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**Molecular Catalysts for Energy Conversion in Fuel Cells**

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Tsukuba, September 7, 2010

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## Introduction

Polymer electrolyte fuel cells (PEFCs) are considered as an important device for future environment technology, and many researches are devoted to their earliest commercialization in stationary and mobile applications. One of the key components is the catalyst, where mostly platinum and alloys are used in the present technology. However, with limited world production and a high cost, alternatives to platinum are strongly desired. Two types of materials are historically investigated. One is transition metal macrocycles (porphyrins, phthalocyanines etc.) and relatives [1], where some derivatives are heat-treated on carbon materials resulting in higher activity and stability. The other is based on inorganic materials, especially carbides and nitrides of IV<sub>a</sub> through VI<sub>a</sub> transition metal elements [2]. Towards its goal, the strategy of bridging these two materials seems to be a plausible option for developing Pt-free electro-catalysts. This idea must be supported by consideration of the electronic structure and geometric properties of the catalyst elements. Note that in designing alloy catalysts, d-band properties and bond distance of surface atoms are crucial factors which determine OH adsorption potential and O<sub>2</sub> reactivity.

Present study is intended first to mimic both the macrocycles and transition metal nitrides, where metal-nitrogen bonds serve as oxygen reduction reaction (ORR)

active centres. Secondly carbon and nitrogen hybrid structure is highlighted as elemental active centres for ORR [3]. High density active sites consisting of iron cation and pyridinic nitrogen in graphitic sheets are attracting attention due to their superior catalytic ability [4], and are worth testing as model catalysts.

## **Background Information**

Oxygen reduction reaction (ORR) is a rather slow step in fuel cell reactions (slower than hydrogen oxidation reaction by  $10^6$  to  $10^7$  times), and needs a high overpotential. In order to avoid usage of large amount of platinum, alternatives were sought from the early stage of the PEFC development. As such candidates, macrocycles were proposed as early as 1960s [5], and applied for fuel cell cathodes. In macrocycles, the metal centre (M) with N<sub>4</sub> moiety was believed to be the active site for ORR [6], which can bind an O<sub>2</sub> molecule and transfer electrons via the peripheral conjugated aromatic rings. The role of M is to adsorb O<sub>2</sub> in the initial step of ORR, while that of the macrocycles molecule is to modify the electronic structure of M and relocate its redox potential so that O<sub>2</sub> can accept electrons from the d-orbital of M [7].

ORR involves 4 electrons as shown in the following scheme (in acid media):



If this process occurs in half-way,  $\text{H}_2\text{O}_2$  is evolved as undesired product:

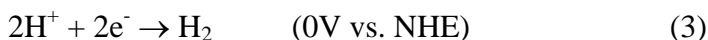


which causes harmful effects of carbon and membrane material degradation. Pt leads to almost perfect reaction route (1), while Au shows reaction (2). On Pt,  $\text{O}_2$  molecule adsorbs with its double bond axis parallel to the surface of Pt lattice (side-on interaction or Griffith model). This needs 2 adjacent sites of Pt, and O-O bond is weakened when its  $\pi^*$ -orbital receives back-donations from d-electrons of Pt. Mukerjee et al. [8], in designing alloy catalysts for ORR, suggested that increasing d-band vacancy of Pt and decreasing Pt-Pt bond distance both favour the ORR by decreasing OH adsorption on Pt and allowing Pt surface free sites.

This situation is not always the case for non-metal electrocatalysts such as macrocycles or inorganic compounds. Most cases are like end-on interaction of  $\text{O}_2$  molecules (Pauling model) with catalyst compounds, and O-O bond cleavage for 4-electron reduction requires special orientation. Anson et al. showed that dicobalt face to face porphyrins gives efficiently  $\text{H}_2\text{O}$  in acid [9]. In this case dioxygen adsorbs between two Co centres with trans-bridged configuration, and Co(II)/Co(III) redox transition activates  $\text{O}_2^-$  intermediates. This orientation may also provide a model for designing efficient

ORR electrocatalysts. More interesting report is that nitrogen in carbon interstitial structure can catalyse ORR [3]. The result infers that metal centres are not prerequisite as active catalyst sites.

Hydrogen oxidation reaction (HOR) catalysts are also important in order to reduce the total amount of precious catalysts in fuel cells. Historically the opposite reaction as hydrogen evolution reaction (HER) has long been investigated as most basic electrochemical reactions [10].



In HER, many parameters were investigated which affects the activity of transition metal electro-catalysts. Work function and heat of adsorption were found to be major characteristics relating to HOR activity. Kita et al. classified the metal into two groups [11], one is d-metals (transition and I<sub>b</sub> metals) and the other is sp-metals (metals after II<sub>b</sub>). In d-metals, the reaction intermediate is the adsorbed hydrogen atom H(a) (catalytic mechanism), and in sp-metals the adsorbed hydrogen molecule ion H<sub>2</sub><sup>+</sup>(a) (electrochemical mechanism). On increasing the number of d-orbital electrons of transition metals, HER activity first increases, drops on the completion of d-orbital, and then increases again with further increase in p-orbital. The highest activity occurs on Pt group metals.

When microscopic reversibility is applied to HOR, the same trend will appear for catalytic activity of elements. Almost filled d-orbital of transition metals will result in high HOR performances. Corrosion resistance in acid environment allows only Pt and its alloys as HOR catalyst candidates. Sometimes tolerance against CO becomes a crucial factor as the anode catalyst, and the second element like Ru is added to Pt.

