MAXIMIZATION OF CO TOLERANCE OF PEMFC SYSTEMS USING RECONFIGURED ANODES

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ABSTRACT

The reconfigured anode (RCA) system is a small modification to the backing cloth placed on the anode side of each MEA in a PEM fuel cell stack. A catalyst layer is placed on the gas feed side of the cloth, to catalyze oxidation of CO utilizing the oxygen introduced in a small air-bleed. The purpose is to achieve a high CO-tolerance at a temperature below 100 °C. The development and status of this technology are described. Investigation of catalyst systems based on inexpensive transition metal oxides continues.

INTRODUCTION

Practical PEM fuel cells for automotive and large stationary applications are expected to operate on reformate, obtained by reforming gasoline, diesel, natural gas, or methanol fuels. A very troublesome impurity in reformate is residual carbon monoxide, CO, which poisons the platinum catalyst surface (1). CO is still at a significant level even if water-gas shift and preferential oxidation reactors are included. In the on-board reformate production option, complex processing to remove CO would have a high capital cost and weight penalty. It would be desirable to be able to eliminate one or both of the conventional preferential oxidation and water gas shift reactors. However, even 50-100 ppm CO is normally enough to shut down operation of a polymer electrolyte fuel cell. Hence, reasonable CO-tolerance requires special measures at the cell operational stage, such as an anode air-bleed. For instance, in previous work at Los Alamos National Laboratory, a minimal air-bleed was added to the fuel stream to catalyze chemical oxidation of CO. Originally, this reaction was catalyzed by the platinum anode catalyst itself (2).

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It was later found more effective for the anode gas to make contact with a CO oxidation catalyst before reaching the anode active layer (1). This led to the development, in our laboratory, of the reconfigured anode (RCA) system (1), to improve performance of low temperature (< 100 °C) Nafion®-based MEAs on reformate fuel. The reconfigured anode operates in conjunction with an air-bleed, added to the fuel stream. In essence, this method is designed to perform a preferential oxidation as the gas is distributed to the fuel cells. Depending on the catalyst, there may be a contribution from the water gas shift pathway, also.

The RCA system is shown schematically in Figure 1. A thin layer of a catalyst, based on an inexpensive transition metal oxide, is immobilized on the side of the gas distribution cloth adjacent to the flow field plate. Oxidation of CO by the oxygen from the air-bleed is catalyzed by the additional layer of chemical catalyst, before the anode gas reaches the electrochemically active layer.

Similar approaches have also been suggested by Ballard (3), and workers at ZSW Ulm (4), but their respective devices used precious metal catalysts or nickel foam structures. Gas filtration through hydrogen-selective membranes has been suggested, but requires much development to bring to practice. In other variants of CO oxidation, other workers have suggested the “ruthenium filter” (5), or the addition of pure oxygen (4,6) or hydrogen peroxide (7) instead of air. Alternative means suggested for achieving high CO tolerance are operation with pulsed current (8), the use of an alloy catalyst with very high intrinsic tolerance to CO (9), and the use of a high temperature membrane, such as acid doped polybenzimidazole (PBI) (10).

OVERVIEW OF EXPERIMENTS

General Experimental Details

All fuel cell tests were carried out at 80 °C, at an anode stoichiometry of 1.5, with anode and cathode backpressures of 30 psig. The anode and cathode feed gases respectively were humidified at 105 °C and 80 °C. MEAs were fabricated by the decal method of pressing thin electrocatalyst layers onto Nafion® 112. Synthetic reformate consisted of 40% H2, 35% N2 and 25% CO2. RCA catalyst loadings (dry ink) were typically 1.0-1.5 mg cm⁻², but a higher loading of 3.5 mg cm⁻² was used for cobalt-exchanged cryptomelane. Test conditions were always allowed to settle for at least 0.5 h before measuring a polarization curve over about 0.5-1 h.

