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# The Catalytic Oxidation of Ammonia in a Ceramic Electrochemical Reactor, Using Metal Oxide Electrodes

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**The oxidation of ammonia to nitric oxide can be realized in a ceramic electrochemical reactor. Electrochemical control of the catalytically active electrode allows for an increased selectivity to the products of interest. This work examines the effect of metal oxide electrodes as catalysts for the above reaction. When $Co_3O_4$ was used, for example, control of the material could be realized and a more active catalytic species could be produced. $Co^{3+}$ was postulated to be a very active species for the reaction and as such its stabilization by an applied potential allowed for an increased selectivity to nitric oxide.** © 1994 Academic Press, Inc.

## INTRODUCTION

Ceramic electrochemical reactors have applications in electrocatalysis as a means of modifying the electrocatalyst and thus allowing increased selectivity of a particular reaction. Catalytic activity and selectivity for reactions such as styrene from ethylbenzene (1), HCN from $CH_4$ and $NH_3$ (2), and $SO_2$ from $H_2S$ (3) have been examined in electrochemical reactors. In these cases the authors were interested in operating the cells for the simultaneous generation of chemical products and electrical power. More recent work has described the modification of catalytic activity as nonfaradaic; that is, the increase in catalytic activity is greater than the rate of oxygen ion transport through the electrolyte (4, 5). This phenomenon is now described as nonfaradaic electrochemical modification of catalytic activity (NEMCA) and has been shown to increase the catalytic rate by a factor of $3 \times 10^5$ over the rate of oxygen ion supply to the catalyst (6, 7). The use of alternative electrolytes has also been examined. $\beta''$-$Al_2O_3$, a $Na^+$ ion conductor, has been used to show that the NEMCA effect can increase the rate of ethylene oxidation on Pt by a factor of $10^3$ to $5 \times 10^4$ over the rate of supply of $Na^+$ ions to the electrocatalyst (4, 7).

The oxidation of ammonia to nitric oxide in a ceramic electrochemical reactor has been previously investigated in a cell of the type (8–10)

$$NH_3,\ \text{metal catalyst}/(ZrO_2/8\ \text{mol\%}\ Y_2O_3)/M,\ O_2$$

where the metal, *M*, catalyzes the reaction

$$O_{2(gas)} + 4e^-_{(electrode)} \rightarrow 2O^{2-}_{(electrolyte)}. \qquad [1]$$

This serves as a means of supplying $O^{2-}$ to the metal catalyst. The exact mechanism is more complicated than that shown and involves a large number of intermediate steps, each with its own kinetic behavior (11, 12). Initial work by Farr and Vayenas (8, 9) and later by Sigal and Vayenas (10) showed that NO could be produced as the primary product, with the cogeneration of power, using a reactor with two platinum paste electrodes. The authors concluded that the dominant anode reaction was

$$2NH_3 + 5O^{2-} \rightarrow 2NO + 3H_2O + 10e^-. \qquad [2]$$

They also remarked that the rate of reaction was controlled by the rate of oxygen diffusion through the electrolyte.

Later work by Manton *et al.* (13) showed that by increasing the current density, the selectivity of NO could be increased. This was due to the effect of passing more oxygen to the anode and thus decreasing the side reaction to nitrogen. Farr and Vayenas (9) showed that the effect of admixing oxygen to the feed stream produced the same selectivity as that of obtaining equal amounts of oxygen through the electrolyte.

The aim of this study was to investigate the effect of applied potential on the catalytic activity of metal oxide catalysts for the oxidation of ammonia. Metal oxides are currently used in solid oxide fuel cells (14) as the anode, cathode, and interconnect materials. However, the electrochemical control of these metal oxides has not previously been studied.

