

New CO tolerant electro-catalysts exceeding Pt–Ru for the anode of fuel cells†

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Novel types of CO tolerant electro-catalysts from Pt and organic metal complexes that are far superior to Pt–Ru and practically usable as anode catalysts in reformate gas fuel cells with 100 ppm CO tolerance have been developed.

In recent research and development of polymer electrolyte fuel cells (PEFCs), the design of electro-catalysts is still an issue. One of the big challenges is to find better alternatives to Pt–Ru alloys as anode catalysts in PEFCs.¹ In reformate hydrogen fuel cells, CO strongly adsorbs onto the Pt surface, and seriously degrades the hydrogen oxidation reaction (HOR) occurring in the anode catalyst layer.^{2,3} Electrode catalysts insensitive to CO poisoning are thus desired in order to realize high conversion efficiency in PEFC. For more than 20 to 30 years since its discovery, the only catalyst that can endure CO for practical uses has been Pt–Ru.⁴ The function of Ru is ascribed to be the source of oxygen containing species,⁵ or its ability to weaken CO bonding on Pt due to d-electron deficiency.^{6,7} Because of the limited availability of Ru, better substitutes for the Pt–Ru catalyst have been sought after for more than a decade.

Several candidates for CO tolerant anode electro-catalysts were proposed in the past. These include platinum based alloy catalysts,^{8,9} ternary platinum alloy catalysts,¹⁰ and oxide based

catalysts.^{11,12} Carbon-supported transition-metal porphyrin catalysts,¹³ metal-phthalocyanines and metal-tetramethylcyclames as cocatalysts¹⁴ have been studied in view of their activity as oxygen reduction, methanol or CO oxidation catalysts. Their performance can be greatly enhanced by heat treatment in an inert atmosphere. In spite of this progress, very few catalysts showing real promise to replace 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.¹⁵ These new components can be expected to provide flexibility in manipulating the molecular design and their new innovative functions compared to metal alloy catalysts.

N,N'-Ethylenebis(salicylideneaminato)oxovanadium(IV)¹⁶ [abbreviated as VO(salen)], and nickel *N,N'*-mono-8-quinolylo-phenylenediamine¹⁵ [abbreviated as Ni(mqph)] were synthesized as reported in earlier works. Mixed catalysts were prepared from the platinum precursor, *i.e.* platinum tetra-amine chloride Pt(NH₃)₄Cl₂·xH₂O, and VO(salen) or Ni(mqph) in a 50–50 mass% ratio. 60 mg of 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 400 to 600 °C for 2 h in a furnace. The average particle size of platinum in the catalyst, calculated by using the Scherrer formula from X-ray diffraction experiments, was 4.5 nm. The obtained powder was characterized by X-ray photoelectron spectroscopy (XPS). 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

† Electronic supplementary information (ESI) available: TEM image of the Pt–VO(salen) heat-treated at various temperatures, and preparation of a half-MEA for the electrochemical CO tolerance tests. See <http://www.rsc.org/suppdata/cc/b4/b415271a/>

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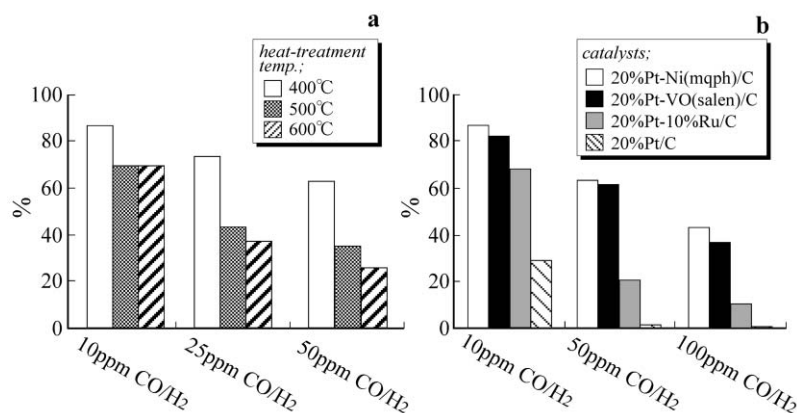


Fig. 1 Comparison of CO tolerance measured in a half-cell with H₂ gas containing various amounts of CO at 70 °C. (a) Effect of heat-treatment temperature of Pt–VO(salen)/C on the H₂ oxidation current containing various amounts of CO. (b) Comparison of Pt–VO(salen)/C and Pt–Ni(mqph)/C, that were heat-treated at 400 °C, with Pt/C and PtRu/C for the H₂ oxidation current containing various amounts of CO.