Initial Experiments (5 cm² Cells)

A number of commercially available transition metal oxides, as well as tungsten carbide and the pure metals: Zr, Sn, Mo, W, and Cu, were combined
with carbon black to produce inks for painting anode gas diffusion layers. Additional copper-based catalysts were also tested. For instance, CuO (ac) was prepared by thermal decomposition of the acetate salt onto carbon black. The ink preparation procedure was as follows: The active material (metal or oxide) was mixed with Carbon Black (Vulcan XC-72), a Teflon suspension, glycerol, and isopropanol. This mixture produced an ink that could be brush painted onto the carbon cloth.

The cloths with reconfigured anode layers were tested in 5 cm² single MEA fuel cells. The cells were operated for periods of about 1 hour on hydrogen (or synthetic reformate) mixes containing CO (typically 100 ppm) with and without air-bleeds of 2-6%, then allowed to recover on neat hydrogen. Cell polarization curves were obtained under each condition, after the cell had stabilized.

Experiments in 50 cm² Cells

It was desired to investigate more fully, oxides of Co and Fe supported on carbon black, prepared by thermal decomposition of the acetate salt of the respective metal. These are denoted CoOₓ (ac) and FeOₓ (ac). A cryptomelane, K₂Mn₆O₁₆, (porous manganese dioxide with residual negative charge) “doped” by exchange with cobalt in place of some of the usual balancing K⁺ ions, was also tested. This catalyst has been reported in the literature (11) as a stable catalyst, selective for CO oxidation in preference to hydrogen. These catalysts were tested with Nafion® – based MEAs with platinum/carbon anode and cathode. The iron oxide catalysts were also tested with “state of the art” alloy anodes (Pt-Ru at standard and reduced loadings) and cathodes (Pt₃Cr). Pt-Ru provides increased intrinsic tolerance to CO (5,8,9).

These RCA layers and MEAs were tested in single cell tests (50 cm² geometric active area) which were carried out on hydrogen and synthetic reformate with up to 500 ppm CO, using air-bleeds of 6% or less. The test cells were compared to cells otherwise identical but without the RCA modification of the anode gas distribution cloth. Sometimes these baseline tests were run simultaneously with a particular test cell.

One definition of full tolerance is: voltage losses no greater than 5% at any attainable cell current, in the presence of CO relative to its absence. For this definition to be applicable to the reconfigured anode, we should be investigating conditions for which the cell voltage drops significantly in response to CO, even with airbleed, in the absence of a reconfigured anode catalyst layer.

For the tests on 5 cm² cells, CO-tolerance was evaluated from the net effect of CO and air-bleed on the cell voltage at 0.6 A cm⁻² for a cell operating on hydrogen fuel. For the tests on 50 cm² cells, CO-tolerance was evaluated from the net effect of CO and air-bleed on the cell voltage at 0.5 A cm⁻², for a cell operating on either hydrogen or simulated reformate fuel.
RESULTS

Performance on Hydrogen

Figure 2 compares results for the tests on 100 ppm CO in hydrogen performed in 5 cm² cells. At both 4% and 6% air, La₂O₃, Cr₂O₃ and WC had negative impacts. Zr and MnO₂ were positive at 6% but negative at 4%. Consistent, positive effects, but less than full tolerance were seen with Sn and Mo. Full tolerance with 6% air was obtained for W and for CoOₓ. Full tolerance at both 4% and 6% air-bleed was observed for TbOₓ, CuO, CuO (ac), Fe₂O₃, and CuO/ZnO.

Figure 3 shows the effect of various levels of air-bleed on a 50 cm² cell operated with CO in hydrogen, in the absence of an RCA layer, for a platinum catalyzed MEA. For 100 ppm CO, Figure 4 compares the performance of several different RCA layers using air-bleed. The CoOₓ (ac) RCA catalyst showed marginally increased CO tolerance with 4% (or 6%) air-bleed. The FeOₓ (ac) RCA catalyst showed complete tolerance at 2% (and 4%) air-bleed and appeared particularly promising in this test. Comparable results were obtained using an MEA with a low loading of Pt-Ru anode electrocatalyst.