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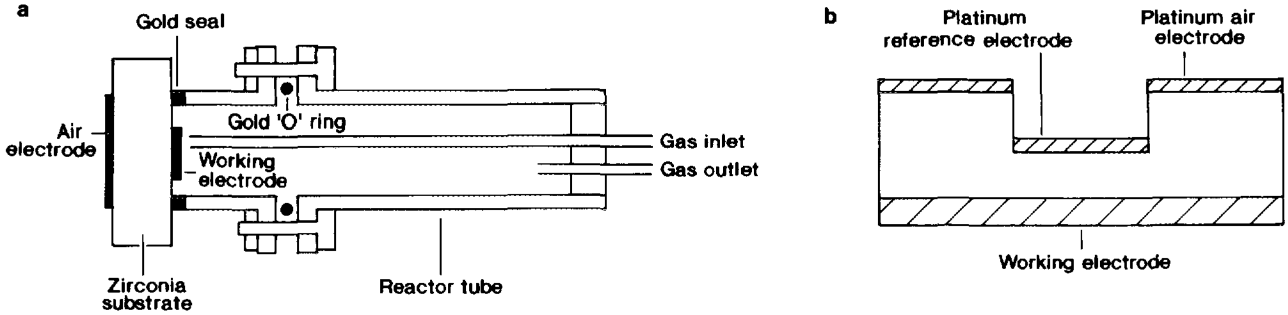

FIG. 1. (a) Schematic of the electrochemical reactor; (b) schematic of the zirconia electrolyte, showing the working, reference, and counter (air) electrodes.

## EXPERIMENTAL

The apparatus used for this work is shown in Figure 1a. The silica inlet tube was attached to a stainless steel tube, which in turn was attached to the outlet of a series of mass flow valves (supplied by Brookes Instruments). Each mass flow valve was attached to the required gas, depending on the concentration and flow rate required. Helium and ammonia were used without further purification, and were passed directly into the reactor. Oxygen was used in certain experiments without further purification. The silica outlet tube was attached directly to a Philips Gas Chromatograph (GC), using a 6-way valve which allowed 1 $cm^3$ of gas to be passed into a Chromosorb 103 column in series with a molecular sieve (MS5A) column, using automatic switching valves. A nitrogen balance was used to determine whether a leak was present within the system. The bulk of the outlet gases were vented to air. The electrode wires were attached to "lead throughs" so that connections could be made to them from outside the furnace. A potentiostat was then incorporated into the system to allow potentiostatic control of the cell. Ammonia and occasionally oxygen, prediluted in helium, was then passed into the reactor.

A fully stabilized zirconia (FSZ) pellet (fabricated from Toyso 8 mol% yttria-stabilized zirconia powder) was used as the solid electrolyte in this work. The powder was pressed into the required shape using a die press and isostatically pressed, using a Stansted Fluid Power Ltd. isopress, at 10,000 psi. The sample was then fired at 1500°C for 3 h, producing a pellet with a relative fired density of greater than 98%. Degussa D308 platinum paint was applied to the electrolyte to act as a reference and counter (air) electrode. The reference electrode was produced by drilling a hole into the electrolyte, using a diamond drill, and attaching the wire into it, as shown in Figure 1b. The platinum electrodes were fired at 1000°C for 1 h to allow complete adhesion to occur.

$Co_3O_4$ (99.9% pure, from Aldrich), was used as provided. $LiCoO_2$ was synthesized by ball milling (using PSZ milling media) stoichiometric amounts of lithium carbonate (99.9%) and cobalt oxalate (99.99%), provided by Aldrich, in ethanol for 24 h. The sample was then dried in a Buchi furnace for 12 h and fired in a platinum crucible for 11 h. The final product was ground and X-ray powder diffraction was undertaken to determine the formation of $LiCoO_2$.

$La_{1-x}Sr_xCoO_3$ ($x = 0$ and 0.2) was synthesized using a standard coprecipitation route, using stoichiometric mixtures of CoO (99.99%), $La_2O_3$ (99.99%), and $SrCO_3$ (99.9%), all provided by Aldrich. The final samples were fired at 900°C and X-ray powder diffraction was undertaken to determine the formation of the perovskite phase. The BET-$N_2$ surface areas of the catalysts were determined using a Quanta chrome surface area analyzer; the results are summarized in Table 1. The catalytic oxide was added to enough glycerol to form a slurry and this was then painted onto the zirconia electrolyte. The sample was dried in air and fired at 800°C for 3 h. The procedure was repeated twice more to produce a continuous catalytic layer.

