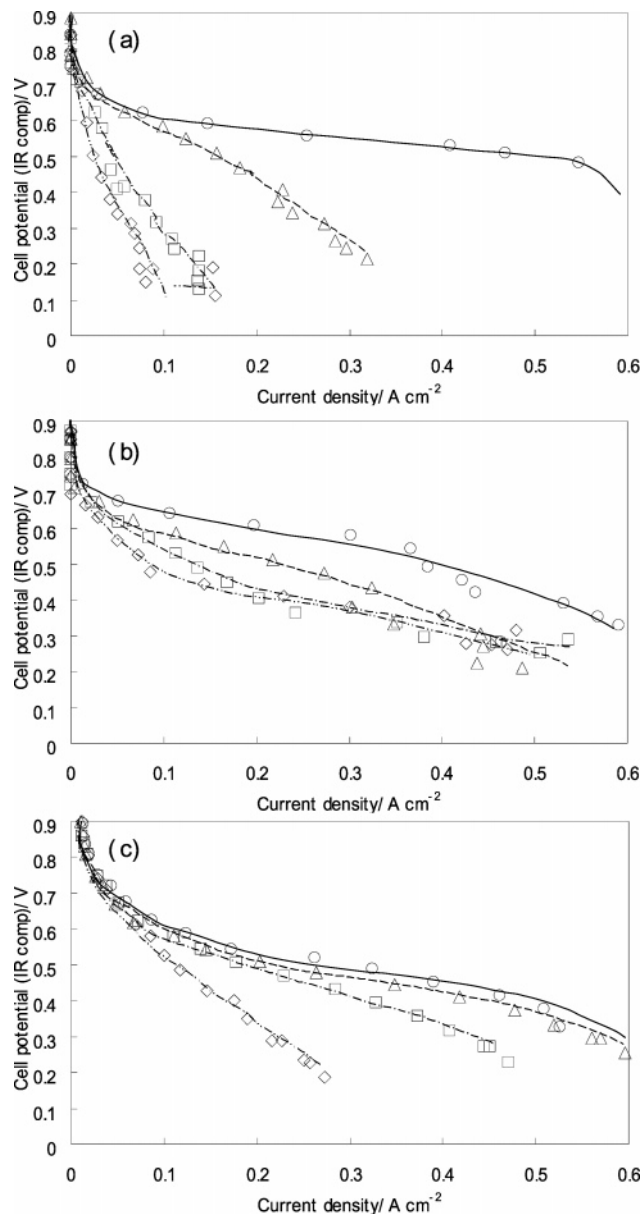


Figure 5. Polarization curves measured in PEFC single cells supplied with pure hydrogen (○), 10 ppm CO/H₂ (△), 50 ppm CO/H₂ (□), and 100 ppm CO/H₂ (◇) at the anode. Anode catalysts: (a) 20% Pt/C, (b) 20%Pt–10%Ru/C, and (c) 20%Pt–VO(salen)/C with 0.3 mg(Pt) cm⁻² loading. Cathode catalyst: 20%Pt/C (ElectroChem) with 1 mg(Pt) cm⁻² loading. Cell temperature: 70 °C. Air and hydrogen humidifier temperature: 60 °C. Anode flow rate: 0.06 L min⁻¹; cathode flow rate: 0.4 L min⁻¹.

catalyst works satisfactorily with less CO poisoning than conventional Pt–Ru/C catalysts.

