NON-NOBLE METAL CATALYSTS FOR PEM OXYGEN REDUCTION BASED
ON SOL GEL DERIVED COBALT NIGROGEN COMPOUNDS

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ABSTRACT

The majority of power loss in PEM fuel cells occurs at the
cathode, due to the sluggish kinetics of the oxygen reduction reaction
(ORR). Much higher loadings of Pt at the cathode, as compared to the
anode, must be used to compensate for this, resulting in high costs. There
have been numerous efforts to develop non-noble metal catalysts for the
ORR, including Co-N₄ chelates, normally arising from porphyrin
precursors and which have been shown to improve in activity with heat
treatment. In this work, Co oxide sol-gel syntheses, known to yield
nanoparticulate composite materials, have been modified by the
incorporation of carbon and nitrogen in the form of ethylene diamine.
These new catalysts have demonstrated very good ORR activity in acidic
solutions after adsorption on carbon and subsequent heat treatment, with
a maximum in performance and minimum in H₂O₂ generation at 700 °C.
Catalyst activity was also found to increase with an increase in the
concentration of the catalyst on the carbon powder and with increased
loadings of the catalyst.

INTRODUCTION

Low temperature fuel cells provide an efficient and clean source of power.
Through the oxidation of hydrogen or methanol at an anode and the reduction of oxygen
at a cathode, with the electrodes separated by a proton exchange membrane (PEM), a
current is generated. One of the limiting factors in fuel cell operation is the kinetics of
the oxygen reduction reaction, which does not proceed at a reasonable rate until large
overpotentials are reached. This results in a substantial power loss to the system. The
best catalyst currently known is Pt, and even when employed in nanoparticulate form, it
is still a very costly component of the fuel cell.

Therefore, numerous non-Pt catalysts have been investigated for their activity as
an oxygen reduction (ORR) catalyst. Materials which have been examined in acidic
media or in PEM fuel cells include Fe porphyrin (1), Co porphyrin (2, 3), ReRuS₄, MoRuS (4), Mo₉RuS₅ (4), CrO₂ (5), Au (6), Ir porphyrins (7) Pt/Ru mixed pyrochlores (8), Pt macrocycles (9) and organo-Cu compounds (10). In terms of Fe and Co porphyrin based catalysts, it has been shown that it is not necessary to retain the porphyrin structure in order to observe catalytic behaviour. Indeed, heat treatment in an inert atmosphere was found to improve both the activity and stability of these catalysts (11). It has been suggested that the active site is a dimeric metal-C-N species (12). Also, active catalysts for the ORR in alkaline solutions are formed from amorphous sputter-coated Co-N-C (1, 13). Promising catalysts have also been formed by passing acetonitrile gas over V, Cr, Fe and Co metal salts at 1000° C, again suggesting that the active centre does not require an intact porphyrin structure (14).

Our recent work has focussed on the sol-gel (SG) synthesis of a wide range of compounds. This approach offers many advantages in the preparation of solid state electrode materials, including ease of formation of binary and ternary films, as well as the resulting high surface area (nanosized particles), with further modifications of the particle size and surface area possible by the adjustment of the drying temperature and time. Our prior work with SG-derived Ni and Co oxides (15) led us to the formation of amorphous Co-N-C ORR catalysts using the SG route. Good catalytic activity has been observed in acidic solutions, better than for comparable Co phthalocyanine (CoPC) prepared using identical procedures.

**EXPERIMENTAL**

**Catalyst synthesis**

The synthesis of the catalysts was carried out by the dropwise addition of 2 to 3 equivalents of ethylenediamine (en), diluted in ethanol and ethyl acetate, over 3 days to a refluxing stirred ethanol and ethyl acetate solution of the standard Co oxide sol (16). A white precipitate that initially formed was determined to be HN₂C₂N₂HNO₃ from its appearance, solubility and the likely chemical reactions taking place, and was filtered off. Water was added, as needed, to enhance the solubility of the purple precipitate which began to form after 3 hours. The reaction was followed by UV-Visible spectroscopy (UV-Vis) and cyclic voltammetry (CV), to determine the change in the bonding environment of Co. The final product of the synthesis was a red solution (Co(en)ₓ sol) and several characterisation experiments were carried out on this material.

To absorb the Co(en)ₓ sol onto carbon powder, it was refluxed with ethanol and C powder for 2-4 hours and then stirred overnight, followed by filtering and rinsing with ethanol. In the case of CoPc (Aldrich Chemicals), the solvent used was THF and sequential rinsings were carried out with hot and cold water. All powders were dried under vacuum overnight before testing. The initial and final solutions were examined by UV-Vis spectroscopy to determine the degree of adsorption of the Co(en)ₓ sol catalyst onto carbon (Co(en)ₓ/C). To prepare higher concentrations of catalyst on the carbon
powder, the carbon powder was saturated with the catalyst solution and then evaporated to a gel, which was stable on an electrode surface only after heat treatment.

