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Polymer Electrolyte Fuel Cells for Transportation Applications

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(1) Introduction

The application of the polymer electrolytic fuel cell (PEFC) as a primary power source in electric vehicles has received increasing attention during the last few years. This increased attention has been fueled by a combination of significant technical advances in this field and by the initiation of some projects for the demonstration of a complete, PEFC-based power system in a bus or in a passenger car. Such demonstration projects reflect an increased faith of industry in the potential of this technology for transportation applications, or, at least, in the need for a detailed evaluation of this potential. Nevertheless, large scale transportation applications of PEFCs require a continued concerted effort of research on catalysis, materials and components, combined with the engineering efforts addressing the complete power system. This is required to achieve cost effective, highly performing PEFC stack and power system. We describe in this contribution some recent results of work performed within the Core Research PEFC Program at Los Alamos National Laboratory, which has addressed transportation applications of PEFCs.

The prerequisite for large scale terrestrial transportation applications of polymer electrolytic fuel cells (PEFCs) can be briefly summarized as a combination of high performance and reliability and low cost. In terrestrial transportation, the source of hydrogen fuel for the PEFC can be, in principle, a carbonaceous fuel like methanol, which has to be steam reformed to produce the hydrogen feed, or hydrogen stored in pressurized or hydride form. In the methanol fueled vehicle, which has the important advantages of simple refueling and larger range, the PEFC operates on reformat and air. This calls for effective answers for two important requirements. The first is high performance of air cathodes, preferably operating at ambient air pressure or slightly pressurized air, and the second is stable anode operation with variable low levels of CO in the anode feed stream. At this point, these two requirements have to be answered with Pt catalysts. An effective replacement catalyst has not been identified as yet, and this is not too surprising considering the low temperature of the cell (typically 80°C) and the acidic (perfluoro sulfonic acid) electrolyte. As shown in our previous work, optimized design of the catalyst layer and of its bonding to the membrane achieves an enhancement of the effective catalytic activity from a given loading of Pt, and a lowering of mass transport barriers within the thin-film catalyst layer (1,2). The latter feature is particularly important for the air cathode. This has resulted in high performance of H₂/air PEFC's, utilizing ultra low Pt loadings corresponding to about 0.2 gr/kW. Furthermore, these PEFC's are based on catalyzed membranes fabricated by a process of good potential for effective scale up (1-3). The significance in terms of materials cost and manufacturability of such catalyzed membranes is substantial. We report in this paper on recent tests of single cells based on these thin film catalyst layers, which demonstrate stability of performance on a time scale of thousands of hours. This stable long-term performance further demonstrates the viability of our catalyzed membranes as one important component of a PEFC technology which combines lower cost, high performance and high reliability.

As to the significant problem of CO poisoning at the anode Pt catalyst, we have demonstrated that it can be effectively solved by the bleeding of low levels of air into the fuel feed stream (4,5). We report further in this paper on some recently demonstrated application of this air-bleeding approach for "rejuvenation" of PEFC's after long-term cell operation.

Returning to the challenge of an effective air cathode, the relative contribution of this component to losses in PEFCs may need some further clarification because past analyses have stressed ionomer membrane losses. In reality, ionomer membranes 100 μm thick, or thinner, enable an overall areal PEFC resistance as low as 0.08 ohm cm^2 , particularly when the equivalent weight of the ionomer has been lowered to 900, or less (see figure 1). Furthermore, with such better membranes, the PEFC resistance in well humidified cells does not increase with the cell current even at current densities as high as 3 A/cm^2 (see figure 1). Membrane properties required to achieve such behavior have been quantified by detailed modeling (6). It seems, therefore, that the ionomer membrane itself is no longer the major barrier for achieving higher cell performance, at least not in PEFCs operating on air rather than neat oxygen. The significant effect of air cathodes on the overall performance of PEFCs can be appreciated from figure 1, which demonstrates the results of iR-correction (R measured typically at 10 kHz at each current density) in the case of oxygen and of air PEFC cathodes. The figure highlights the large contribution of mass transport limitations in the air cathode (figure 1b) to the overall loss in the PEFC. In contrast, in the case of cathode operation on neat oxygen (figure 1a), cathode transport losses are much less significant in the same current density range. Consequently, good understanding of the nature of losses in the PEFC air cathode, based on detailed experimentation and modeling, is a key for enhancing the performance of such cells under conditions relevant to transportation applications. We report in the last part of this paper on the development of effective diagnostics for the PEFC cathode, based on combined modeling and experiment. We offer some conclusions on possible further improvements of PEFC air cathodes.