Characterization of Pt–VO(salen)/C Mixed Catalysts by TEM, EDX, XRD, XPS, and XAFS. The TEM images of Pt–VO(salen)/C heat-treated at 300, 400, and 600 °C are shown in parts (a), (b), and (c), respectively, of Figure 6. The size of the particles increased with increasing heat treatment temperature. Concerning the electrochemical performance of the catalysts, it is concluded that the catalysts prepared at 400 °C generate the highest activity, and at this temperature the particle size observed by TEM is about 1–2 nm. The catalyst reveals good dispersion of metal particles on the carbon support. In the TEM micrographs the presence of agglomerates of metal particles on the micro- and nanoscale is not observed in Figure 6b. Raising the temper-

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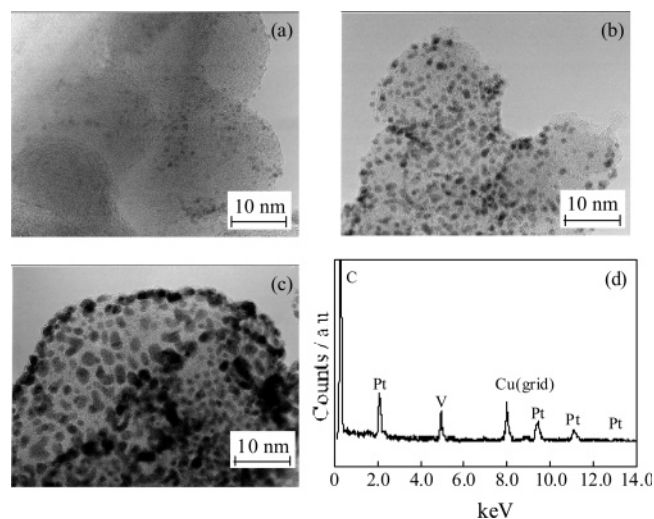


Figure 6. Transmission electron micrograph images of the 20%Pt–VO(salen)/C powder with heat treatment at (a) 300, (b) 400, and (c) 600 °C in an argon atmosphere. (d) Typical EDX spectra of metallic particles on Vulcan carbon support heat-treated at 400 °C.

Table 2. Contents of V and Pt in EDX Analysis for the Pt–VO(salen)/C Catalysts Prepared by Heat Treatments at 400 and 600 °C

heat treatment temperature	on particle		heat treatment temperature	on carbon	
	element	wt %		element	wt %
400 °C	V-K	20.5	400 °C	V-K	41.0
	Pt-L	79.5		Pt-L	59.0
600 °C	V-K	7.1	600 °C	V-K	3.5
	Pt-L	92.9		Pt-L	96.5

ature up to 600 °C resulted in particle agglomeration to the size of 3–5 nm as seen in Figure 6c.

The particles were analyzed for the elements by EDX attached to scanning TEM and by the image of the HAADF (high-angle annular dark field) STEM. Typical spectra were obtained, as shown in Figure 6d. In the spectra platinum and vanadium atoms were detected in addition to copper atom that comes from the sample grid. The compositions of elements in the particle and on the carbon support are listed in Table 2. In the case of the heat treatment at 400 °C, the amounts of vanadium atom on the carbon and in the particle are both higher than those at 600 °C. It appears that, at 400 °C, the vanadium complex may surround the platinum nanoparticles and protect them from agglomerating on the carbon support.

Figure 7 shows the X-ray diffraction (XRD) patterns of the Pt–VO(salen)/C mixed catalysts prepared at 400, 500, and 600 °C. The characteristic diffraction peaks of the fcc Pt indicate that reduction of Pt precursor to metallic form has been achieved by heat treatments. The low-intensity peak at 2θ of about 25° is associated with the Vulcan XC-72 carbon black as a support. From spectra of (111) and (220), the average crystallite size is estimated to be 4.5 nm with the use of Scherrer formula, which corresponds to the results of TEM analysis. The 2θ values of the (111) peak for Pt–VO(salen)/C prepared at 400, 500, and 600 °C were 39.32°, 39.71°, and 39.81°, respectively. Also the Pt (220) peaks appeared at 45.79°, 46.08°, 46.37°, respectively. XRD results show that the diffraction peaks slightly shift to higher Bragg angles with increasing heat treatment temperature, indicating