Heat treatment involved subjecting the Co(en)$_x$/C to a flow of nitrogen for at least 1 hour before transfer to a pre-heated tube furnace. The samples were heated at 500° to 900° for 2 hours and then allowed to cool under a flow of N$_2$. Whether heat treated (Co(en)$_x$/C-ht) or not (Co(en)$_x$/C), the catalyst powder was ground by mortar and pestle for at least 2 minutes before mixing with Nafion solution.

An 11% Nafion solution (1100EW) was diluted with acetonitrile or ethanol and mixed with the Co(en)$_x$/C-(ht) in the appropriate ratios. Just before application to the electrode surface, the suspension Co(en)$_x$/C-(ht)-Naf was sonicated for 10 minutes.

Electrochemical evaluation of ORR kinetics and mechanisms

A 5 or 7 mm diameter glassy carbon (GC) rotating disc electrode (RDE) or a Au /Pt or GC/Pt RRDE (5 mm disc for both) were used as the electrode substrate to determine the ORR activity of the catalysts. A measured volume (14 µL for a 7 mm disc) of the Co(en)$_x$/C-(ht)-Naf was applied by micropipette to the centre of the electrode disc to give a loading of 0.6 mg/cm$^2$ of dry catalyst powder. With a Co loading of 1.2 % Co/C, this gives a loading of 0.008 mg/cm$^2$ of Co. The electrode was then air-dried for approximately 5 minutes before drying for 1 minute using a heat gun.

The standard electrochemical conditions employed were 0.5 M H$_2$SO$_4$, purged with vigorously bubbling nitrogen or oxygen for at least sixty minutes and then with nitrogen or oxygen at a flow rate of 50 mL/min for 5 minutes. A three electrode electrochemical cell was used, containing a Pt black mesh counter electrode and a reversible hydrogen electrode reference electrode. CVs were collected first in nitrogen purged aqueous solution at 2 or 10 mV/s to obtain a baseline for comparison to the ORR data. The cell was then saturated with oxygen, as described above, and a CV was run at 2 or 10 mV/s at different rotation rates (0-2000 rpm) using a Pine analytical rotator (ASR2). Data collection was achieved using either Corrware (RDE) or PineChem (RRDE) software.

RESULTS AND DISCUSSION

Co(en)$_x$ sol synthesis

Fig. 1 shows the changes in the UV-Vis spectrum of the Co product formed as a function of the ratio of Co to en during the synthesis. The goal of this experiment was to ascertain that Co was indeed being complexed by the nitrogen of the ethylene diamine (en) and to establish whether oxygen continued to be in the Co bonding environment. A cobalt oxide sol-gel (O-Co-O-Co) and Co(H$_2$O)$_6^{2+}$ both have the same $\lambda_{\text{max}}$ at 510-514.
nm (515 nm (17). When the cobalt is complexed to nitrogen, as in pure Co(en)$_3^{3+/2+}$, the $\lambda_{\text{max}}$ shifts to 464-476 nm (Fig. 1). In the data of Fig. 1, it is seen that the molar absorptivity increases with increasing ligand ratio and that the $\lambda_{\text{max}}$ shifts to lower wavelengths, indicating at least partial complexation of Co with en. The final product exhibits a $\lambda_{\text{max}}$ at the same position as Co(en)$_3^{3+}$, but with a much broader peak and a shoulder near the Co-O peak. This suggests that both Co-N and Co-O bonds exist in the SG in solution, and it is assumed (but cannot be verified from these spectra) that each Co centre is complexed both to O and N.

![Figure 1: Evidence for Co-ethylene diamine complexation in Co oxide sol gel](image)

Figure 2 shows the CV response of the non-carbon supported catalyst in alkaline solution. Also shown is the CV response of a pure Co oxide SG, formed using identical conditions to the catalyst (but without added en), revealing the known Co$^{2+/3+}$ oxide and Co$^{3+/4+}$ oxide redox transitions, typical of Co oxide dried at less than 200°C (15). In comparison, the Co(en)$_x$ sol reveals a different response, with significantly shifted potentials. This is evidence for the alteration of the Co centre in these catalysts vs. in Co oxide. Had the catalyst contained a mixture of Co oxide and Co-C-N, we would have expected to obtain the CV signatures of both Co oxide and the new material. The results in Fig. 1 and Fig. 2 therefore support the contention that all of the Co centres are in a mixed environment involving oxygen and nitrogen bonded to Co.
The Co(en)$_x$/C catalysts initially exhibited quite low ORR activity. Consistent with the literature, the catalytic activity improved greatly upon heat treatment. Fig. 3 shows the improved activity after heat treatment at 650 °C for 2 hours under flowing N$_2$, demonstrating also that the Tafel slopes are lowered, consistent with a more active catalyst. Cobalt phthalocyanine (CoPC), prepared in parallel with our catalyst, also shows an improvement in ORR activity with heat treatment, as reported in the literature (2) for CoPC prepared using different processing steps. The exact mechanism by which heat treatment improves the activity of CoN$_4$ based catalysts is not known, but numerous suggestions have been made, including improvement in the dispersion of the catalyst, the formation of new bonds of the chelate to the carbon powder, the formation of a new type of Co species or carbon species (18), and the formation of dimeric CoN$_4$ sites (12).