Conductivity measurements were undertaken on the powders to determine whether or not an electronic conducting electrode (a current collector) would have to be mixed with the oxide. The powders were die pressed into pellets and fired at 800°C for 4 h. Measurements of ac impedance (using a HP 4192a LF Impedance Analyzer interfaced with an IBM PC) were then undertaken on the

TABLE 1

**BET $N_2$ Surface Areas of the Catalysts Used as Anode Materials ($m^2/g$)**

| Sample | Surface area ($m^2/g$) |
|---|---|
| $Co_3O_4$ | 10.6 |
| $LiCoO_2$ | 10.0 |
| $LaCoO_3$ | 10.5 |
| $La_{0.8}Sr_{0.2}CoO_3$ | 11.9 |

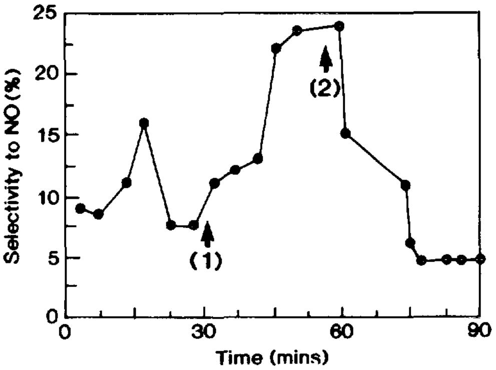

FIG. 2. Selectivity as a function of time for the $Co_3O_4$ catalyst. The feed was 1% ammonia in helium, with a catalyst temperature of 800°C. The potential was kept at 0 V. [1] = addition of 0.4% oxygen, [2] = oxygen off.

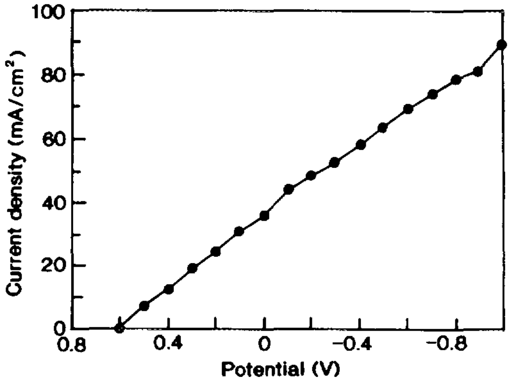

FIG. 3. Current density/potential plot for a 10% ammonia/6% oxygen feed at 800°C.

samples for the temperature range 100–500°C. The $Co_3O_4$ and $LiCoO_2$ samples were found to have resistivities over 100 times that of zirconia; thus, an inert current collector (gold) was added to the oxide electrode. The current collector had previously been examined for its catalytic activity and was found not to be an electrocatalyst for the reaction of interest. The pelleted $LaCoO_3$ and strontia-doped $LaCoO_3$ were found to be electronically conducting at room temperature, with the implication that no such current collector was required.

## RESULTS AND DISCUSSION

Figure 2 shows selectivity to nitric oxide with respect to time. Using an applied potential of 0 V, a selectivity of approximately 15% (at a total conversion rate of 68%) was obtained, for a 1% ammonia concentration in helium. The flow rate was kept at 1000 cm³/min and the temperature at 800°C. After approximately 20 min, the selectivity started to fall, and after a 30-min period it had fallen to below 7% (with an overall conversion rate of 56%). When 0.4% oxygen was bled into the feed, the selectivity increased to approximately 25%, with a conversion rate of 82%, and remained at this value. When the oxygen was removed, the selectivity immediately fell to below 5%, thus showing a loss in the catalytic activity during the experiment because of the effect of

(a) time at temperature and
(b) reduction due to the presence of the ammonia.

This is in accordance with the work of Andrew and Chinchen (15) who showed that a cobalt oxide catalyst loses its activity because of the sintering effect at high temperature. However, when an ammonia : oxygen ratio of 1.7 or less is used as the feed gas, the $Co_3O_4$ catalyst does not appear to reduce, even after lengthy periods at temperature. Powder X-ray diffraction showed no change in phase of the catalyst after removal from the reactor. Figure 3 shows a typical potential/current density curve for the catalyst at 800°C. In this case 10% ammonia plus 6% oxygen was used as the reactant mixture, at a total flow of 25 cm³/min. An open circuit potential of 0.6 V was obtained, and at 0 V a current density of 35 mA/cm² was realized. This corresponds to a selectivity of over 50% at a conversion rate of 57% (see Fig. 4). At lower concentrations (5% ammonia: 3% oxygen), selectivities of over 80% and a conversion rate of 72%, can be obtained at 0 V. It is to be hoped that as high a concentration of fuel as possible is used, because any diluent that requires heating produces an industrially unfavourable system.