A cell with the FeOₓ (ac) RCA catalyst and Pt electrocatalyst layers (0.2 mg Pt cm⁻²) was tested with hydrogen containing levels of up to 500 ppm CO. In short term tests, full tolerance was observed for the conditions 100 ppm CO + 2% air-bleed, 200 ppm CO + 4-6% air-bleed, 300 ppm CO + 4-6% air-bleed, and 500 ppm + 6% air-bleed (Figure 5). This is a preliminary demonstration of full tolerance to 500 ppm CO in hydrogen.

With a Pt-Ru anode (0.2 mg Pt cm⁻²) and a Pt₃Cr cathode, in a cell with the FeOₓ (ac) RCA catalyst, the anode was much less susceptible to poisoning by a given CO concentration, as is already known from the literature (9). In the present experiments, full tolerance to 100 ppm CO in hydrogen could be achieved with a 1% air-bleed and no RCA catalyst. Therefore, under these conditions, it was not possible to determine whether there is an improvement by adding RCA catalyst with air-bleed.

Recently, additional tests have been carried out in cells with a Pt-Ru anode at a reduced loading (0.1 mg Pt/cm²) and a Pt₃Cr cathode. In hydrogen containing 500 ppm CO, the combination of 6% air-bleed with FeOₓ (ac) RCA catalyst gave full tolerance. Under these conditions, full tolerance was not achieved in the absence of an RCA catalyst layer.

Performance with Synthetic Reformate
Some experiments were carried out on the 5 cm² cells. Results are presented in Figure 6. From this, it was concluded that the Fe₂O₃ catalyst allowed full tolerance to 100 ppm CO in reformate, using 4-6% airbleed. An air-bleed of only 2% gave poor results.

Figure 7 shows data for a stream containing 100 ppm CO through a 50 cm² cell with a platinum catalyzed MEA and no catalyst on the backing layer. Figure 8 shows the effects of a combination of 100 ppm CO and various levels of air-bleed on similar cells incorporating each of several catalysts in the backing layer. Similar trends are seen, to those in Figure 4.

In Figure 7, curve D shows data for no catalyst on the backing layer, with a higher CO level (250 ppm). Figure 9 shows the net effect of this level of CO and air-bleed for each catalyst. For MEAs with a Pt-Ru electrocatalyst at low loading, FeO₃ (ac) and CoO₃ (ac) had similar activity. The results for platinum-catalyzed MEAs are somewhat different from those in Figure 4 for hydrogen, in the presence of the FeO₃ (ac) or CoO₃ (ac) RCA catalysts. They indicate that CoO₃ (ac) becomes the better RCA catalyst on reformate. Even 250 ppm CO was tolerated fully, with a 6% air-bleed in two cases with Pt electrocatalytic layers: using CoO₃, and using cobalt-exchanged cryptomelane mixed with a carbon ink. However, this data is of a preliminary nature, since few experiments were completed in this region of operation. For the latter catalyst, which contained K⁺, there appears to be an ageing effect. The initial, good results, shown in Figure 9, could not be repeated with the same batch of catalyst.

For a Pt-Ru anode (0.2 mg Pt cm⁻²), 100 ppm CO was tolerated fully, with a 4% air-bleed and no RCA layer. Even 250 or 500 ppm CO was tolerated fully with a 6% air-bleed and no RCA layer. Under these conditions, marginal benefits were obtained at high air-bleeds with an RCA layer. Additional tests have been carried out in cells with a Pt-Ru anode at a reduced loading (0.1 mg Pt cm⁻²) and a Pt₃Cr cathode (0.4 mg Pt cm⁻²). In reformate containing 250 ppm CO, 6% air-bleed gave full tolerance with either FeO₃ (ac) or CoO₃ (ac) RCA catalyst.

The contrast between Pt-Ru anodes (0.1 mg Pt cm⁻²) and Pt anodes (0.2 mg cm⁻²) is illustrated in Figure 10. Even for the former type of anode, full tolerance has not been achieved at 500 ppm CO. The best result to date is that of curve E in Figure 10. With no RCA catalyst, full tolerance was only achieved at the 100 ppm CO level, using 6% air-bleed.