As for non-precious catalysts for fuel cell anode, very few are reported successful because Pt outperforms in HOR activity (in exchange current density,  $i_0=10^{-3}$  A cm<sup>-2</sup>). Seeking for similar electronic structure as Pt, WC and MoS<sub>2</sub> have been proposed as alternatives, but the activity was low [12]. Molecular catalysts were also investigated, but very few successful reports were published so far. In this regard, enzyme catalysts in biochemical systems will be good models such that hydrogenase enzymes in bacteria which produce H<sub>2</sub> or H<sup>+</sup> by decomposing organic materials or nitrogenase enzymes which produce NH<sub>3</sub> during nitrogen fixation from N<sub>2</sub>. In hydrogenase enzymes, Fe-Fe or Fe-Ni bridged by S are thought to be the active centres for H<sub>2</sub> cleavage and H<sup>+</sup> production. In [NiFe] hydrogenase, H<sub>2</sub> is first adsorbed on Fe site, then split to H bridged on Fe-Ni and H<sup>+</sup> on cysteine S [13]. In energetics, the H-H bond cleavage occurs at the first energy barrier and H<sup>+</sup> transfer occurs at the second and third energy barriers. Electron

is transferred from the Fe-Ni dimer to Fe-S clusters. Nørskov et al. reported by DFT calculation that free energy of H bonding to the enzyme is close to that of Pt, and using this criterion proposed new MoS<sub>2</sub> catalyst [14].

## Strategy

### *ORR electro-catalyst*

In the periodic table, Pt group metal shows the most active and stable catalytic performance of ORR in acid media. Whether or not other elements could mimic the electronic structure of Pt had been a great concern in designing non-precious catalysts. Nørskov et al. found through DFT calculations a correlation between the bond energy of M-O and ORR reactivity [15]. The bond energy neither too strong nor too weak results in a high ORR activity (Volcano curve), which also relates to d-band vacancies of the metal [16].

O<sub>2</sub> molecule has a unique electronic structure with triplet spin configuration at the ground state, i.e., it has two unpaired electrons in doubly degenerate  $\pi^*$ -anti-bonding orbital. The bond order is two with four bonding orbitals and two anti-bonding orbitals. This configuration makes O<sub>2</sub> rather stable, and makes it difficult to convert. Transition metals that have vacant d-orbitals can catalyse complete O<sub>2</sub> reduction. When O<sub>2</sub> adsorbs on metal surface, electrons are donated from



$\pi$  orbital of  $O_2$  to  $dz^2$  orbital of the metal, and  $d\pi$  from the metal is back-donated to  $\pi^*$  anti-bonding orbital of  $O_2$  [17]. Then O-O bond is weakened and convert to  $H_2O$  through O-O bond cleavage.

On designing ORR catalysts from macrocycles, the mode of interaction of  $O_2$  with central metal M should be an important factor that determines the efficiency of 4-electron reduction. Dicobalt face-to-face porphyrin forms a *trans*- $\mu$ -peroxo intermediate that favours  $H^+$  access and O-O bond rupture [9]. On the other hand, for iron phthalocyanines, side-on configuration of  $O_2$  on M promotes back donation of d-electrons from M to  $O_2$ , and facilitates O-O bond cleaving [6]. This may be called the geometric or configuration effect, and the orientation of  $O_2$  against the metal adsorption site should be controlled by designing ligand structures. From this consideration binuclear complex rather than mononuclear complex is chosen for synthesis [18]. Whether *trans* or *cis* adsorption of  $O_2$  on M-M dimer centre favours ORR activity would be an interesting topic that should be solved [19].

The strategy for ORR on macrocycles is also considered through a control of the electronic structure so that the redox potential of M shifts downward near the electronic level of  $O_2$  during ORR [20]. Since the electron transfer occurs between  $O_2$  and M when their electronic levels are not too far apart, energy of  $O_2$  HOMO (highest occupied molecular orbital) and

d-band energy of M should be near the same level [21]. The structure of ligand would be a factor to modify this electronic effect and thus the ORR activity.

A new strategy is to build an M-N complex from the transition metal nitrides. For example, Mo<sub>2</sub>N that was synthesized as NH<sub>3</sub> production catalyst [22] is expected also as ORR catalyst because of its H<sub>2</sub> and N<sub>2</sub> dissociation ability. Ota et al. reported TaO<sub>x</sub>N<sub>y</sub> and ZrO<sub>2</sub> as good ORR catalyst with high stability in acid media [23]. They recently proposed partially oxidized transition metal carbide-nitride as cathode catalyst for fuel cells [2]. How to synthesize such inorganic catalysts in a simple process is a great concern, so as to realize the ORR reaction site in the most active state. It should be noted that Fe coordinated by pyridinic nitrogen in carbon structure can form very active ORR sites. Dodelet et al. designed the pyrolysed catalyst from Fe precursor (Fe acetate), the pore filler phenanthroline in high surface area carbon black, which were heat-treated in NH<sub>3</sub> at high temperature [4].

Looking for the alternatives of Pt, two approaches, i.e. one from organic metal complexes and the other from inorganic compounds such as metal nitrides can be combined and be made a third candidate, where M-N interactions modify the electronic structure of metal active sites.