Figure 4 shows that an optimum selectivity to NO is found at a potential of −0.4 V. It is suggested that the stabilization of the $Co^{3+}$ ion in the $Co_3O_4$ electrode causes this increased selectivity. The application of the applied potential causes an increased oxygen partial pressure at the electrode, thus causing a greater nonstoichiometry (16). This in turn causes a greater percentage of $Co^{3+}$ ions

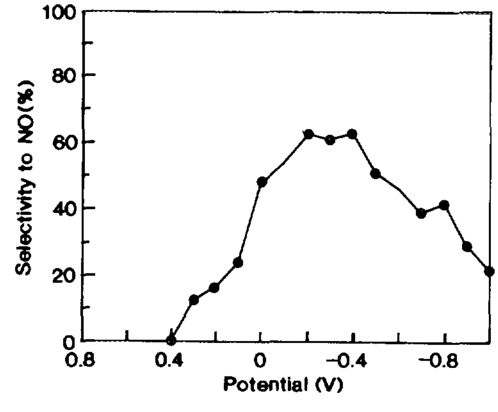

FIG. 4. Selectivity as a function of potential for the experimental conditions of Fig. 3.

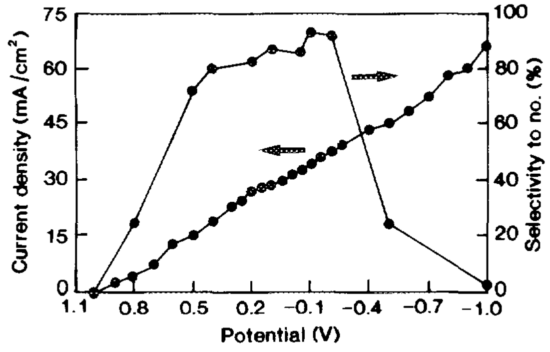

FIG. 5. Current density/selectivity as a function of potential for the $LiCoO_2$ catalyst. The ammonia feed was diluted to 0.5% in helium and the catalyst temperature was 750°C.

to be present in the system, which are postulated to be more catalytically active. It is generally agreed that Co vacancies are the predominant point defect in $Co_3O_4$ (17, 18). When $Co_3O_4$ is used as an anode material in the ceramic electrochemical reactor, the rate of reoxidation of the oxide by the electrolytic oxygen is faster than the rate of reduction due to the ammonia (assuming that the flux of oxygen through the ceramic is greater than the concentration of ammonia at the anode). If this were not the case then the oxide material would reduce to a lower oxide with time. It is suggested that the reason for this is due to the structure of the oxide; the majority defect is cation vacancies ($V_{Co}$) which are not used to oxidize the ammonia. If the predominant defects were oxygen anion vacancies, then they could carry oxygen to the ammonia, possibly faster than the rate of reoxidation, and thus cause a reduction of the structure, which was not found with the $Co_3O_4$ anode.

Because it was perceived that the $Co^{3+}$ ion was more catalytically active toward the partial oxidation of ammonia to NO, $Li^+Co^{3+}O_2$ was synthesized as an electrode material. $LiCoO_2$ was applied to the zirconia substrate by the technique described above, using a gold current collector due to the high resistivity of the oxide. Figure 5 shows the current density and selectivity to nitric oxide against the applied potential for a 0.5% concentration of ammonia in helium. The flow rate was kept at 100 $cm^3$/min and the optimum temperature was found to be 750°C. The maximum selectivity was found to be over 90% (at total conversions of >95%) with an applied potential of −0.2 V. This was again perceived as being due to the stabilization of a more active catalytic species. A fuller understanding of the mechanism of reactivity and selectivity on the $Co^{3+}/Co^{2+}$ active species needs to be pursued. On examination of Fig. 5, it can be seen that greater applied potentials cause a decrease in the selectivity, rather than an expected increase (due to the increased oxygen flux). It is postulated that large applied anodic overpotentials cause the $LiCoO_2$ structure to revert from the original NaCl-type structure to an alternative structure. This phase change is thought to be responsible for the deterioration in the catalytic selectivity of the oxide. It should be noted that the selectivity drop with large applied potentials was obtained for all conditions employed and was reproducible over the period of time investigated.