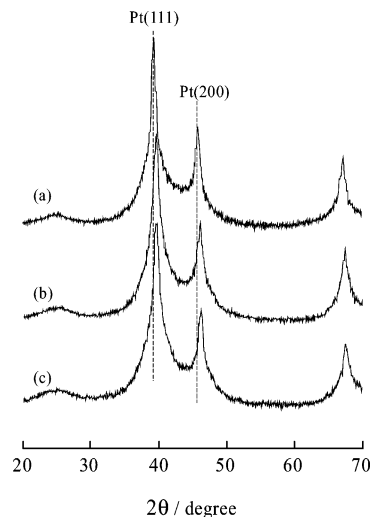


Figure 7. X-ray diffraction patterns of 20%Pt–VO(salen)/C powder with heat treatment at (a) 400, (b) 500, and (c) 600 °C.

that the platinum atoms in the lattice are replaced by the smaller sized vanadium atoms, and led to smaller average lattice constant.

The results of XPS spectra of the Pt–VO(salen)/C mixed catalysts are shown in parts (a), (b), and (c) of Figure 8 in the energy regions of Pt 4f, V 2p, and N 1s, respectively, measured before and after the heat treatment in flowing argon at 300, 400, 500, and 600 °C for 2 h. The binding energies and relative intensity of these components are given in Table 3. In Figure 8a, the Pt 4f region displays two doublets from the spin–orbital splitting of the $4f_{5/2}$ and $4f_{7/2}$ states, and in the case of non heat treatment, the peak position occurs at the binding energy of Pt(II) (77.2 and 73.9 eV), corresponding to a Pt(II) chlorinated species.²¹ After the heat treatment, platinum changes to the reduced state from Pt(II) in the metal precursor to Pt(0). The Pt 4f signal of specimens heat-treated at 300 °C consists of three pairs of doublets. The most intense doublet (72.14 and 75.55 eV) is due to metallic Pt. The second set of doublets (72.95 and 76.44 eV), which is observed at the binding energy (BE) 0.8 eV higher than that of Pt(0), could be assigned to the Pt(II) chemical state. The third doublet of Pt is the weakest in intensity and occurred at even higher BEs (74.37 and 77.70 eV). These two components coincide with the Pt(II) chlorinated species as shown for the case of non-heat-treated powder. A critical examination of the XPS data presented in Table 3 suggests that the content of the platinum chloride species in the carbon-supported Pt–VO(salen)/C catalyst heat-treated at 300 °C is higher than any other specimens heat-treated at higher temperatures. The slight shift in the Pt(0) peak to higher binding energies is a known effect for small particles, as has been reported by Roth et al.²² It is indicated that the chemical state arising from platinum tetra-ammine chloride was reserved at this temperature, although only in a minor amount.

In Figure 8b, two peaks were observed at 523.5 and 516.2 eV, which can be assigned to the $2p_{1/2}$ and $2p_{3/2}$ states of

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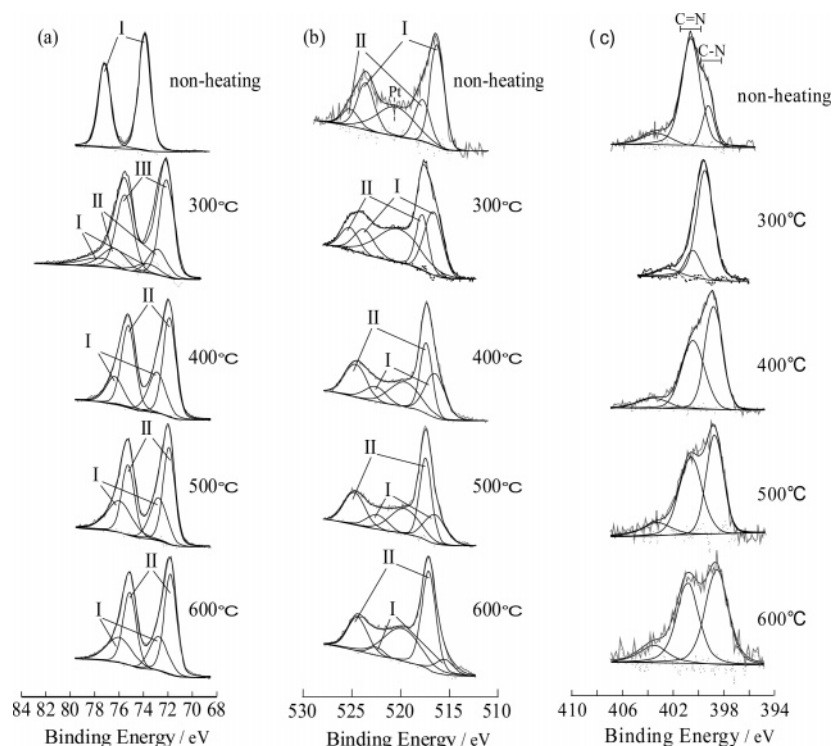