*HOR electro-catalyst*

The energy of H<sub>2</sub> bonding is 436 kJ mol<sup>-1</sup>, and that of O<sub>2</sub> is 498 kJ mol<sup>-1</sup>. This shows how the HOR reaction:



needs stable H(a) adsorption sites in the first step (here H(a) indicates adsorbed H atom on the catalyst site). On Pt in acid electrolyte, Horiuti et al calculated quantum-chemically that H(a) resides in the surface hollow site of Pt lattice [10]. In relation to HOR catalysts from organic molecules like macrocycles, it seems thus inappropriate that single metal centre in an organic metal complex could split H<sub>2</sub> to H(a) and then discharge atomic H(a) to H<sup>+</sup> in a simple route. Metal dimer site may be the key structure that can split H<sub>2</sub>, and take special configuration that after electron is transferred, H<sup>+</sup> is released through the peripherals of the organic metal complex to the electrolyte, as in hydrogenase enzyme.

Tungsten carbide (WC) had been investigated as a Pt alternative, because similar electronic structure as Pt was anticipated. If this is the case, the same concept would be applied for the design of HOR inorganic catalysts. Although very few are reported so far, MoS<sub>2</sub> may be a model compound. Transition metals with high d-electron deficiency will bind strongly with O<sup>2-</sup> or S<sup>2-</sup>, and take almost filled d-orbitals. Aiming at the similar electronic structures as Pt merely do not guarantee the HOR catalytic ability, because splitting of H<sub>2</sub> on

the catalyst sites must be an important process. Also other factors like corrosion resistance should be taken into account.

### *CO tolerant anode catalyst*

In H<sub>2</sub>-air fuel cells, CO poisoning becomes the issue when reformed H<sub>2</sub> gas is used in the anode because Pt is susceptible to strong CO adsorption. Similar and important reaction related to CO poisoning is methanol oxidation reaction (MOR). In liquid feed fuel cells like methanol fuel cells, CO is formed as by-product and poison the anode catalyst. The catalyst surface should meet two aspects:

- (1) As the site requirements for methanol adsorption, more than 3 vacant sites are free [24].
- (2) The metal site should be maintained poison free during MOR. CO should be oxidized or eliminated from the metal surface.

The first requirement means that active metal site like Pt is inevitable. In order to cope with this problem, Pt-Ru alloy catalysts had been developed where the second element Ru adsorbs oxygen derived species on the surface, and help Pt to regenerate CO-free sites, either by bifunctional effect [25] or by ligand effect [26].

Because Ru is also the element of scarce production, new electro-catalyst is desired in order to reduce the cost of CO tolerant catalysts. Addition of co-catalyst to Pt is proposed

along this line, and the composite catalyst of Pt and organic metal complex turned out to be a good candidate. The role of the organic metal complex is intended to be the site of CO spillover, ligand effect or adsorption barrier of CO. The advantage of this composite catalyst is a wide variety of molecular design, where many possibilities in tailoring materials could open new functions for the performance improvement of the anode catalysts

## **Synthetic Procedure**

### *ORR catalysts based on heat-treated organic metal complexes on carbon substrates*

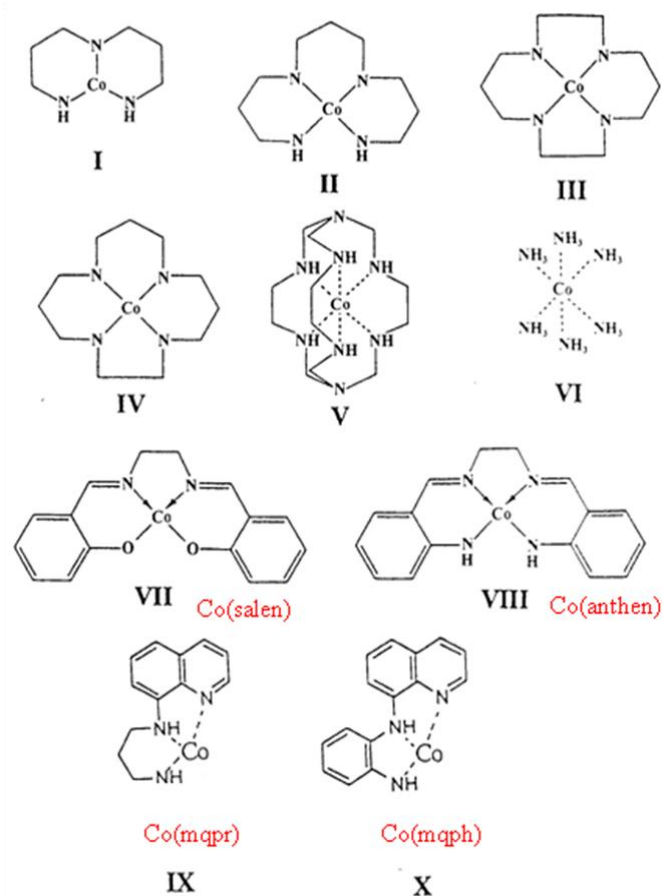
The first attempt for organic metal complexes in the present strategy was Co porphyrins heat-treated in Ar atmosphere on carbon substrate [27]. Anionic and cationic Co porphyrins, cobalt tetrakis(4-carboxyphenyl) porphyrin (CoTCPP) and cobalt tetrakis(1-methyl-4-pyridyl) porphyrin (CoTMPyP) were mixed in methanol to make porphyrin aggregates with planar faces stuck one another, and constructed as cofacial complexes. The compound was supported on graphite powder (Aldrich 1-2  $\mu\text{m}$ ; 50% by mass) in anhydrous pyridine, dried and heat-treated for 2 h in Ar atmosphere at temperatures 200 to 1000  $^{\circ}\text{C}$ .