Stability of RCA Chemical Catalysts

Various catalysts have been characterized by TGA, XRD, XRF, and EDAX. Detailed results are to be presented elsewhere (12). In brief, the CoO₃ (ac) RCA catalyst consists of mainly Co₂O₃. The FeO₃ (ac) RCA catalyst contains both Fe₃O₄ and Fe₂O₃. The cryptomelane crystal structure was verified.
by XRD. Exchanging cobalt produced slight line broadening, which may be due
to reduced grain size or increased lattice strain.

Preliminary endurance experiments (3 days) were run at 0.60 V on
combinations of hydrogen, CO and air-bleed, which had displayed complete
tolerance over about 1 hour. Two cells with the FeOx (ac) RCA catalyst were
operated under these conditions. One had Pt electrocatalytic layers (both 0.2 mg
Pt/cm²) and the other had Pt-alloy electrocatalytic layers (Pt-Ru at 0.2 mg Pt/cm²
for the anode and Pt₃Cr at 0.4 mg Pt/cm² for the cathode). A slow decay in
performance was seen, with an average of 25% loss after 3 days with 100 ppm
CO + 4% airbleed. The cell with alloy electrocatalytic layers was slightly less
affected than the Pt-catalyzed cell.

Additional, ex-situ work is being carried out using a facility for measuring
catalyst activity and/or catalyst mass changes, while monitoring gas streams by
gas chromatography (GC). The purpose is to test catalyst activity by purely
chemical mechanisms at temperatures around 80 °C, where Nafion®-based MEAs
operate. These methods will also be used to evaluate potential new catalyst
formulations.

DISCUSSION

From the trends in Figure 2, we suggest that the metals (or most probably
their oxides) that promote the oxidation of CO more effectively are those with
two stable, low oxidation states (+4 or lower). Examples of these are: Cu, Fe, Co,
and Sn. This hypothesis is consistent with the poor performance of Zr and La₂O₃;
Zr and La have only one stable oxidation state (+4 and +3 respectively). Cr and
Mn on the other hand, may be found in much higher oxidation states (+6 and +7
respectively) as chromates and permanganates. Borderline are Mo and W, which
show moderate performance and have stable oxidation states from +2 to +6. Sn
(+2 and +4) was not as effective as the metals with two lower oxidation states (+3
or lower). Indeed other non-precious metals, with two stable, low oxidation
states, such as Eu, Ti, Tl, Ni, or Pb, could be tested for CO tolerance.

The answers to the questions, which anode is best and which re-configured
anode layer is best, could depend strongly on the fuel stream, the CO level, and
the amount of air-bleed allowable. (a) For hydrogen and a low air-bleed (2%),
FeOₓ (ac) gave the best RCA performance, and for 100 ppm CO, the Pt anode was
actually superior to Pt-Ru. (b) If an air-bleed is to be used, a suitable RCA layer
will be about as effective as using a Pt-Ru (0.2 mg Pt cm⁻²) catalyst in the anode
layer of the MEA. It will also be much cheaper. (c) For reformate using a 6% 
air-bleed, there appear to be several RCA catalyst options for 100 or even 250
ppm CO. In this case the use of Pt-Ru (0.2 mg Pt cm⁻²) is in competition with
adding an RCA layer to a cell with a Pt electrocatalyst. So far, the very best result
obtained for the latter situation was with the partially cobalt-exchanged
cryptomelane. However CoOₓ (ac) also gave acceptable results, more repeatably.
Above 100 ppm CO in reformate, results with the iron oxide catalyst were poor,
except when a Pt-Ru electrocatalyst was used. (d) At 500 ppm CO in reformate, Pt-Ru anodes (0.2 mg Pt cm\(^{-2}\)) continued to give good results with 6% air-bleed, even without an RCA layer. In contrast, this fuel feed rapidly disabled cells with Pt anodes, even at 6% air-bleed. In this regard, the combination of high CO and reformate seems to be more detrimental than CO and hydrogen.

We aimed to find conditions under which 500 ppm CO in reformate could be tolerated. Tests have confirmed that a 4-6% air-bleed without RCA layer allows operation of Pt-Ru anodes under these conditions, at least on the timescale of an hour. Further tests in progress, using anodes with reduced loadings of Pt-Ru, are designed to get a better ranking of the promise of various RCA catalysts for cells with Pt anode electrocatalysts. It is hoped that the best catalyst we can develop for these conditions will eventually achieve full tolerance to 500 ppm CO in reformate when a Pt anode is used.