Figure 8. X-ray photoelectron spectra of (a) Pt 4f_{7/2}, (b) V 2p_{3/2}, and (c) N 1s of Pt-VO(salen)/C before and after the heat treatments at various temperatures.

Table 3. Results of XPS Spectra of the Pt-VO(salen)/C Mixed Catalysts in the Energy Regions of Pt 4f and V 2p

Pt-VO(salen)/C	doublet	binding energy (eV)			relative intensity (%)	doublet	binding energy (eV)			relative intensity (%)
		Pt 4f _{5/2}	Pt 4f _{7/2}	assignment			V 2p _{1/2}	V 2p _{3/2}	assignment	
non heat treatment	I	77.2	73.9	Pt ²⁺	100	I	523.5	516.2	V ⁴⁺	70.8
						II	525.1	517.7	V ⁵⁺	29.2
heat treatment temperature: ^a										
300 °C	I	77.7	74.4	Pt ²⁺	7.2	I	523.8	516.6	V ⁴⁺	53.5
	II	76.4	73.0	Pt ²⁺	19.6	II	525.2	517.8	V ⁵⁺	46.7
	III	75.6	72.1	Pt ⁰	73.2					
400 °C	I	76.0	72.9	Pt ²⁺	28.0	I	522.3	516.4	V ⁴⁺	38.6
	II	75.1	71.9	Pt ⁰	72.0	II	524.5	517.3	V ⁵⁺	61.4
500 °C	I	76.1	73.0	Pt ²⁺	25.0	I	522.3	516.4	V ⁴⁺	26.2
	II	75.1	71.9	Pt ⁰	75.0	II	524.7	517.4	V ⁵⁺	73.8
600 °C	I	76.0	72.9	Pt ²⁺	21.6	I	521.4	515.4	V ⁴⁺	13.4
	II	75.0	71.8	Pt ⁰	78.4	II	524.4	517.1	V ⁵⁺	86.6

^a Heat-treated at 300, 400, 500, and 600 °C for 2 h in flowing argon.

tetravalent vanadium. These are composed of two components I and II, which can be assigned to V(IV) and V(V) states, respectively. The reduction of platinum valence state occurred in parallel with the oxidation of vanadium, i.e., V(IV) (516.4 eV) to V(V) (517.3 eV), as seen in Table 3. The relative intensity of V(V)/V(IV) in the catalysts increased with increasing heat treatment temperature from 0.4 (non heat treatment) to 6.4 (heat-treated at 600 °C). These results suggest that the valence states of vanadium in Pt-VO(salen)/C mixed catalysts play a crucial role in manipulating the oxidation state of platinum.

The catalytic activity of Pt-VO(salen)/C can be related to the oxidation of V to higher valence states. Activation of the CO molecule may be achieved through its coordination to the central metal of the chelate in a higher oxidation state, resulting in a reduced back-donation from the metal, which

in turn increases a nucleophilic attack by H₂O.¹⁵ The role of the carbon black supporting material may also become important in order to account for the stability of complexes after the heat treatment of the Pt-VO(salen)/C mixed catalysts.