Other cobalt macrocycles were synthesized by mixing metal-free ligands with equimolar amounts of cobalt acetate tetrahydrate for 1 h at room temperature in degassed ethanol. Cobalt compounds tested are depicted in Fig. 1 [28]. Complexes were mixed with graphite powder, heat-treated at 600°C for 2 h in Ar.

Co(salen) (**VII**), Co(anthen) (**VIII**), Co(dqpr) (**IX**) and Co(mqph) (**X**) were electropolymerized on the basal plane of pyrolytic graphite disk electrode from a solution containing  $2 \times 10^{-3}$  M of Co(complex) and  $5 \times 10^{-2}$  M of tetramethylammonium tetrafluoroborate in acetonitrile (AN) or dimethylformamide (DMF) saturated with Ar at 25°C. The potential was scanned 5-10 cycles between -1.7 and 1.7 V vs. Ag wire quasi-reference electrode (ca. 0.049 V vs. SCE) at 0.1 V s<sup>-1</sup>.

#### *Binuclear ORR catalysts based on phenoxide and C=N ligands*

Binuclear transition metal complexes that were intended to form *cis*-bridge interaction with O<sub>2</sub> were synthesized by bridging two diformylphenols with diamines. Interatomic distances between two metal atoms were designed to be in the range 2-3 Å. Catalysts were supported on Ketjen black and heat-treated at 400 to 600 °C for 2 h in N<sub>2</sub> atmosphere [18].



**Fig. 1** Chemical structures of cobalt complexes.

*Binary transition metal nitrides on carbon nanotubes*

Metal nitrides were synthesized from acetylacetonate (acac) reagents of V, Cr, Mo, Mn, Fe, Co and Ni. Single

$M(\text{acac})_n$  or a combination of two  $M_1(\text{acac})_n + M_2(\text{acac})_n$  dissolved in tetrahydrofuran (THF) were supported on carbon nanotubes (CNT) in  $N_2$  atmosphere, filtered and dried, then heat-treated first at  $400^\circ\text{C}$  in 10%  $H_2/N_2$  then at  $700^\circ\text{C}$  in  $NH_3$  (abbreviated as M-N/CNT or  $M_1$ - $M_2$ -N/CNT).

### *CO tolerant composite catalysts of Pt-M(complex)/C*

Nitrogen and oxygen ligand containing organic metal complexes, N,N'-bis(salicylidene)ethylenediamine (*salen*), N,N'-bis(salicylidene)phenylenediamine (*salophen*), N,N'-mono-8-quinolyl-o-phenylenediamine (*mqph*) and N,N'-bis(anthranilidene)ethylenediamine (*anthen*), coordinated to V, Mn, Fe, Co, Ni, Cu, Mo, Pd and Sn were synthesized and tested [29]. Major differences are the number of N ligands, i.e. 2N+2O for *salen* and *salophen*, 3N for *mqph* and 4N for *anthen*. Mixture of platinum precursor  $[Pt(NH_3)_4]Cl_2 \cdot xH_2O$  and each of the organic metal complexes are supported on graphite powder (1-2  $\mu\text{m}$ ) and heat-treated at  $600^\circ\text{C}$  for 2 h in Ar gas. This heat-treatment is important to finish the catalysts with high catalytic performance and robustness in long-term use. Methanol oxidation reaction (MOR) was measured in acid electrolyte containing methanol.

The gas electrode using  $H_2$  with CO was evaluated using the same catalyst. Platinum precursor  $[Pt(NH_3)_4]Cl_2 \cdot xH_2O$  and organic metal complexes are



supported with 50:50 mass % ratio on the carbon black (Vulcan XC-72R), and heat-treated in the same way [30].

## **Method of Catalyst Evaluation and Characterization**

Catalysts synthesized were mounted on a carbon disk-platinum ring electrode using Nafion solution (Aldrich) binder (dry Nafion to carbon ratio was 0.5), and evaluated for ORR in a 3-electrode electrochemical cell at 25°C. Test solution was 0.05 M H<sub>2</sub>SO<sub>4</sub> saturated with either N<sub>2</sub> or O<sub>2</sub>, and cyclic voltammograms and polarization curves were measured using dual potentiogalvanostat. The efficiency of O<sub>2</sub> reduction to H<sub>2</sub>O (%H<sub>2</sub>O) was evaluated by RRDE, by detecting H<sub>2</sub>O<sub>2</sub> emerging from the disk by means of the ring current.

For MOR activity measurements, the catalyst powder (abbreviated as Pt-M(*complex*)/C) was put on a glassy carbon disk electrode, and electrochemical measurements were performed in 1M CH<sub>3</sub>OH + 0.05M H<sub>2</sub>SO<sub>4</sub>, using a glass cell with 3-electrode configuration.

The catalyst performance for HOR was tested in a single fuel cell mode at 70°C. The catalyst-supported carbon powder was mixed with 5wt% Nafion solution to get an ink of the mixture, which was then pasted on the wet-proofed carbon paper. The amount of Pt in the mixed catalyst was  $5.4 \times 10^{-1}$

mg(Pt) cm<sup>-2</sup>, for the apparent electrode area. Membrane electrode assemblies (MEAs) having active areas of 2×2 cm<sup>2</sup> were prepared by hot-pressing the catalyst-loaded carbon paper and Nafion 115 membrane. Anode and the cathode gases were H<sub>2</sub> containing CO and Air, each humidified at 60°C.

X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM) and thermo-gravimetry (TG) were also conducted to characterize the catalysts.