Since a gold current collector was present in the above reactors, due to the fact that the anode materials were not electronically conducting, it was decided to use an electronically conducting perovskite material, $La_{1-x}Sr_xCoO_3$ (with $x$ at 0 and 0.2). However, $LaCoO_3$ was found to be much more difficult to apply to the zirconia substrate than was originally thought. It was apparent that the oxide material did not form a coherent layer across the electrolyte, and thus a nonconducting anode was formed. Thus, a gold current collector was also used in these electrode configurations. Figure 6 shows a plot of the current density against time for a cell of the type $NH_3$, NO, $NO_2$, $N_2$, Au/$LaCoO_3$|FSZ|Pt, air. The feed gas was 1.5% ammonia diluted in helium, producing an open circuit potential of 1.03 V. The cell was held at 0 V and the current density at $t = 0$ is seen to be approximately 29 mA/$cm^2$. However, the current density dropped to 15 mA/$cm^2$ at $t = 125$ min and then fell off very rapidly; at $t = 175$ min, the value had fallen to below 5 mA/$cm^2$. On the addition of oxygen to the feed stream (1.5%), the current density reached approximately 80% of its original value. It has been previously noted that $LaCoO_3$ reduces to a series of suboxides and does not reoxidize back to the original structure. Janecek and Wirtz (19) found that the X-ray diffraction pattern of the reoxidized $LaCoO_3$ contained lines of $La_2CoO_4$, $La_4Co_3O_{10}$, $La_2O_3$, CoO, and $Co_3O_4$. Thus, when oxygen was introduced into the feed stream, the original oxide would not have been reformed, but a series of lower oxides would be present. Hence, the original value for the

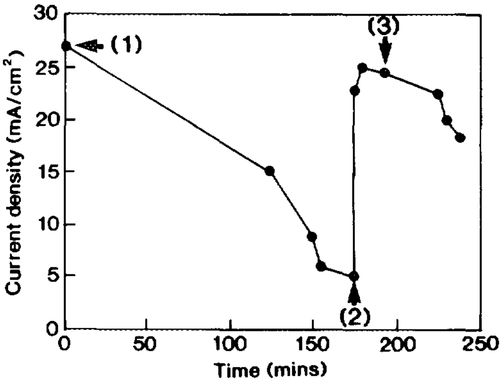

FIG. 6. Current density as a function of time for a 1.5% ammonia in helium feed at 800°C. The catalyst was the $LaCoO_3$ electrode. The potential was kept at 0 V. [1] 0% oxygen, [2] 1.5% oxygen, [3] 0% oxygen.

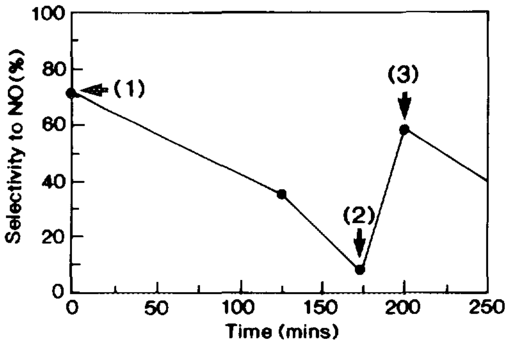

FIG. 7. Selectivity as a function of time for the experimental conditions of Fig. 6.