Using a reconfigured anode and a Pt electrocatalyst, at least 250 ppm CO in reformate can be tolerated for a timescale of 1-2 hours under steady state conditions. Therefore, this system can certainly deal with transient CO levels of this order during continuous operation at generally lower CO. This makes it attractive for applications on reformate fuel with some other CO clean-up process which may not operate at its rated CO output all of the time, especially during start-up or changes in load. Such a cell system will be cheaper than cells with high levels of platinum and another precious metal as the electrocatalyst.

For future commercial exploitation in fuel cell stacks, the advantages of the reconfigured anode technique for maximization of CO tolerance include the following. It works with the proven MEA material Nafion® at temperatures as low as 80 °C. It avoids or minimizes the use of relatively expensive catalyst materials such as ruthenium, which have been suggested for other CO removal systems, and as a major component of the anode catalyst. Finally, it does not significantly increase the dimensions or mass of a fuel cell stack, but may help to minimize bulky purification stages following reforming.

There is a definite concern about the long-term stability of iron oxides and cryptomelanes under fuel cell conditions. The studies to date, prove the principle of the reconfigured anode. However, further study is required to find catalysts, which will maximize lifetime as well as initial performance. Although FeO\(_x\) (ac) has shown the best performance on hydrogen, when synthetic reformate is fed to the cell, CoO\(_x\) (ac) appears superior over the full range of anode electrocatalysts and CO levels.

A possible explanation for the marked interactions with an air-bleed, on changing the anode from Pt to Pt-Ru (0.2 mg Pt cm\(^{-2}\)), may lie in the fact that Pt-Ru favors the surface water gas shift reaction over its reverse (6). Further evidence for suppression of the reverse water gas shift is found in the literature (13, 14). In reformate, the combination of high initial CO\(_2\) and H\(_2\) (or surface adsorbed H) concentrations could ensure that no net CO\(_2\) would be formed from CO by the water gas shift reaction reaction. In this feed stream, the reaction with oxygen would be the dominant pathway for CO removal. This would hold for
either a Pt-Ru or a Pt electrocatalyst. In hydrogen, the water gas shift reaction on Pt-Ru could provide a faster pathway for CO conversion to CO₂, in the absence of CO₂ initially. However, in this case, oxygen additions and reaction over the RCA catalyst may produce enough CO₂ to suppress the water gas shift reaction on the Pt-Ru, leading to an apparent, negative overall effect of air-bleed. These effects would not occur for a Pt electrocatalyst.

The reasons for the improvement in behavior of the CoOₓ (ac) RCA catalyst, on going from hydrogen to reformate, and the degradation of the performance of FeOₓ (ac), with a Pt anode, are not clear. Again, interactions between the water gas shift reaction and the chemical oxidation reaction may be involved. It is also possible that, with CoOₓ (ac), peroxo intermediates may interfere with oxygen utilization in hydrogen, but be decomposed back to oxygen by the high CO₂ level in reformate. Alternatively, catalytic activity may be a function of potential, altered by the RCA layer being in contact with the anode via the electronically conducting carbon cloth. These phenomena will be probed to the extent possible, by ex-situ and in-situ tests with GC analysis.

Future work on the reconfigured anode scheme will concentrate on catalyst optimization, endurance experiments with reformate containing 500 ppm CO, investigation of dispersion of catalysts on mesoporous support materials, and stack studies.
CONCLUSIONS

The reconfigured anode system is a means of increasing the CO tolerance of platinum catalyzed Nafion® MEAs to a level similar to that achieved with alloyed electrocatalysts, e.g. Pt-Ru, at 80 °C. This system can deal with transient CO levels of at least 250 ppm during continuous operation at generally lower CO. Such a cell system will be cheaper than cells containing high levels of platinum and another precious metal as the electrocatalyst. Unlike some other systems, it will not add significant volume or mass to a PEM fuel cell stack.

The use of reconfigured anodes could be attractive for applications on reformate fuel with some other CO clean-up process which may not operate at its rated CO output all of the time, especially during start-up or changes in load.