## **Some Rules concerning Chelate Structure and Catalyst Performances**

### *ORR electro-catalyst*

Co porphyrin ion complexes heat-treated on carbon revealed much higher ORR ability than non heat-treated ones. Also it is seen from Table 1 that in every case the ion complex (CoTCPP+CoTMPyP) shows better ORR performances than monolithic porphyrin compounds (CoTCPP or CoTMPyP), indicating structural dependences for the ORR ability of the catalyst. Heat-treatment temperature was a crucial factor that determines ORR activity. As seen in Fig. 2, the highest activity appeared around 600 °C, where Co and N surface concentrations by XPS became highest on the carbon surface.

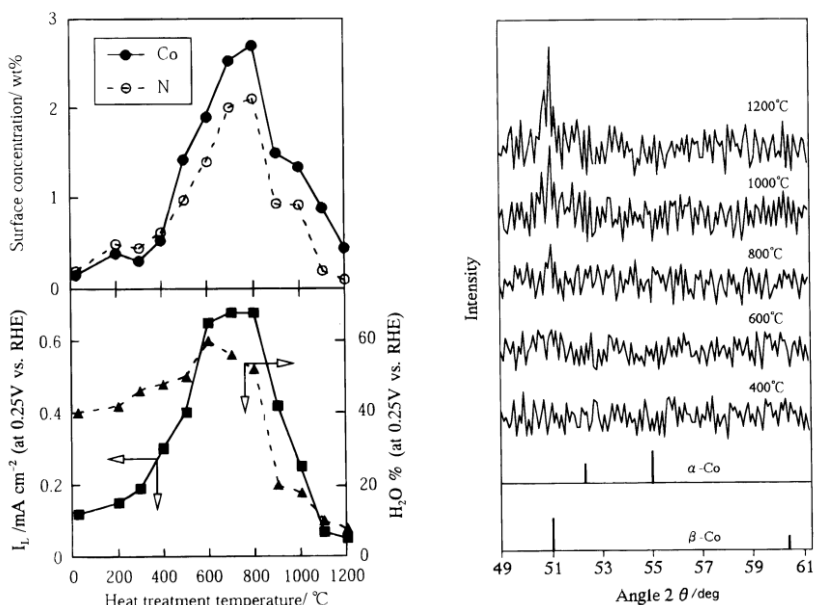
On the other hand, above 800 °C, activity declined and metallic Co clusters began to deposit as observed by XRD.

The results indicate that the chelate structure Co-N<sub>4</sub> was not totally destroyed during heat-treatment as long as the temperature was not too high, and some stable reaction sites remained in the metal centre on carbon surfaces. In order to see if the original structure affects the ORR activity after the heat-

**Table 1** ORR characteristics of non heat-treated and heat-treated Co-porphyrin compounds. Catalyst amount: 3.5-4 mg cm<sup>-2</sup> (apparent area of electrode).

Catalyst	$I_L$ /10 <sup>-3</sup> A cm <sup>-2</sup>	$I_k$ /10 <sup>-3</sup> A cm <sup>-2</sup>	%H <sub>2</sub> O
Non heat-treated			
CoTCPP + CoTMPyP	0.69-0.73	2.4	40-57
CoTCPP	0.35-0.48	1.5	10-14
CoTMPyP	0.34-0.44	1.5	10-12
Heat-treated at 600 °C			
CoTCPP + CoTMPyP	0.75-0.83	2.5	57-62
CoTCPP	0.62-0.72	1.8	30-39
CoTMPyP	0.59-0.65	1.7	27-36
Heat-treated at 800 °C			
CoTCPP + CoTMPyP	0.79-0.86	2.5	52-56
CoTCPP	0.66-0.73	2.0	33-40
CoTMPyP	0.60-0.66	2.0	30-38
Smooth Pt	1.00-1.05	5.9	96-98

treatment on carbon, several Co complexes with different chelate structures were tested which were supported on graphite powder and heat-treated at 600 °C. Table 2 shows the ORR performances as compared with Pt. The results are summarized as follows [28]:



**Fig. 2** Left: XPS surface concentration of Co and N (top), and electrochemical activity of ORR on CoTCCP+CoTNP/C heat-treated at various temperatures (bottom). Right: XRD patterns of the ion complex heat-treated at various temperatures [27].

**Table 2** ORR characteristics of heat-treated catalysts measured at 25 °C in 0.05 M H<sub>2</sub>SO<sub>4</sub><sup>a</sup>. Amount of Co complex: 1×10<sup>-6</sup> mol cm<sup>-2</sup> (apparent area of electrode).

Catalyst	Heat-treatment temperature /°C	$I_L$ /10 <sup>-3</sup> A cm <sup>-2</sup>	$I_k$ /10 <sup>-3</sup> A cm <sup>-2</sup>	$E_{p, 1/2}$ /V vs. SCE	%H <sub>2</sub> O
<b>I</b>	600	0.70	1.1	0.12	39
<b>II</b>	600	0.76	1.2	0.15	41
<b>III</b>	600	1.36	3.6	0.22	59
<b>IV</b>	600	1.13	2.5	0.21	55
<b>VII</b>	600	0.78	1.1	0.01	48
<b>VIII</b>	600	1.08	2.0	0.23	52
<b>X</b>	600	1.15	2.7	0.24	39
12% Pt/graphite	600	2.72	8.0	0.33	94
Smooth Pt	-	2.81	30	0.42	98

<sup>a</sup> Rotation speed: 300 rpm.  $I_L$ : limiting current density of ORR at 300 rpm;  $I_k$ : charge transfer current density at the half-wave potential  $E_{p, 1/2}$ ; %H<sub>2</sub>O: efficiency of O<sub>2</sub> reduction to H<sub>2</sub>O.

