Methanol Oxidation over Doped-LaCoO₃ Electrodes in a Solid Oxide Fuel Cell

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The oxidation of methanol to CO and CO₂ can be realised in a solid oxide fuel cell (SOFC) or a ceramic electrochemical reactor. Electrochemical control of the active anode species allows for increased activity (and hence conversion) to the desired products. This paper examines the effect of La_{1-x}Sr_xCoO_{3+δ} (x = 0.2-0.4) as a SOFC anode, using methanol as a feed stock. Stability and increased activity were realised at temperatures below 650°C and at an applied potential of approximately -0.2V. It was, however, apparent that under the highly anodic environments experienced by the anode for SOFC applications, the material degraded and a loss in efficiency was noted. It was therefore concluded that p-type oxides could only be used for systems such as electrochemical reactors, rather than in solid oxide fuel cell applications.

1 INTRODUCTION

The greatest challenge in the development of a solid oxide fuel cell (SOFC) is the possibility of internal reformation of the hydrocarbon-based fuel, and thus reduction of the overall size of the SOFC unit. It is well known that methane (whether dry or containing a realistic volume percentage of water vapour) forms a carbon deposit on the conventional Ni-cermet anode¹⁻²). The deposited carbon filaments then cause a reduction in the efficiency of the anode and an increase in the overpotential (and thus a decrease in the overall power output). There is some evidence to suggest that the formation of a methanol intermediate, via reaction [1], may overcome the problem of carbon deposition³).

The methanol intermediate can then form synthesis gas (CO + H₂) which can readily be oxidised, in-situ, forming electricity. This reaction is perceived as being possible over an oxide catalyst, particularly a perovskite-based system³).

The use of methanol as a feed stock is being considered world-wide. However, the material has a lower heat of combustion than natural gas and is thermodynamically less favourable. In countries where methanol is produced (for example, New

Zealand), the material could be used as a fuel and decomposed, on the active catalytic anode, to synthesis gas which can be efficiently used as the fuel gas. It has been shown that Ag and V₂O₅-based catalysts can selectively decompose and dehydrogenate methanol to, for example, formaldehyde⁴). Ukropec *et al.*⁵) have shown that a selectivity of 75% can be realised for a Y₂O₃-doped V₂O₅ catalyst, with increasing amounts of CO and CO₂ with increasing temperature. Nguyen *et al.*⁶) and later Neophytides and Vayenas⁷) have reported the oxidation of methanol, in a cell of the type:

where Me^I is Ag, Au or Pt, Me^{II} is the active cathode and YSZ is the yttria stabilised zirconia electrolyte. In these electrochemical cells, oxygen can be pumped to or from the catalyst (in this case Ag), via the reduction of oxygen, where the active cathode acts as a source of electrons as given by equation [3].

The authors⁷) found that an increase in the catalytic activity could be realised by varying the oxygen across the electrolyte and the phenomena was termed 'non-Faradaic electrochemical modification of catalytic activity (NEMCA)'. This phenomena has been observed for a number of other gas feedstocks, including, for example, ethylene oxidation⁸), ammonia oxidation⁹), CO hydrogenation and NO decomposition¹⁰). In the case of methanol, rate enhancements of over 600x were observed when O²-species were pumped

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away from the catalyst. However, in the majority of electrocatalytic investigations previously undertaken, a precious metal was used as the anode species. Later work, on the oxidation of ammonia to nitric oxide^{9,11)}, showed that increased activity of the electrocatalytically-active anode could be realised by using a metal-oxide system. In the case of ammonia, the authors^{9,11)} found that by increasing the localised oxygen partial pressure at the anode, by pumping oxygen to the catalyst via the solid electrolyte, the selectivity to nitric oxide was greatly enhanced. This was suggested as being due to the increased stability of the Co^{3+} ion in the Co_3O_4 electrocatalyst, even under the highly reducing conditions prevalent at the anode. In the present work the possibility of using a fuel cell (or an electrochemical reactor run as a fuel cell) to internally reform methanol on a metal-oxide catalyst, is examined. It was decided that the perovskite type oxide, doped- LaCoO_3 , be used as the electrocatalyst due to a number of reasons, including high electronic conductivity¹²⁾, its good response as a fuel cell cathode material¹³⁾ and its excellent potential as a catalytically active material towards methanol oxidation¹⁴⁾. The perovskite is, however, a well known p-type semiconductor and is prone to reduction under low oxygen partial pressures. It was, therefore, the object of this work to investigate the electrocatalytic properties of the metal oxide and to examine whether an applied potential across the cell could allow for stabilisation of the oxide.

2 EXPERIMENTAL

Ultrapure He (99.99%) was saturated with methanol by being bubbled through a saturator containing methanol, typically at 0.1 bar and mixed with water (3%), or oxygen (3.4%). The products were analysed by an on-line Pye Unicam gas chromatograph, using an automatic switching valve and a 6' x 1/4" concentric glass lined stainless steel column (outer column is activated molecular sieve and the inner column is a porous polymer) through a TCD detector. A carbon mass balance was performed to check that the methanol reactant stream (calculated as moles of carbon in) equalled the CO_x and hydrocarbon product stream (calculated as moles of carbon out). The total conversion was expressed as the ratio of the flow rate of ($\text{CO} + \text{CO}_2$) in the product stream to that of the methanol in the feed stream.