The generation of H$_2$O$_2$ during the ORR was also examined for our SG-derived catalyst, in comparison with CoPC. The direct four-electron mechanism to water is the preferred reaction pathway, vs. the two-electron generation of H$_2$O$_2$, both because of the higher currents and voltages obtained, but also as corrosive H$_2$O$_2$ is not formed. Using the RRDE in oxygen-saturated 0.5 M sulphuric acid, it was found that 30% of the oxygen which reacted at the disc formed H$_2$O$_2$ when our catalyst was non-heat treated, compared to 50% for non-heat treated CoPC. After heat treatment at 650 °C, the value for the SG-formed Co(en)$_x$/C dropped to 20%, while the % H$_2$O$_2$ generated at CoPC did not change.
consistent with previously reported results (2). These results demonstrate an additional advantage of the SG route for Co(en)$_x$ sol synthesis.

Figure 3: Effect of heat treatment on the ORR activity of CoPC compared to our catalyst.

To determine the optimum heat treatment temperature, for these catalysts, temperatures were varied from 500 to 900° C. Fig. 4 shows a plot of the potential at a selected current density of 2 mA/cm$^2$ as well as the % H$_2$O$_2$ generation as a function of

Figure 4: Optimisation of heat treatment temperature.
drying temperature, clearly revealing the benefits of temperatures over 700°C. Under these conditions, the ORR activity is the highest, while the amount of H₂O₂ formed is very small. An optimum heat treatment temperature of between 600° and 800° C has been generally reported (2, 12, 14) for CoPc, although a maximum at 600°C has also been reported (19).

In an effort to further increase catalyst performance towards the ORR, multiple layers of the Co(en)ₓ/C-ht-Naf were applied to the GC electrode to determine the effect of loading on the achievable reaction rate. The inset in Fig. 5 reveals the increasing amount of catalyst on the surface, based on the larger charging currents of the carbon support. Indeed, the ORR currents also increase and, in other experiments, it has been shown that up to 3 to 5 loadings of the catalyst can be applied, after which no further increases in the ORR activity are seen.

![Figure 5: Increase in ORR activity with multiple loadings](image)

Other experiments focussed on increasing the ORR activity by increasing the ratio of Co(en)ₓ sol to the carbon support. Fig. 6 demonstrates the success of this approach up to a maximum loading of 20% by weight of the Co on carbon, after which the activity decreases again. This was observed with two separate batches of catalyst. The need for a relatively high amount of carbon points towards its involvement in generating the desired active sites. In our work, this is also clearly observed in other ways, e.g., as catalysts heated to 650 °C in the absence of carbon support yield only a very poor ORR activity of 10 to 20 %, relative to those that are pyrolized with carbon.
Figure 6: The effect of a higher concentration of Co on C powder

Fig. 7 demonstrates the improved performance of our SG-formed Co(en)$_2$/C-ht catalyst over approximately the last year of research.

Figure 7: Improvements in catalytic activity with changing variables

The increase in activity shown from left to right in Fig. 7 was achieved by changing only one catalyst preparation variable at a time. Non-heat treated catalyst was relatively inactive, similar to other materials which we have prepared. Heat treatment
was found to improve the activity significantly, while the method of initial drying of the 
catalyst after applying it to the electrode was also found to be very important. Initially, 
the catalyst was dried for 15 minutes at 175° C in air (in a furnace), but drying the 
catalyst for only one minute with a heat gun led to a notable activity increase. As 
described earlier (Fig. 6), increasing the catalyst loading led to a further substantial 
increase in activity, although a maximum was observed at 20% Co. Fig. 7 also shows 
that Pt (0.12 mg/cm²) still gives ca. 100 times better performance than the Co(en)x/C-ht, 
although at an approximately 800 times higher cost.

CONCLUSIONS

In this work, Co oxide sol-gel syntheses, known to yield nanoparticulate 
composite materials, have been modified by the addition of ethylene diamine in order to 
incorporate carbon and nitrogen into the Co environment. The successful achievement of 
this goal has been verified using UV-Visible spectrophotometry and cyclic voltammetric 
analysis in alkaline solutions. These new catalysts demonstrate very good oxygen 
reduction activity in acidic solution after adsorption on carbon and subsequent heat 
treatment. Based on the improved kinetics (both lowered Tafel slopes and higher 
exchange current densities), as well as the lower amount of H₂O₂ generated, the optimum 
heat treatment temperature was found to be 700 °C. By comparison, Co phthalocyanine 
catalysts, prepared identically, also showed an increase in activity with heat treatment, 
but less than that of Co(en)x/C, and with no decrease in the amount H₂O₂ produced.

Catalyst activity was also found to increase with an increase in the concentration 
of the Co(en)x sol on carbon powder. However, this is limited to 20 wt % Co on carbon, 
after which the ORR activity decreased again. Increasing the quantity of catalyst 
impregnated carbon powder on the electrode surface also increased the activity, 
suggesting that the catalyst is a porous network. The beneficial effect of increasing the 
loading was limited to 3-5 layers (0.6 mg/cm² each), perhaps due to the blocking of 
active sites by the outer layers of catalyst.

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