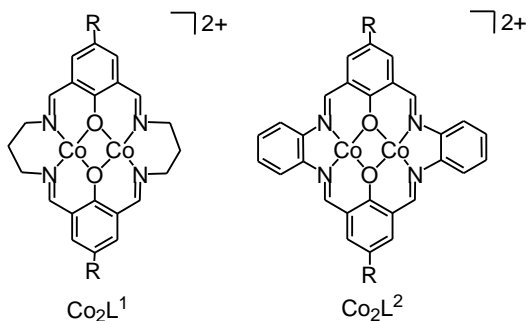
- (1) The number of ligands surrounding the central Co should be larger than three and less than six. Coplanar chelate structure of Co complex is crucial as O<sub>2</sub> coordination sites.
- (2) Closed-ring structure of metal complex is preferable to an open-ring structure.

- (3) Metal-ligand bond should be strong in order to ensure the stability of active sites during the heat-treatment.
- (4) The interaction between the substrate (carbon) and the chelate site is an important factor that determines the stability, orientation and surface density of the active centres.
- (5) The monolithic metal complex evolved  $\text{H}_2\text{O}_2$  as the major product, and the molecular design for binuclear complex is expected as the second step.

What is the basic structural feature of organic metal complexes that fulfill the requirements of the ORR active sites is a big question which is not answered yet. There have been several discussions about the “real structure” of organic metal complex catalysts after the heat-treatment on carbon substrates. Yeager assumed “carbonaceous compounds” where the metal oxides or clusters are adsorbed on carbon-nitrogen complex on the surface [31]. Van Veen et al. proposed that metal- $\text{N}_4$  chelate structure is the essential unit that reduces  $\text{O}_2$  into water [32]. Also Dodelet et al. assert that metal-carbon-nitrogen mixtures are formed on the surface and act as ORR active sites [33].

Based on these hypotheses, and on the expectation that *cis*- $\mu$ -peroxo intermediates could form if adjacent Co-Co sites rather than Co- $\text{N}_4$  cofacial structure (as in porphyrin

**Table 3** ORR activity and %H<sub>2</sub>O on dinuclear catalysts. Amount of Co complex: 0.014 mg cm<sup>-2</sup> (apparent area of electrode).



Catalyst	Heat-treatment temperature /°C	ORR mass activity /A g(metal) <sup>-1</sup>	%H <sub>2</sub> O /%
$\text{Co}_2\text{L}^1$	nil	0.65	59
	500	60	90
$\text{Co}_2\text{L}^2$	nil	40.8	64
	450	350	80
Pt	-	220	>98

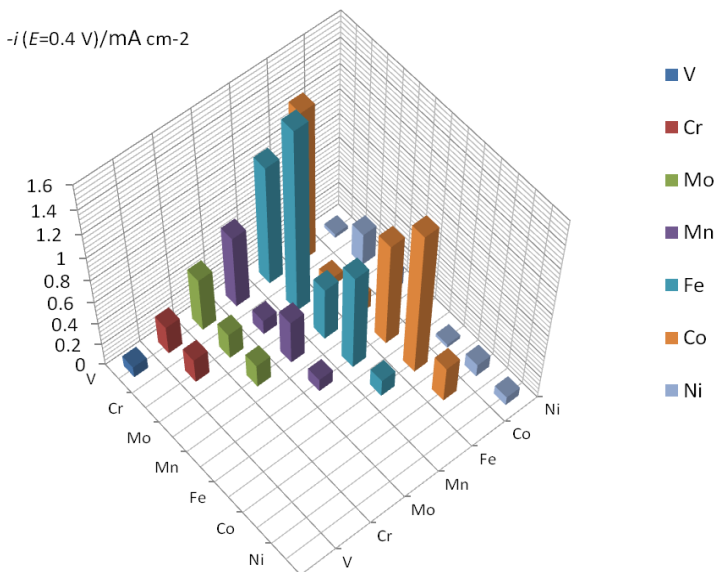
complexes) were realized, di-nuclear Co complexes were tested for ORR [18]. Table 3 shows this is really true, and it is inferred that chemical structures with stiff aromatic rings would prefer when the complex is heat-treated on carbon substrates because of the strong  $\pi$ - $\pi$  interactions between the complex and the carbon surfaces.

Further to corroborate theories that M-N<sub>x</sub> structure may be the active site for ORR, transition metal nitrides were tested that were formed on CNT by the gas phase reaction with NH<sub>3</sub>. Figure 3 summarizes ORR performances on M-N/CNT or M<sub>1</sub>-M<sub>2</sub>-N/CNT. CNT proved to be a good substrate, and even without metal particles that were incorporated on the surface, fair ORR activity appeared. As for the transition metal nitrides, very good synergistic effect was observed, and Fe-Cr-N/CNT, Fe-Co-N/CNT and V-Co-N/CNT appear to be good ORR catalysts considering also %H<sub>2</sub>O as high as 95-98 %. How these good ORR performances appeared on binary (not unitary) transition metal nitride systems is a matter to be clarified in future study. An interesting trend is that the number of d-electrons of these transition metal is nearly half (4 or 6) of d-orbitals. N has a high electro-negativity than C, and the central metal would shift to high d-vacancy, which is favourable for O<sub>2</sub> adsorption and O-O bond weakening. Considering their cost and availability, these new ORR catalysts would be a promising future candidate in the application for PEFC cathode catalysts.

