

Dioxygen Fixation by a Cobalt(II)–Ammoniacal Complex and its Electroreduction in a Nafion Coated Solid-state Three-electrode Cell

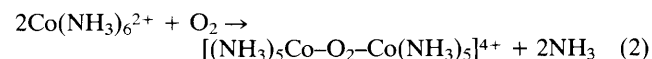
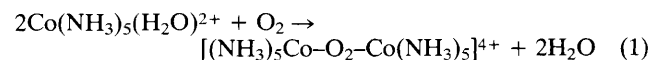
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The reduction potential for the $\text{Co}^{\text{II}}\text{-NH}_3\text{-O}_2$ system at a glassy-carbon electrode in a solid-state Nafion-coated cell is about 800 mV more positive than obtained for a glassy-carbon–Nafion film electrode when immersed in an aqueous solution containing Co^{II} , ammonia, and dioxygen (+0.3 and -0.5 V vs. Ag/AgCl, respectively); this is attributed to two different electrode reactions: reduction of $[(\text{NH}_3)_5\text{Co-O}_2\text{-Co}(\text{NH}_3)_5]^{4+}$ in the absence of a contacting liquid electrolyte solution and free O_2 in aqueous Co^{II} –ammoniacal solution.

We recently described the catalytic properties towards dioxygen reduction of cobalt tetrakis(*o*-aminophenyl)porphyrin [abbreviated Co(tapp)]. This catalyst was electropolymerized onto glassy-carbon (GC) and the modified electrodes were studied in aqueous solutions.¹ We also showed that when using ionic conducting polymers such as polyethylene oxide (PEO)² or Nafion,^{3,4} it is possible to conduct the electrochemistry of various redox couples in the absence of a contacting electrolyte solution and in a macro electrode configuration, provided that the set-up is exposed to a wet gas (such as Ar– H_2O). Polymeric films of Co(tapp) exposed to a Ar– H_2O bathing gas in the Nafion solid-state configuration exhibited two $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ waves at +0.37 and +0.20 V vs. Ag/AgCl. A substantial current increase was observed when the bathing gas was replaced by air– H_2O and the half-wave potential for the catalytic reduction of dioxygen (+0.25 V vs. Ag/AgCl) was similar to that obtained for the polymeric Co(tapp)/GC-modified electrodes immersed in an air-saturated 0.5M H_2SO_4 solution.¹

It is well known that many Co^{II} complexes take up molecular dioxygen from organic and aqueous solutions.⁵ The best known dioxygen adduct is $[(\text{NH}_3)_5\text{Co-O}_2\text{-Co}(\text{NH}_3)_5]^{4+}$. The reversibility of the reaction of the Co^{II} ammoniacal complexes with dioxygen has been investigated by numerous authors using spectroscopic, potentiometric, and kinetic methods [reactions (1) and (2)].⁶



In the present work, we have studied reduction of dioxygen in the presence of the Co^{II} –ammonia system using a Nafion solid-state configuration. As in the previous study,⁴ the arrangement consisted of two electrodes (0.47 cm²) cast in polyester and serving as working and auxiliary electrodes. The gap between the two electrodes was about 0.5 mm. A Nafion tube containing a polymeric Ag/AgCl reference electrode³

was pressed over the two other electrodes and a Nafion film was cast by spreading 100 μl of the 1% polymer solution over the electrodes followed by drying in air at room temperature.

Figure 1 shows the cyclic voltammograms obtained when the three-electrode solid-state configuration contains Co^{II} ions in the Nafion film and is exposed to Ar– H_2O and O_2 – H_2O bathing gases [curves (a) and (b), respectively]. In the absence of ammonia, dioxygen reduction occurs at negative potentials [$E_p \sim -0.4$ V vs. Ag/AgCl, curve (b)]. However, when NH_3 is introduced into the bathing gas (by adding NH_4OH to the solution through which the bathing gas passes), a cathodic peak appears with $E_p +0.3$ V vs. Ag/AgCl [curve (c)]. This peak almost completely disappears when O_2 is replaced by an inert gas, such as Ar [curve (d)]. It can also be seen from Figure 1 that high anodic currents are obtained for the oxidation of NH_3 (or NH_4OH) which are not observed (in the +0.7 to -0.4 V potential range) in the absence of NH_3 [curves (d) and (a), respectively].

Similar experiments were conducted using the modified electrode concept, *i.e.*, using a GC electrode with a Nafion film (obtained by dipping in a 1% Nafion solution and air drying the electrode) which was then immersed in a 0.1 M NaClO_4 solution. The cyclic voltammograms obtained in the absence and presence of Co^{II} ions in the deaerated 0.1 M NaClO_4 solution are shown in Figure 2 [curves (a) and (b) respectively]. A broad oxidation wave at +0.3 V vs. Ag/AgCl is observed when NH_4OH is added to the deaerated solution [curve (c)]. When some air is introduced in the solution, a peak for dioxygen reduction appears with $E_p -0.5$ V vs. Ag/AgCl [curve (d)]. This potential is similar to that obtained for dioxygen reduction in the ammoniacal– NaClO_4 solution in the absence of Co^{II} ions (not shown in Figure 2). This seems to indicate that, as concluded from similar experiments conducted with uncoated electrodes in Co^{II} –ammoniacal solutions,⁷ the species being reduced at the electrode is free O_2 in labile equilibrium with the $[(\text{NH}_3)_5\text{Co-O}_2\text{-Co}(\text{NH}_3)_5]^{4+}$ complex.