(2) Experimental

Single cell testing for PEFCs prepared with membranes coated by the thin-film catalyst (1,2) has been carried out under complete control of temperature, pressure and humidification conditions. Humidification conditions have been set by the control of the temperature in stainless steel humidification bottles upstream the cell, equipped with glass bubblers. Automatic control and safety features enable continuous operation at elevated temperature and pressure for the long duration of the life-test. Polarization curves were collected automatically with a system employing an electronic load (HP 6060) and a Labview program (National Instruments) in conjunction with a MacIntosh PC. The high frequency resistance was measured (with a Voltech TF2000 frequency response analyzer) as function of cell current, by applying an ac perturbation through the electronic load and measuring the amplitudes of the ac voltage across the cell and of the ac current through the small series resistor employed for cell current measurements. Details of the preparation of the thin film catalyst and its bonding to the membrane are given in references 1-3. X ray diffraction (XRD) measurements were performed on a Siemens D5000 X ray diffractometer and analyzed with the Warren Averbach program provided with the instrument.

(3) Results: Single Cell Life Testing

(3a) Thin-film catalysts for the PEFC - Enhanced long-term performance stability of cells with ultra low Pt loadings

We begin our report with recent improvements in the properties of the thin-film catalyst layers developed by us recently (1-3). These improvements have enabled a significant extension in the useful life of our PEFC. We have previously reported on the fabrication of catalyzed membranes with ultra low Pt loadings, based on the preparation of an "ink" with general composition Pt/C + dissolved ionomer + glycerol, which can be either applied directly to the membrane or pre-dried on a "blank" and then hot-pressed onto the membrane. In our previous contributions, we reported on the ionomeric component of the ink in either the H⁺ (1) or Na⁺ (2) form. (The ionomer is always reprotonated before introduction of the catalyzed membrane into the fuel cell). We report here on the enhanced long-term performance stability of PEFCs which employ thin-film catalyst layers prepared with the thermoplastic, tetrabutylammonium (TBA) form of the (perfluorosulfonate) ionomer. Figure 2 gives a comparison between the long-term losses observed with catalyst layers prepared from the Na⁺ form of the ionomer and those observed with catalyst layers prepared from the TBA form of the ionomer. The experiment followed cell current at a constant cell voltage of 0.5V. Following the first gradual current decay, observed in all the cells during the first 1000 hours of continuous cell operation, the performance of the cells prepared with the TBA form of the ionomer has stabilized at about 70% of the initial level (see section 3c for further evaluation of this initial performance loss). In contrast, cells with catalyst layers prepared with the Na⁺ form of the ionomer exhibit later in their life a further, rather strong fall in performance. This further performance loss is completely eliminated in our newer cells prepared with the thermoplastic form of the ionomer. This improvement is apparently achieved thanks to enhanced robustness of catalyst layers prepared with the thermoplastic form of the ionomer. The flow of the ionomeric component during hot-press, enabled by the property of thermoplasticity, may enhance the interparticulate bonding within the catalyst layer. Also, the higher temperature employed in catalyst preparation with the TBA form enables better annealing, and, thus, better crystallinity of the ionomer. Consequently, excessive swelling of the catalyst layer, which could be responsible for oxygen transport limitations within an "aging" cathode catalyst layer, is apparently less severe in the case of catalyst layers prepared with the TBA form of the ionomer. Further stabilization of the long term performance of such PEFC's is discussed in section 3c.

(3b) Pt catalyst Agglomeration - Does it contribute to long term performance losses in the PEFC?

One suspicion as to the origin of long term losses in such PEFC's has been directed towards the phenomenon of catalyst agglomeration (or catalyst ripening). It can be understood why this mechanism of performance loss would be of particular concern for cells employing such ultra low Pt loadings. The phenomenon of Pt catalyst agglomeration, or ripening, has been well documented for the case of the phosphoric acid cell (7). Arguments for lower rates of agglomeration in PEFC's have been suggested based on the much lower temperature of the PEFC and the more benign nature of the electrolyte.

However, experimental evidence to support such arguments has not been previously provided. We report here on the measurement of Pt catalyst ripening in PEFCs based on ultra low Pt loadings, which operated continuously for 2500 hours at a cell voltage of 0.5V on pressurized hydrogen and air. The cathode catalysts in such cells were analyzed with x-ray diffraction (XRD) techniques which did not require removal of the catalyst from the ionomer membrane substrate. This enabled direct XRD measurements on catalysts of cells disassembled following a long period of continuous operation. The catalyst particle size distribution could be analyzed from the shape and width of the XRD intensity peaks. Results are given in figure 3 for the cathode catalyst. The results show that slow catalyst ripening does take place in these PEFCs. The typical degree of ripening can be summarized as a decrease of Pt surface area from an initial value of $100 \text{ m}^2/\text{gr}$ to $70 \text{ m}^2/\text{gr}$ after 1000 hours and to $40 \text{ m}^2/\text{gr}$ after 2500 hours. Such a surface area loss suggests that the catalytic activity should decline by about 60% between the beginning and the end of the life test. This should be reflected by a decrease of the measured current density by the same factor around 0.9V, where the performance is controlled only by catalytic activity. However, in reality the long-term performance losses observed in these PEFCs seem to be confined to the voltage domain associated with larger current densities (see figures 5,6). Long-term effects observed at 0.9V between beginning and end of the life test are, in most cases, much less pronounced than the expected 60% current decrease. One likely explanation is provided by the results described in another report to this ECS meeting (8). We show there the loss of Pt surface area could be compensated by a higher specific activity per unit surface area of the larger catalyst particles. We conclude that this rather substantial Pt catalyst ripening phenomenon, observed in PEFC cathode Pt/C catalysts following long term cell operation, probably does *not* contribute significantly to the long-term performance losses observed in our PEFCs. Further support for this conclusion is brought in section 3c.