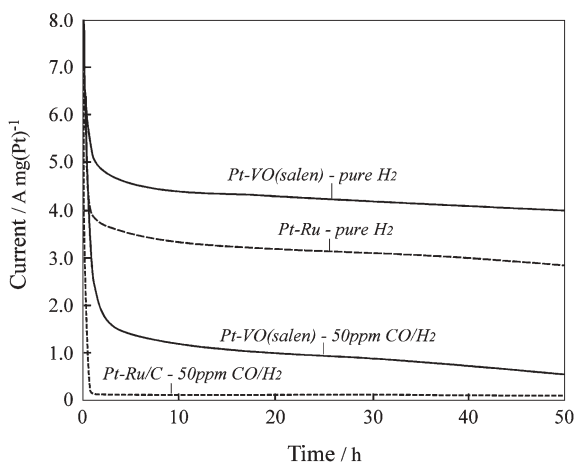


Fig. 2 Time variation of the hydrogen oxidation current at 100 mV RHE, measured for Pt-VO(salen)/C and Pt-Ru/C, in neat H₂ and H₂ containing 50 ppm CO gas.

(284.8 eV) signal. Curve fitting of the spectra was made by a combination of Gaussian and Lorentzian functions on a Shirley-type background.

CO tolerance tests for anode catalysts were conducted 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, 25, 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 hydrogen electrode (RHE) were used as the counter and 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, with the use of a Solartron model SI 1287 potentiostat.

Fig. 1(a) shows the HOR currents at 100 mV RHE derived from the polarization curves measured with H₂ gas containing various amounts of CO normalized by those measured in pure H₂, for the mixed catalysts of Pt-VO(salen)/C, which were previously heat-treated at various temperatures. In Fig. 1(b), the performances of Pt-VO(salen)/C and Pt-Ni(mqph)/C are compared with those of 20% Pt/C (ElectroChem, Inc) and 20% + 10% Pt-Ru/C (Johnson Matthey, Inc, Co) of the same Pt amount. The mass activity (current per unit mass of Pt contained in the catalysts) in neat H₂ were 7.6 A mg (Pt)⁻¹, 4.1 A mg (Pt)⁻¹, 4.8 A mg (Pt)⁻¹, and 4.1 A mg (Pt)⁻¹, for Pt/C, Pt-Ru/C, Pt-VO(salen)/C and Pt-Ni(mqph)/C (the latter two being heat-treated at 400 °C), respectively.