The present results, therefore, suggest that the electrochemistry of the Co^{II} – NH_3 – O_2 system in the absence of a contacting electrolyte differs from that of the same system

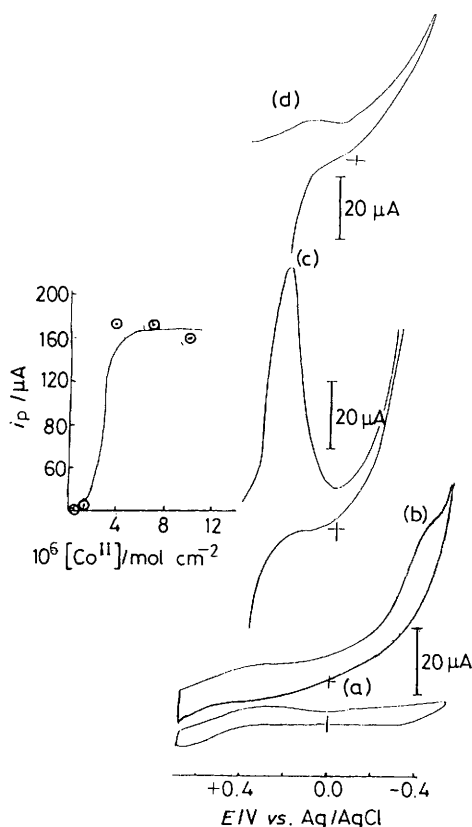


Figure 1. Cyclic voltammograms (20 mV/s) for a Nafion-GC film electrode exposed to (a) Ar-H₂O, (b) O₂-H₂O, (c) O₂-NH₃-H₂O, and (d) Ar-NH₂-H₂O bathing gases. *Inset:* peak current for dioxygen reduction as function of the Co^{II} surface coverage when the cell is exposed to O₂-NH₃-H₂O.

when tested in an aqueous solution. While O₂ is directly reduced in electrolyte solutions containing cobalt-ammoniacal complexes, reduction of the (NH₃)₅Co-O₂-Co(NH₃)₅ complex is achieved using the solid-state ionic conductive polymer configuration. Since the experiments with the Nafion-modified electrodes were conducted in the presence of a high Co^{II} concentration in the solution (10⁻² M), it is improbable that the cobalt-dioxygen adduct is reduced because of a higher Co^{II} content of the Nafion membranes in the solid-state system.

The catalysis of dioxygen reduction is much more effective in the Nafion solid-state configuration than it is in aqueous solutions [curves (c) in Figure 1 and (d) in Figure 2, respectively]. Dioxygen reduction in the solid-state cell occurs at a potential 800 mV more positive than obtained when O₂ is reduced at a modified Nafion electrode immersed in an aqueous Co^{II}-ammonia solution (+0.3 and -0.5 V vs. Ag/AgCl, respectively). Activation of molecular dioxygen by transition-metal complexes has been suggested to occur via a one-electron, two-electron, and four-electron-transfer, which will generate superoxide ion, peroxide ion, or oxide ion in aprotic media.^{8,9} We have previously shown that a large amount of H₂O₂ is produced during O₂ reduction catalysed by

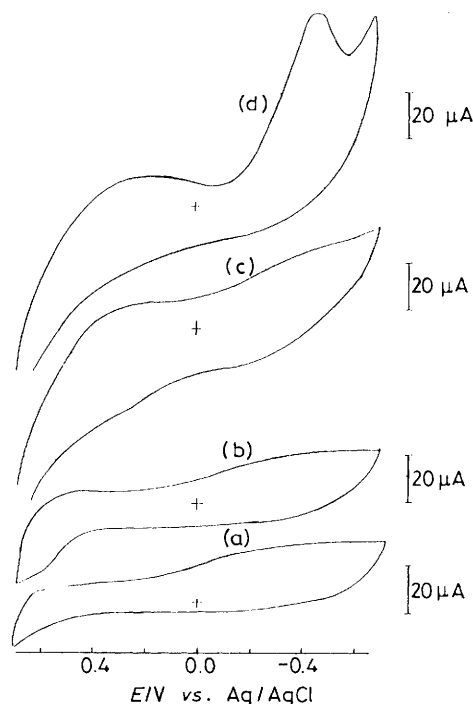


Figure 2. Cyclic voltammograms (20 mV/s) for a Nafion-modified electrode immersed in a deaerated 0.1M NaClO₄ solution in the absence [curve (a)] and presence of 10⁻² M Co^{II} ions [curve (b)]. Curve (c) is as in (b) after adding 2 M NH₄OH and deaerating the solution. Curve (d) is as in (c) after introducing some air.

Co(tapp) present in a PEO solid-state four-electrode electrochemical cell.² Preliminary experiments, conducted with a similar configuration, show considerable production of hydrogen peroxide (ca. 30%) for electroreduction of the cobalt-ammonia-O₂ adduct in the solid-state Nafion-coated cell.

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