The electrochemical cell (or SOFC) was fabricated from a stabilised zirconia pellet of dimensions 2.3cm ϕ , 0.5mm thickness (Tosoh 8Y), and sealed, using a Pyrex seal, to a glass lined

zirconia tube. Platinum paste (Degussa D308) was painted onto the electrolyte as the reference and counter (oxygen) electrodes, and fired at 1000°C for 1 hour. This high temperature allowed for excellent stability of the platinum during use. $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ($x = 0.2-0.4$) was prepared using the modified Pechini method, described elsewhere¹⁵⁾. The oxide powders in ethanol, or alternative carriers, dispersants and binders, were sprayed onto the anode side of the zirconia electrolyte by a novel airbrush technique using a continually stirred slurry. Firing of the anode material onto the electrolyte was performed at 1200°C for 2 hours and excellent adhesion was noted. Scanning electron microscopy was performed using a Hitachi S4000 and EDX analysis was undertaken using a Kevex microanalyser. BET analysis was undertaken using a Nova 1000 surface area analyser.

During the course of the experiments, potentiostatic control was undertaken, using a PJT24-1 Tacussel potentiostat/galvanostat system.

Fig. 1 Current/Cell Potential plot for a cell of the type: H_2O , CH_3OH , $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ | YSZ | Pt, O_2 at 650°C.

Fig. 2 Conversion for 10.3% methanol/3.4% O₂ over La_{0.8}Sr_{0.2}CoO₃ at 550°C

The superficial surface area of the anode was measured as 2.8 cm². The true surface area of the oxide was taken using a standard size coated zirconia sheet, within the BET line and was found to be 570 cm²/cm² of superficial surface area for La_{0.8}Sr_{0.2}CoO₃, and 170 cm²/cm² for La_{0.6}Sr_{0.4}CoO₃. When the average from a number of runs was performed, the surface area could be obtained. The samples used for surface area analysis were coated at the same time as those of the actual system used. The reactor temperature was controlled to within $\pm 2^\circ\text{C}$ by use of a controlling thermocouple and a measuring thermocouple very close to the sample under scrutiny.

3 RESULTS AND DISCUSSION

Figure 1 shows a typical cell potential/current density plot, at 650°C, for a cell of the type:

What is apparent is the relatively low level of current density produced from the cell, which can be explained in terms of the low temperature employed, and the rate determining step being the oxygen flux through the electrolyte. However, methanol was found to degrade at temperatures above 650°C, via the possible reaction given in equation [4].

Other variations of reaction [4] are possible,

however, it was apparent that a large percentage of carbon was deposited at the higher temperatures. This was reduced when water (or oxygen) was present in the feed, but this only served to lower the available current density (and thus the power density) from the fuel cell system.

The cell voltage on the current density given in figure 1 is rather complex due to several competing reactions taking place at the anode. At low current densities, the cell voltage is greater than 0.9V and it can, therefore, be suggested that the dominant reaction be given in equation [5] ¹⁶⁾

where O²⁻_(elect) is the oxygen produced from the electrolyte via the standard vacancy mechanism.

The hydrogen is formed from the catalytic degradation of the methanol. When all the hydrogen has been consumed at the anode, then other reactions, forming CO and CO₂ would predominate, as shown in equations [6] and [7].

Other reactions are possible, but further work is required to determine all the mechanisms of methanol degradation.

At intermediate current densities, the cell voltage decreases quasi-linearly with current and the slope is near to the total cell resistance. This is indicative of ohmic polarization. The final non-linear portion of the curve is possibly due to diffusion overpotential ^{17,18)}.

Figure 2 shows a typical conversion to CO and CO₂ for a 10.3% methanol feed and 3.4% oxygen addition, at 550°C, over the La_{0.8}Sr_{0.2}CoO₃ catalyst. The variation in the conversion was measured as a function of the cell potential. It is interesting to note that when no oxygen is present in the feed at temperatures below 650°C, very little conversion (or change in conversion with increasing overpotential) was apparent. When a small percentage of oxygen (or water) was added to the feed in percentages lower than stoichiometry (for complete heterogeneous catalytic oxidation to CO/CO₂) the increased conversion was quite marked. The open cell potential, found in figure 2, was 0.83V (lower than that for the theoretical voltage, due to the presence of the oxygen), with a conversion of methanol to CO + CO₂ of 64%. When an overpotential was applied to the cell, using the potentiostat, there was an increase in the percentage formation of the products. An optimum was found at approximately -0.2V. At potentials lower than this, the

Fig. 3 Effect of time on conversion of methanol, for conditions in figure 2, at 0.86V and -0.2V potential.

a)

b)

Fig. 4 SEM micrograph of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ sample, on the electrolyte. a). before being used in the reactor, b). after 200 hours on-load.

performance was again seen to be lower. It should be noted that the long term performance of the catalyst was examined. Figure 3 shows the effect of time on the conversion of methanol to CO and CO_2 , for the conditions employed in figure 2. It is apparent that when no potential was applied to the anode (open circuit, 0.86V), it is found to lose its activity due to the highly reducing environment present. In this work only CO and CO_2 were produced by the reaction, for all conditions examined. The reduction in the formation of the products was postulated as being due to the lack of stability of the system under the prevalent conditions. XRD confirmed this, as there were extra peaks in the trace which were due to sub-oxides being formed. However, when a potential of -0.2V was applied to the anode, no such loss in activity was observed, showing that stabilisation of the system could be realised. Figure 4 shows the SEM micrographs for the sample given in figure 3 and confirms that there was no change in the microstructure after over 200 hours on-load.