A further application may be to allow operation on a relatively high CO containing reformate stream, by combining the RCA layer with an anode of high intrinsic tolerance to CO (such as Pt-Ru at 0.1 mg Pt cm⁻²) and/or a high temperature membrane, since the tolerance of Pt to CO increases markedly with temperature.

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Figure 1. RCA schematics and functionality. 1) Non-precious-metal-based chemical catalyst layer; 2) anode gas distribution carbon cloth; 3) Pt-based anode electrocatalyst layer; 4) ionomer membrane; 5) Pt-based cathode electrocatalyst layer; 6) cathode gas distribution carbon cloth.

Figure 2. Comparison of substances tested as RCA catalysts with base performance without RCA layer. Voltage loss for 100 ppm CO + air-bleed measured at 0.6 A cm\(^{-2}\) and referred to neat hydrogen (5 cm\(^2\) cell with 0.2 mg Pt cm\(^{-2}\) anode and cathode electrocatalyst layers).
Figure 3. Performance of cell with no RCA layer on hydrogen, in response to air-bleed. (50 cm² cell with 0.2 mg Pt cm⁻² anode and cathode electrocatalyst layers).

Figure 4. Comparison of three RCA catalysts with base performance as shown in Figure 3. Voltage loss measured at 0.5 A cm⁻² and referred to neat hydrogen. A₀ = no RCA layer; A₁ = FeOₓ (ac); A₂ = CoOₓ (ac); A₃ = Co-exchanged KMn₈O₁₆. A Series = Pt anode electrocatalyst (0.2 mg cm⁻²); C Series = Pt-Ru at 0.1 mg Pt cm⁻².
Figure 5. Effect of air-bleed with up to 500 ppm CO in a hydrogen feed on the performance of FeOx (ac) catalyst (A1) in RCA layer in cell with 0.2 mg Pt cm$^{-2}$ anode and cathode electrocatalyst layers.

Figure 6. Performance of Fe$_2$O$_3$ catalyst with synthetic reformate containing 100 ppm CO, and various levels of air-bleed (5 cm$^2$ cell with 0.2 mg Pt cm$^{-2}$ anode and cathode electrocatalyst layers).
Figure 7. Performance of cell with no RCA layer on synthetic reformate under various conditions of CO level and air-bleed (50 cm² cell with 0.2 mg Pt cm⁻² anode and cathode electrocatalyst layers).

Figure 8. Comparison of three RCA catalysts with base performance at 100 ppm CO. Voltage loss measured at 0.5 A cm⁻² and referred to synthetic reformate with no CO. A0 = no RCA layer; A1 = FeOₓ (ac); A2 = CoOₓ (ac); A3 = Co-exchanged KMn₄O₁₆. A Series = Pt anode electrocatalyst (0.2 mg cm⁻²); C Series = Pt-Ru at 0.1 mg Pt cm⁻².
Figure 9. Comparison of three RCA catalysts with base performance at 250 ppm CO. Voltage loss measured at 0.5 A cm\(^{-2}\) and referred to synthetic reformate with no CO. A0 = no RCA layer; A1 = FeO\(_x\) (ac); A2 = CoO\(_x\) (ac); A3 = Co-exchanged KMn\(_8\)O\(_{16}\). A Series = Pt anode electrocatalyst (0.2 mg cm\(^{-2}\)); C Series = Pt-Ru at 0.1 mg Pt cm\(^{-2}\).

Figure 10. Effects of anode type and FeO\(_x\) (ac) reconfigured anode layer on tolerance to 500 ppm CO in synthetic reformate, using a 6% air-bleed. Measured in 50 cm\(^2\) cells. Curve A: Pt Anode (0.2 mg cm\(^{-2}\)), RCA layer, no CO or air-bleed; Curve B: As in A, but with 500 ppm CO; Curve C: As in B, but with 6% air-bleed; Curve D: Pt-Ru anode (0.1 mg Pt cm\(^{-2}\)), no RCA layer, 500 ppm CO, 6% air-bleed; Curve E: As in D, but with RCA layer.