As shown in Figure 8c, an N 1s single peak is observed at 400.6 eV originating from the C=N groups, while a shoulder appeared at lower binding energy at 399.2 eV, due to the presence of C-N groups. There is general agreement in the literature that the functional groups of high reactivity produced between metal and nitrogen-containing polymers are C-N (398.8 eV) and C=N (400.2 eV) groups,²³ while the third component centered at 403.3 eV and present in

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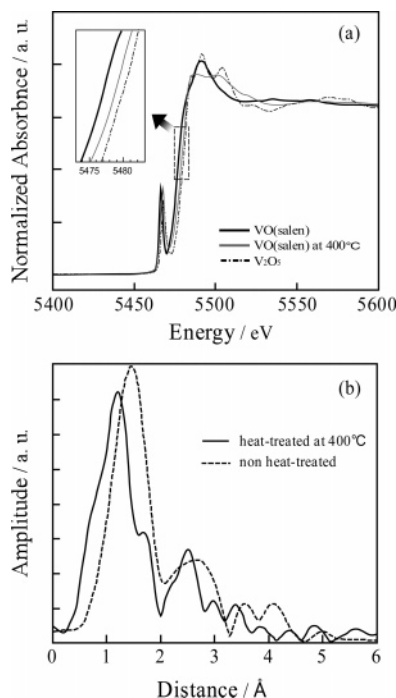


Figure 9. (a) Vanadium K-edge XANES and (b) Fourier transform of normalized k^3 weighted EXAFS spectra of the Pt–VO(salen)/C powder before and after the heat treatment at 400 °C. V_2O_5 is used as the reference sample.

significantly lower concentrations has been assigned to nitrogen substituted in a graphite-like structure.²⁴ It assumed from the results of the N 1s spectra that coordinated states between V and N exist even after the heat treatment between 300 and 600 °C, suggesting that VO(salen), although it might start to partially decompose, is not totally destroyed after the heat treatment.

X-ray absorption near-edge structure (XANES) spectra were analyzed to obtain detailed information on the local structure and coordination geometry of the central vanadium atoms in the Pt–VO(salen)/C after the heat treatments. Figure 9a shows the K-edge XANES spectra of V in the Pt–VO(salen)/C mixed catalysts before and after the heat treatment at 400 °C, together with that of the reference V_2O_5 . In the spectra, the absorption position from K-edge was in the order of Pt–VO(salen)/C (non heat treatment) < Pt–VO(salen)/C (heat-treated at 400 °C) < V_2O_5 , indicating that the local structure around V species was strongly influenced by the heat treatment. The pre-edge peak position of the Pt–VO(salen)/C sample was 5467.5 eV, which was consistent with the peak position of the oxidation state of V(IV).²⁵ The inflection point of the edge of Pt–VO(salen)/C shifted in the positive direction by 1.5 eV after the heat treatment, approaching the line for V_2O_5 . These results clearly show that the heat treatment at 400 °C in argon caused the oxidation state to shift from vanadium(IV) to vanadium(V), which is in agreement with the results of XPS analysis.

The Fourier transforms of normalized k^3 weighted EXAFS spectra of the Pt–VO(salen)/C before and after the heat