current density was not reached. However, Vidyasagar *et al.* (20) and later Rao and Gopalakrishnan (21) found that the mixed oxide $La_4Co_4O_{10}$, shown previously to exist as an intermediate in the reduction of $LaCoO_3$ by Seppänen *et al.* (22) and Lombardo *et al.* (23), could be reoxidized to the original perovskite, $LaCoO_3$. Thus, if the oxide has not been reduced too far it may be possible for it to be reoxidized to the original structure, but on its reduction to oxides lower than $La_4Co_4O_{10}$, the reoxidation cannot occur. When the oxygen is again removed from the feed, the current density deteriorates. Because of the small percentage of gold present in the $LaCoO_3$/Au cermet, any reduction of the catalyst (causing a loss in conductivity) causes an increase in the resistivity of the cermet. Thus, a decrease in conductivity of the anode causes a decrease in the available current density. Therefore, when oxygen is bled into the reactor, the anode reoxidizes to a structure closer to the original. The loss in current density with time corresponds to a loss in selectivity of the catalyst toward nitric oxide production and is shown in Fig. 7. At $t = 0$, the selectivity is over 70% (with 75% total conversion), while at $t = 175$ min, the selectivity has fallen to below 10%, with maximum total conversion down to 53%. Thus, if no gold current collector were present (if a coherent layer of $LaCoO_3$ was applied to the electrolyte), the loss in selectivity with time would probably be greater than that shown here. However, it has been shown that the application of a potential to the catalyst should stabilize the structure even under the reducing conditions encountered by the ammonia oxidation reaction. It should be noted that the potentials were applied (for an oxygen flux density high enough to oxidize the ammonia selectively to nitric oxide) before the ammonia was passed into the reactor, to ensure that no reduction of the electrode occurred. After the electrode was held at an oxidizing potential, ammonia was passed into the reactor and loss in selectivity was still noted. This was not the case for the $Co_3O_4$ and $LiCoO_2$ oxide anodes and the discrepancy between these two systems and the perovskite systems needs to be investigated. It has been generally established that nonstoichiometric $LaCoO_3$ is an oxygen-deficient (22) *p*-type conductor (6, 24). Oxygen vacancies were analyzed as being the major ionic defect and the formula is usually written as $LaCoO_{3-\delta}$. The defect equilibrium can be expressed as

$$O_O^x + 2Co_{Co}^{\cdot} \Leftrightarrow 2Co_{Co} + V_{\ddot{O}} + \tfrac{1}{2}O_2, \qquad [3]$$

where, $O_O^x$ = oxygen on normal sites, $Co_{Co}^{\cdot}$ = $Co^{4+}$ on $Co^{3+}$ sites, $Co_{Co}$ = $Co^{3+}$ on normal sites, and $V_{\ddot{O}}$ = oxygen vacancies.

The maximum electronic conductivity is found at the highest oxygen activities, because the equilibrium, in Eq. [3], moves to the left. The $[Co_{Co}^{\cdot}]$ defects are, in effect, equivalent to electron holes. The concentration of these species increases with increasing oxygen partial pressure, thus causing an increase in the conductivity (*p*-type). Under low oxygen activities, the equilibrium moves to the right, forming oxygen vacancies. This causes a lowering of the $[Co_{Co}^{\cdot}]$ concentration and thus a lowering of the conductivity. When $LaCoO_3$ is used as an ammonia oxidation catalyst, the ammonia reacts with the lattice (or adsorbed) oxygen incorporated in (or on the surface of) the perovskite. This causes the equilibrium to move to the right and thus lower the $[Co_{Co}^{\cdot}]$ concentration. This causes the conductivity to decrease and the number of oxygen vacancies to increase. Hence, the loss in conductivity, shown in Fig. 7, can be explained in terms of the reduction of the perovskite to $LaCoO_{3-\delta}$. At lower oxygen activities, however, the formation of lower oxides occurs (for example, $La_2CoO_4$ + CoO). The loss in conductivity cannot be explained by the above process alone. When the lower oxides are formed, the loss in conductivity is postulated to be due to two effects:

(1) the formation of CoO, which is a *p*-type semiconductor with a conductivity lower than that of $LaCoO_3$ (25, 26);

(2) the presence of lower oxides which cause a network of phases with varying conductivities which in turn may give rise to an overall conductivity lower than the original (21, 22).