#### *MOR and HOR electro-catalyst*

As shown in Fig. 4, polarization curves of MOR for 50:50 mixed catalysts Pt-Co(*complex*)/C reveals a strong ligand dependence on the MOR catalytic activity. Performance





Catalyst	$-i(E=0.4\text{ V})/10^{-3}\text{ A cm}^{-2}$
20 wt% Pt/Vulcan	3.45
Fe-Cr-N/CNT	1.56
V-Co-N/CNT	1.28
Fe-Co-N/CNT	1.24
Fe-V-N/CNT	1.03
CNT	0.607

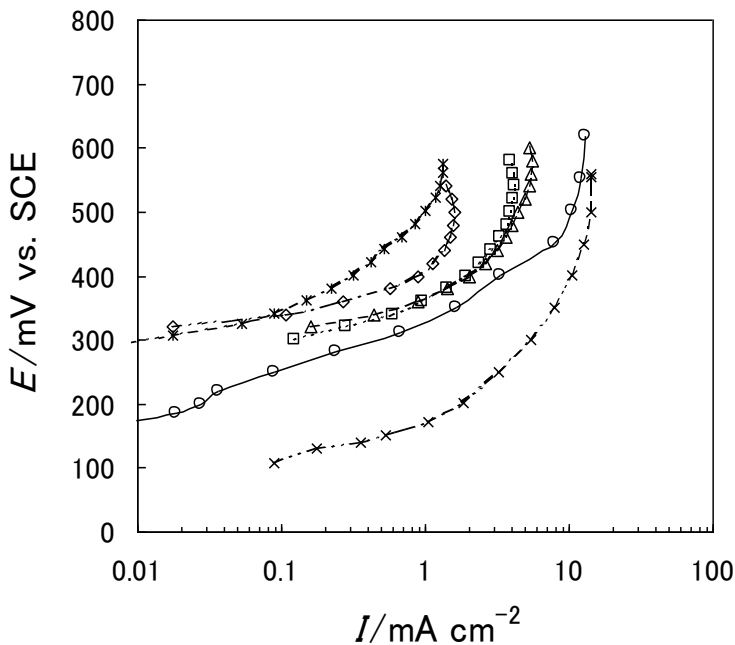
**Fig. 3** ORR activity (current density at  $E=0.4\text{ V}$  vs RHE) of M-N/CNT and  $M_1\text{-}M_2\text{-N/CNT}$  ( $M = \text{V, Cr, Mo, Mn, Fe, Co, Ni}$ ) synthesized by reaction with  $\text{NH}_3$  at  $700\text{ }^\circ\text{C}$ .

follows the order: Pt-Ru/C > Pt-Co(*mqph*)/C > Pt-Co(*anthen*)/C > Pt-Co(*salen*)/C > Pt-Co(*salophen*)/C > Pt/C. XRD and thermal decomposition by TG-DTA indicated full decomposition to metallic particles for Pt-Co(*salophen*)/C, but for other composite catalysts decomposition was gradual and partial, and Co complexes are not completely destroyed. XPS and EXAFS supported this result, and Co-N interaction remained after the heat-treatment.

Results of polarization curves of H<sub>2</sub>-Air fuel cells for Pt-VO(*salen*)/C and Pt-Ni(*mqph*)/C as anode catalysts are summarized in Table 4, where peak power density (W cm<sup>-2</sup>) and the cell voltage (V) at fixed current are compared. As long as the reformat gas containing 10 ppm to 50 ppm CO is used, the new composite catalysts performed quite good, which is in agreement with other electrochemical experiments.

Structural characterization by XPS revealed decomposition processes during heat-treatment. At around 300 °C, platinum precursor decomposes to Pt particles on the carbon surface. Between 300 °C and 600 °C, Ni(*mqph*) is partially decomposed and made a mixture with metallic Pt, but the initial complex structure is retained. Above 600 °C, the metal complex starts to decompose to form nickel metal clusters or alloys with Pt.

For Pt-VO(*salen*)/C, two peaks observed for the non-



**Fig. 4** Polarization curves of MOR on mixed catalysts with 50/50 mixing ratio, Pt-Co(*salophen*)/C ( $\diamond$ ), Pt-Co(*salen*)/C ( $\square$ ), Pt-Co(*anthen*)/C ( $\Delta$ ) and Pt-Co(*mqph*)/C ( $\circ$ ), supported on graphite powder and heat-treated at 600 °C. As a comparison, polarization curves on 12% Pt/C (\*) and 20% Pt-Ru/C (ElectroChem, ( $\times$ )) are also shown. Solution: 1 M CH<sub>3</sub>OH+ 0.05 M H<sub>2</sub>SO<sub>4</sub> at 25 °C, in deaerated condition with N<sub>2</sub> gas.

heat-treated specimen in the 2p<sub>1/2</sub> and 2p<sub>3/2</sub> region of V can be assigned to V(IV) and V(V) states. The oxidation of vanadium, i.e., from V(IV) to V(V) occurs in parallel with the reduction of platinum valence state. The relative intensity of V(V) / V(IV)