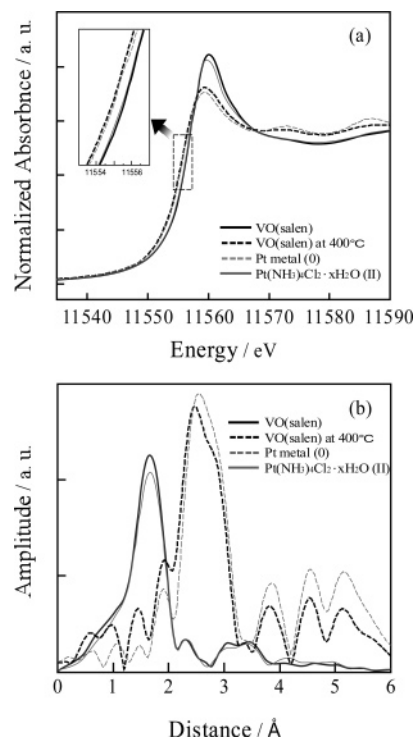


Figure 10. (a) Platinum L-edge XANES and (b) Fourier transform of normalized k^3 weighted EXAFS spectra of the Pt–VO(salen)/C powder before and after the heat treatment at 400 °C. Pt metal and $Pt(NH_3)_4Cl_2 \cdot xH_2O$ are used as the reference samples.

treatment at 400 °C are shown in Figure 9b. In this figure, two peaks appeared around 1.5 and 2.8 Å for non-heat-treated Pt–VO(salen)/C catalysts and around 1.2 and 2.5 Å for the heat-treated catalysts, respectively. The first and the second peaks are assigned to V=O and V–N bonds, respectively. These results confirm that in the Pt–VO(salen)/C catalyst coordination states between V and N are sustained after the heat treatment and that V=O and V–N distances in the Pt–VO(salen)/C are slightly decreased after the heat treatment as compared to those before the heat treatment.

Characterization of platinum species in the catalysts is also conducted by XANES. Figure 10a shows the Pt L_{3} -edge XANES spectra of the non-heat-treated Pt–VO(salen)/C and heat-treated Pt–VO(salen)/C at 400 °C, together with those of the reference $Pt(NH_3)_4Cl_2 \cdot xH_2O$ and Pt foil. As shown in the inset for the absorption edge, there are observed coincidences of the absorption positions between non-heat-treated Pt–VO(salen)/C and $Pt(NH_3)_4Cl_2 \cdot xH_2O$ and between heat-treated Pt–VO(salen)/C and Pt metal.

Fourier transforms of normalized k^3 weighted EXAFS spectra as shown in Figure 10b confirm that the nearest neighbor distance depends on the valence state of Pt. The nearest neighbor distance is around 1.6 Å for the non-heat-treated sample and 2.7 Å for the heat-treated sample, which is attributed to Pt(II) and Pt(0) oxidation states, corresponding to those of $Pt(NH_3)_4Cl_2 \cdot xH_2O$ and Pt foil, respectively.

Conclusion

The electrochemical performance of organic–metal complex VO(salen) as a cocatalyst to Pt was studied by half- and single-cell PEFC experiments, and this new catalyst was proved to be an excellent candidate as a CO-tolerant HOR

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catalyst. The formation of nonhomogeneously dispersed catalyst particles on the nanoscale was anticipated from TEM and XRD analyses.

It is suggested that the valence state of vanadium in the Pt–VO(salen)/C mixed catalysts plays a crucial role in manipulating the oxidation state of platinum. In addition, as anticipated from the V–N coordination evidenced from EXAFS analysis, bonding states between V and N are sustained after the heat treatment at 400 °C. The role of the carbon black supporting material may become important to account for such stability of complexes after the heat treatment.

It is proved that Pt–VO(salen)/C is catalytically very active in the electro-oxidation of reformed hydrogen gas used for PEFCs. The function of VO(salen) as a cocatalyst may

originate during the heat treatment of the mixed catalysts on carbon, which is assumed to be different from the traditional Pt–Ru alloy catalysts. It is suggested from cyclic voltammograms of CO oxidation on the mixed catalysts that CO preferentially adsorbs on the pentavalent vanadium center of VO(salen), rather than –OH or H₂. This is in contrast to the case of Pt–Ru/C where Ru adsorbs and supplies oxygen-containing species or weakens the bonding of adsorbed CO on the Pt atom. Comparing the cost performances of the mixed catalysts Pt–VO(salen)/C with that of Pt–Ru/C alloy catalysts, the present series of catalysts may be promising in designing and synthesizing a new class of electro-catalysts for PEFC applications.

CM0608037