This could explain the loss in conductivity of the perovskite (and therefore the increase in the resistance of the total cell) if no oxygen was present. However, the electrolytic oxygen was available to reoxidize the oxide, causing the conductivity to return to its initial value, but this was found not to be the case (as shown in Fig. 7). The applied potential produced an oxygen flux high enough to cause an oxygen-rich environment which should have caused the $LaCoO_3$ structure to have stabilized and the conductivity to have remained at the original value. It is therefore postulated that the rate of reoxidation of the $LaCoO_3$ anode is slower than the rate of reduction by the ammonia. This is contrary to the experimental work on the oxidation/reduction behavior of $LaCoO_3$ carried out previously (22, 27, 28). It is therefore postulated that the reaction mechanism for the ammonia oxidation, in an electrochemical reactor with a $LaCoO_3$ anode, can be represented as follows:

(1) Initially, a potential is applied to the electrolyte, causing electrolytic oxygen to be given up to the perovskite anode:

$$O_{o(\mathrm{Electrolyte})} = V_{\ddot{O}} + 2e^{-} + \tfrac{1}{2}O_2. \quad [4]$$

(2) The applied potential causes the stabilization of $LaCoO_3$.

(3) When ammonia is introduced into the reactor, it reacts with the lattice oxygen, causing the formation of lower oxides:

$$LaCoO_3 \Rightarrow LaCoO_{3-\gamma} + \tfrac{1}{2}\gamma O_2. \quad [5]$$

(4) The reduction in the lattice oxygen causes the oxygen deficient perovskite structure to be reoxidized by the electrolytic oxygen. However, the rate of reduction by the ammonia is greater than the rate of reoxidation by the electrolytic oxygen (thus a loss in conductivity is noted), which is thought to be due to the formation of oxygen vacancies. The catalytic properties of the oxide containing oxygen vacancies are different from the properties of the oxide containing cation vacancies. It is proposed that the variation in oxidation/reduction behavior (and thus catalytic properties) between $LaCoO_3$ and $Co_3O_4$ is due to the variation in the majority defect concentrations.

$LaCoO_3$ is therefore not a suitable anode material for the selective oxidation of ammonia in a solid state reactor. It should also be noted that the same loss in selectivity was observed for the $La_{0.8}Sr_{0.2}CoO_3$ material. However, the presence of strontia causes an increase in the conductivity of the oxide which is attributed to the formation of $Co^{4+}$ ions as a result of charge compensation in the lattice. The increased formation of $Co^{4+}$ causes the equilibrium shown in Eq. [3] to move to the right. This would cause *p*-type conduction to exist under more highly reducing environments than those experienced by the "pure" $LaCoO_3$. However, the conductivity of $La_{0.8}Sr_{0.2}CoO_3$ also decreased, thus showing that the rate of reduction was greater than the rate of reoxidation. Once the conduction fell slightly, the oxygen flux decreased and thus the environment became very reducing causing the conductivity to decrease even further.

## CONCLUSIONS

$Co_3O_4$, and to a greater extent $LiCoO_2$, can be used as anodes in the electrochemical reactor without degradation. The oxides can be utilized under relatively reducing environments and selectivities to nitric oxide can be achieved with results far superior to those obtained in a platinum reactor. In the reactor containing the $Co_3O_4$ anode, application of a high overpotential produces an improved selectivity up to an optimum value. The increased selectivity is thought to occur for two inherent reasons:

(a) increased flux of oxygen ions though the electrolyte, and

(b) stabilization of oxides with higher oxidation states by application of an anodic potential.

Therefore, the higher oxidation state and increased flux increase the selectivity to nitric oxide. However, at overpotentials greater than the optimum value, the selectivity was found to decrease. It is suggested that the optimum is due to the stabilization of the $Co^{3+}$ ion; overpotentials greater than the optimum are thought to stabilize higher oxidation states, which are possibly detrimental to the catalytic properties. The $LiCoO_2$ anode produces an optimum selectivity at a certain overpotential. The oxide has a superior catalytic selectivity over the $Co_3O_4$ anode, which is thought to be the result of

(a) increased stabilization of the $Co^{3+}$ ion, and

(b) formation of active $Li^{+}$ $O^{-}$ centers.