Catalyst	Gas	H <sub>2</sub>	H <sub>2</sub> + 10ppm CO	H <sub>2</sub> + 50ppm CO	H <sub>2</sub> + 100ppm CO
Pt/C(E-TEK) 0.41 mg Pt cm <sup>-2</sup>		0.21 (100%)	0.063 (30%)	0.029 (14%)	0.018 (8.6%)
		0.52, 0.51	0.02, ~0	~0, ~0	~0, ~0
Pt/C(ElectroChem) 0.30 mg Pt cm <sup>-2</sup>		0.28 (100%)	0.092 (34%)	0.031 (11%)	0.020 (7.2%)
		0.57, 0.54	0.32, 0.24	<0.05, ~0	~0, ~0
Pt-Ru/C(JM) 0.30 mg Pt cm <sup>-2</sup>		0.24 (100%)	0.14 (58%)	0.13 (54%)	0.15 (63%)
		0.59, 0.58	0.48, 0.38	0.36, 0.33	0.40, 0.38
Pt-VO(salen)/C 0.29 mg Pt cm <sup>-2</sup>		0.19 (100%)	0.18 (93%)	0.13 (69%)	0.070 (36%)
		0.52, 0.50	0.48, 0.46	0.45, 0.41	0.23, 0.13
Pt-Ni(mqph)/C 0.29 mg Pt cm <sup>-2</sup>		0.22 (100%)	0.20 (90%)	0.12 (53%)	0.080 (37%)
		0.51, 0.48	0.51, 0.48	0.43, 0.38	0.32, 0.22

**Table 4** Test results of single fuel cell performances with various kinds of anode catalysts measured at 70°C. In each row, the top figure shows peak power density (W cm<sup>-2</sup>) with retention in reference to pure H<sub>2</sub> in the parenthesis, and the bottom figure shows cell voltage (V) at 0.25 A cm<sup>-2</sup> and 0.3 A cm<sup>-2</sup> obtained from the polarization curve. Anode gas: H<sub>2</sub> with various amounts of CO, cathode gas: Air [30].

in the catalysts increases with increasing heat- treatment temperature. These results show that the change of valence state of vanadium in Pt-VO(salen)/C catalysts reflects the oxidation state of platinum.

## Conclusions

Transition metal-nitrogen coordination sites on carbon substrate are an interesting topic in the fuel cell catalyst applications. The important factors to be considered in designing non-Pt cathode catalysts may be summarized as follows.

- (1) M-N<sub>x</sub> chelate structures that are stabilized on carbon surfaces,
- (2) Adjacent M-M sites that can adsorb a O<sub>2</sub> molecule with side-on structures as in Pt,
- (3) Interaction of M-N reaction sites with graphene surfaces that shows high electron conductivity and strong electronic interaction with M-N reaction sites.

As for the anode catalyst, Pt is the main catalyst site but in the case of CO poisoning, organic metal complexes can serve as a co-catalyst. Here M-N centre is designed to be a CO adsorption site, where higher oxidation state of the metal activates CO, results in reduced back-donation and induces a nucleophilic attack by H<sub>2</sub>O.

Metal nitrides on carbon substrate, especially those of binary transition metal systems are good candidates as ORR catalyst. Here N is supposed to increase the metal binding force on carbon on one hand, and on the other hand increased d-vacancy of each of the metal centre will interact strongly with O<sub>2</sub>. This will facilitate bond breaking of O-O.

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**Summary:** For true commercialisation of low temperature fuel cells, non-precious electro-catalysts for gas phase reactions are inevitable. Especially in the cathode, since the oxygen reduction reaction causes a high overpotential, large amount of platinum is used in the present technology, and development of active and low cost catalysts is desired. In this work, such efforts are summarized first historically, and then a strategy for the alternatives is discussed. As the candidate of non-precious electro-catalysts, organic metal complexes are proposed since 1970s, but so far not many seem to be successful. Inorganic compounds such as metal carbides, nitrides and oxides are extensively studied recently, although still their power density being low. Advantages and disadvantages of these candidates, together with a new strategy that incorporates both features are also discussed. So far the anode catalysts are rather rare because platinum group metal catalysts (Pt, Pd, Ru etc.) perform extensively well and no other candidates are found to meet the desired catalytic abilities. Biomimetic approach (hydrogenase etc.) looks attractive, but is not yet established. How to design such anode catalysts is also the topic of this work.

## 要旨

低温型燃料電池の真の実用化のために、ガス反応における非貴金属触媒の開発が不可欠となっている。特に、燃料電池カソードにおいては、酸素還元反応が高い過電圧の原因となることから、現在は大量の白金が使用されており、活性の高い低価格触媒の開発が希求されている。

本研究では、そのような研究を歴史的に振り返り、白金代替物触媒の実現に向けての戦略を議論する。非貴金属電極触媒の候補として、有機金属錯体が 1970 年代以来提案されてきたが、成功に至ったものは多くはないようである。最近では金属炭化物、窒化物、酸化物などの無機化合物が精力的に研究されているが、それらの電力はまだ低い状況である。これらの候補物質の優れた点とそうでない点、更に両者の特徴を取り入れた新しい方法論についても議論する。

これまでのところ燃料電池アノード触媒については、白金触媒 (Pt、Pd、Ru など) の性能が非常に優れているため、必要とされる触媒能を満たす他の候補が見つからないこともあって、研究例はむしろ少ない。生体物質模倣 (ヒドロゲナーゼなど) の観点からのアプローチは魅力的であるが、確立されているわけではない。本研究では、そのようなアノード触媒を如何に設計するかについても議論する。

**List of published works relating to the topic of the thesis  
(cited papers, excluding citations by the author, are shown  
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