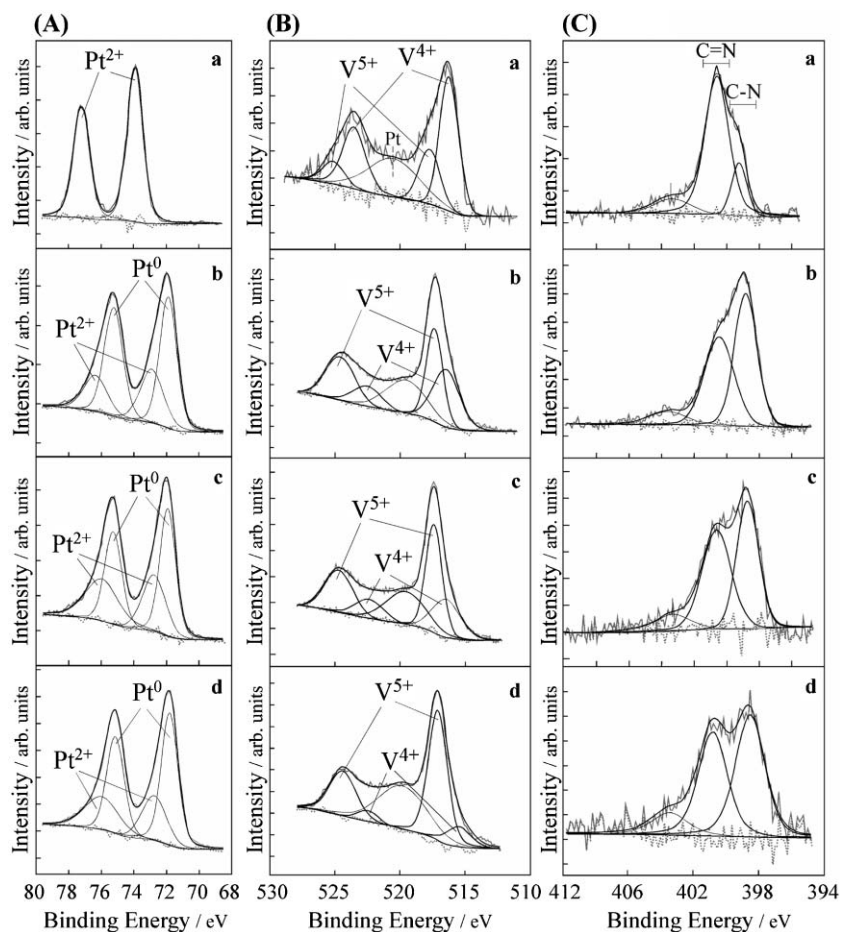


Fig. 3 X-Ray photoelectron spectroscopy of (A) Pt 4f_{7/2}, (B) V 2p_{3/2} and (C) N 1s peaks of Pt-VO(salen)/C, (a) non-heat treated and heat treated at (b) 400 °C, (c) 500 °C and (d) 600 °C.

In pure H₂, Pt/C and Pt–Ru/C catalysts showed an activity equal to or higher than that of Pt–VO(salen)/C and Pt–Ni(mqph)/C catalysts heat-treated at temperatures of 500 and 600 °C. However, the catalytic activity of Pt/C and Pt–Ru/C dramatically decreased with increasing the concentration of CO. On the other hand, Pt–VO(salen)/C and Pt–Ni(mqph) heat treated at 400 °C revealed very high CO tolerance, maintaining their catalytic ability to 100 ppm CO level. This result indicates that the performances of these organic complex catalysts are high enough to sustain efficient H₂ oxidation in the presence of CO.

In Fig. 2, the hydrogen oxidation activity of Pt–VO(salen)/C under 50 ppm CO is evaluated in comparison with Pt–Ru/C. While Pt–Ru/C rapidly deteriorates down to 0.09 A mg (Pt)^{−1} in the current *versus* time curve measured at 100 mV RHE, Pt–VO(salen)/C endures over 10 hours. In the durability test under neat H₂, the current level of 4 A mg (Pt)^{−1} was constantly sustained during the 50 h electrolysis, indicating the stability of the chemical structure and character of the catalyst. After 50 hours of polarization in the presence of 50 ppm CO, the HOR current declined to 0.6 A mg (Pt)^{−1}, but for a shorter period of operations as in the case of the starting-up time of fuel reformers, the CO tolerance of Pt–VO(salen)/C is satisfactory.

HOR performances were also evaluated for other mixed catalysts of platinum and organic complexes. A few other catalysts revealed high CO tolerance. It is very promising to find out the satisfactory CO tolerant catalysts using organic complexes with simple structures and low cost, when comparing the cost performances with Pt–Ru alloy catalysts.

X-Ray photoelectron spectroscopy (XPS) spectra of the Pt–VO(salen)/C mixed catalysts are shown in Fig. 3 in the energy regions of Pt 4f, V 2p and N 1s, and the spectra before the heat-treatment and those after the heat-treatment at various heating temperatures are compared. In Fig. 3(A), the Pt 4f region displays two doublets from the spin–orbital splitting of the 4f_{7/2} and 4f_{5/2} states, and in the case of non-heat treatment, the peak position indicates the binding energy of Pt(II) (73.9 eV), corresponding to a Pt(II) chlorinated species.¹⁷ After the heat-treatment, platinum becomes reduced from Pt(II) in the metal precursor to Pt(0). This reduction in the valence state could occur in parallel with the oxidation of vanadium, *i.e.*, V(IV) (516.4 eV) to V(V) (517.3 eV), as seen in Fig. 3(B).

These results suggest that the valence states of vanadium in Pt–VO(salen)/C mixed catalysts play a role in manipulating the

oxidation states of platinum. In addition, as anticipated from the N 1s spectra in Fig. 3(C), coordinated states between V and N are existent. 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.¹³ 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 Pt–VO(salen)/C or Pt–Ni(salen)/C mixed catalysts.

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