The increase in selectivity is due to an increased oxygen ion flux and possibly the formation of a more catalytically active surface. The loss in selectivity with an applied overpotential greater than the optimum is postulated to be due to the breakdown of the anode. The perovskite structures containing the $Co^{3+}$ ion were found to reduce very easily, even under potentials that should have stabilized the original structure, when ammonia was present in the feed. This was concluded to be due to the presence of oxygen vacancies which are the predominant point defect within nonstoichiometric $LaCoO_{3-\delta}$. The oxygen vacancies are believed to cause a high initial oxidation rate of the ammonia, but the rate of reduction of the oxide is thought to be faster than the reoxidation rate due to the electrolytic oxygen. It can thus be proposed that the oxidation of the ammonia is due to adsorbed (or lattice) oxygen, while the electrolytic oxygen reoxidizes the oxide.

## REFERENCES

1. Michaels, J. N., and Vayenas, C. G., *J. Catal.* **85,** 477 (1984).
2. Kiratzis, N., and Stoukides, M., *J. Electrochem. Soc.* **134,** 1925 (1980).

3. Yentekakis, I. V., and Vayenas, C. G., *J. Electrochem. Soc.* **136,** 996 (1989).
4. Vayenas, C. G., Beblis, S., and Ladas, S., *Nature* **343,** 6529 (1990).
5. Neophytides, S., and Vayenas, C. G., *J. Catal.* **118,** 147 (1989).
6. Tabata, K., Matsumoto, I., and Kohiki, S., *J. Mater. Sci.* **22,** 1882 (1987).
7. Vayenas, C. G., Bebelis, S., and Despotopoulou, M., *J. Catal.* **128,** 415 (1991).
8. Farr, R. D., and Vayenas, C. G., *J. Electrochem. Soc.* **127,** 1478 (1980).
9. Farr, R. D., and Vayenas, C. G., *Science* **208,** 593 (1980).
10. Sigal, C. T., and Vayenas, C. G., *Solid State Ionics* **5,** 567 (1981).
11. Schouler, E. J. L., and Kleitz, M., *J. Electrochem. Soc.* **134,** 1045 (1987).
12. Steele, B. C. H., *Sci. Ceram.* **10,** 655 (1980).
13. Manton, M. R. S., Sawin, H., Scharfman, R. M., Sigal, C. T., Vayenas, C. G., and Wei, J., *Energy Technol.* **11,** 794 (1984).
14. Riley, B., *J. Power Sources* **29,** 223 (1990).
15. Andrew, S. P. S., Chinchen, G. C., *in* "Catalyst Deactivation" (B. Delmon and G. F. Froment, Eds.), Studies in Surface Science and Catalysts, Vol. 6, p. 141, Elsevier, Amsterdam, 1980.
16. Sammes, N. M., *J. Mater. Sci. Lett.* **11,** 162 (1992).
17. Kofstad, P., "Non Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides," Wiley Series on the Science and Technology of Materials, (E. Burke, B. Chalmers, and J. A. Krumhams, Eds.), Wiley–Interscience, New York, 1972.
18. Perton, A. D., Schmalzried, H., and Sticher, J., *Ber. Bunsenges. Phys. Chem.* **83,** 241 (1979).
19. Janecek, J. J., and Wirtz, G. P., *J. Am. Ceram. Soc.* **61,** 242 (1978).
20. Vidyasagar, K., Reller, A., Gopalakrishnan, J., and Rao, C. N. R., *J. Chem. Soc. Chem. Commun.* **1,** 7 (1985).
21. Rao, C. N. R., and Gopalakrishnann, J., *Acc. Chem. Res.* **20,** 288 (1987).
22. Sepänen, M., Kyto, M., and Taskinen, P., *Scan. J. Met.* **9,** 3 (1980).
23. Lombardo, E. A., Tanaka, K., and Toyoshima, I., *J. Catal.* **80,** 340 (1983).
24. Nakamura, T., Misono, M., and Yoneda, Y., *J. Catal.* **83,** 151 (1983).
25. Bransky, I., and Wimmer, J. M., *J. Phys. Chem. Solids* **33,** 801 (1972).
26. Logothesis, E. M., Park, K., Meitzler, A. H., and Laud, K. R., *Appl. Phys. Lett.* **26,** 4, 209 (1975).
27. Nakamura, T., Petzow, G., and Gaukler, L. K., *Mater. Res. Bull* **14,** 649 (1979).
28. Sis, L. B., Wirtz, G. P., and Sorenson, S. C., *J. Appl. Phys.* **44,** 12 (1973).