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is known to be reduced to a series of sub-oxides at low oxygen partial pressures. Janacek and Wirtz¹⁹⁾ found that the material, on reduction, and even after re-oxidation contained La_2CoO_4 , $\text{La}_4\text{Co}_3\text{O}_{10}$, La_2O_3 , CoO and Co_3O_4 . Later, Vidyasager *et al.*²⁰⁾ and Rao and Gopalakrishnan²¹⁾ found that the intermediate, $\text{La}_4\text{Co}_4\text{O}_{10}$ could be re-oxidised back to LaCoO_3 . Thus, if the reduction process has not been allowed to go too far, then stabilisation of the original perovskite is possible. The application of a potential to the catalyst stabilises the structure, due to the localised oxygen partial pressure produced by equation [3], even under the reducing conditions found at the anode¹¹⁾.

It has generally been established that non-stoichiometric LaCoO_3 is an oxygen deficient p-type conductor and oxygen vacancies are found to be the majority defect, given by the defect equilibrium in equations [8] and [9], using Kröger-Vink notation.

Formation of an oxygen vacancy:

Reduction of Co^{3+} to Co^{2+} :

The concentration of $[\text{CoCo}_\text{o}']$ decreases with increasing oxygen partial pressures, allowing for an increase in the p-type conductivity; the reverse is noted at lower oxygen partial pressures, with an increase in the oxygen vacancy concentration.

When $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is used as a methanol electro-catalyst, it can be postulated that the

reactant will either react with the adsorbed oxygen or the lattice oxygen incorporated in the perovskite, or form $\text{CO} + \text{H}_2$ by catalytic cracking. As no loss in the activity of the catalyst was noted and no phase changes in the perovskite material were observed, it can be assumed that the methanol catalytically cracks to form CO and H_2 and reacts with the adsorbed oxygen to form CO_2 and water. The presence of an overpotential allows for an increase in the localised oxygen partial pressure and therefore the formation of a non-stoichiometric $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ system. As the localised oxygen partial pressure was kept constant, the value of δ can be assumed to remain at a constant value. Thus, the increased conversion and increased stability of the electro-catalyst can be postulated to be due to the formation of a particular $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ system. A drop in the conversion noted in figures 2 and 5 may be explained in terms of the formation of an alternative $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3+\delta}$ system due to the changing δ value. When methanol is passed over the active electro-catalyst,

Fig. 5 Methanol conversion over $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ at 550°C and 650°C, with applied potential.

no reduction takes place, due to the fixed oxygen partial pressure, and the catalyst possibly acts to crack methanol via equation [10].

The addition of oxygen in the feed causes an increase in the activity of the catalyst, and is not in quantities large enough to cause secondary reactions to occur. Thus the small percentage of oxygen is thought to increase the surface reactivity of the anode, via either incorporation into the lattice, or adsorption on the surface of the catalyst.

At this stage the increased activity, due to the small percentage of oxygen in the feed, cannot be fully explained.

Figure 5 shows the effect of methanol conversion to $\text{CO} + \text{CO}_2$ over the $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ system, at 550°C and 650°C, for a methanol feed of 12.3% and 3.4% oxygen. What is apparent is that the increased Sr on the A-site of the perovskite does not cause a large increase or decrease in the activity. The principle reaction controlling the stoichiometry of the ABO_3 -based compound can be given by equation [11].

It can therefore be assumed that the Co^{3+} ion is playing an active role in the catalytic nature of the material. At temperatures below 650°C, the activity of the catalyst is dependent on the applied potential, and increases with increasing cathodic potentials, with an optimum being found at approximately, -0.2V. This is, of course, of little benefit for the SOFC system, as an anodic potential of approximately 0.8V is usually employed. However, it is still apparent that when a small percentage of oxygen is fed into the stream, sufficient conversion can be obtained to allow for power generation from the cell, at relatively low temperatures.

4 CONCLUSIONS

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ is an active catalyst for the oxidation of methanol to CO and CO_2 . However, because this is a p-type oxide, degradation takes place under the highly reducing environments prevalent at the anode. The application of a fixed potential of approximately -0.2V stabilised the anode and allowed for a more active catalytic species to be present. However, under the conditions employed for SOFC anodes, the highly reducing potential would not allow for long term stability and thus long term power generation. The system could, however, be used for the electrochemical modification of methanol to the desired products. What is apparent is that the concept of using methanol as a fuel cell feed is a very real one and that further work is being undertaken to investigate other more stable systems.

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