(3C) Long-Term Performance Losses in PEFCs - The Contribution of The Anode

As tests of cells with TBA-based, thin-film catalyst layers continued, we have discovered that a large part of the cell performance loss recorded during the first 1000 hours of cell life could, in fact, originate from increased losses at the cell *anode*. This came as somewhat of a surprise, having suspected all along mainly enhanced losses in the cell cathode. Our discovery was made during the study of effects of low levels of CO in the fuel feed stream, and their possible remediation according to the approach developed by us previously (4,5). Additions of 10-100 ppm of CO to the hydrogen feed stream of a life tested cell began in one case 3000 hours into the life test. As expected, such CO additions brought about significant lowering in cell performance and oxygen bleeding into the fuel feed stream, at a level not exceeding 4%, was applied to remediate the catalyst poisoning. Surprisingly, following the addition of O₂ to the fuel feed stream, not only was the deleterious effect of CO completely removed, but the performance of the cell was actually enhanced significantly above that recorded prior to the additions of CO + O₂ to the anode feed stream. This is shown in figure 4. Figure 4 does not show the drops in cell current when only CO was added to the H₂ feed stream; it shows only the overall performance enhancements twice observed following air injection into the CO contaminated fuel feed stream. The higher performance level of the "rejuvenated" cell could be subsequently maintained by intermittent bleeding of low levels of air into the fuel feed stream.

The conclusions from the results shown in figure 4 on the long term performance stability of our PEFC's are important. Figure 4 demonstrates that PEFC's based on thin film catalysts of ultra low Pt loadings can actually operate for 4000 hours with a performance

loss of only 10%, measured from the onset of the life test. This can be achieved by treating accumulated anode impurity effects by the bleeding of oxygen into the anode feed stream. Consequently, it can also be concluded that the long-term integrity of thin-film catalysts based on the thermoplastic form of the ionomer (TBA) is, in fact, very good. Further support for this conclusion is shown in figures 5 and 6. These figures show that, following the cleansing of the anode catalyst by oxygen bleeding 3000 hours into the life test, there is practically no detected variation in the cell's O₂/H₂ polarization curve compared with the very first day of the life test, whereas only a small performance loss at high current density can be seen for air/H₂ operation. These polarization curves suggest only minor losses in the transport properties within the cathode catalyst layer and/or within the cathode backing after 3700 hours of continuous cell operation (see figure 6), whereas losses in catalytic activity after this long-term operation are apparently negligible (see figure 5).

Finally, it remains to explain the nature of the long-term anode catalyst deactivation which takes place during the first 1000 hours of cell operation (see figures 2 and 4), and which could be corrected by oxygen bleeding into the fuel feed stream. The two most likely possibilities are (i) very low levels of CO in the "pure" H₂ feed used in the life test, and, (ii) some other contaminant which forms within the cell at the anode catalyst by a slow process of chemical reduction or electroreduction. The latter process may be a slow reduction of oxidized sulfur moieties (e.g., sulfonate from the ionomer) to sulfur or to sulfide species, both of which are known to specifically adsorb on a Pt catalyst surface and poison it. Oxidative removal of such surface impurities by oxygen bleeding is conceivable.

(4) PEFC Modeling and Diagnostics

Several recent contributions have been made to the modeling of the PEFC (3,6,9-12). Perhaps the most important result of such modeling should be a set of diagnostic experiments which, with the aid of the model, would enable an effective identification of the origin and magnitude of losses in the operating cell. To develop effective PEFC diagnostics, one would start with a combination of (i) observed patterns in the polarization characteristics of these cells (e.g., effects of oxygen partial pressure, of total gas pressure, of humidification levels at the cathode and at the anode), (ii) experimental derivation of interfacial kinetics and of transport parameters for the component parts of the cell, and (iii) a model for the complete cell which describes the complete polarization characteristic, including the enhanced fall in cell voltage associated with mass-transport limitations in the air cathode. The model has to utilize, to the largest extent possible, experimentally derived key parameters (see, e.g., ref. 6 as an example for the case of membrane modeling). We describe here only a segment of our recent modeling work which highlights two important sources of PEFC losses: the "nitrogen blanket" in the backing layer of the cathode, and the effects of limited ionic conductivity and gas permeability within the catalyst layer. Mathematical treatments of these two aspects were described in previous contributions (11,12), and will not be repeated here for the sake of brevity. All of the experimental results shown here, and fitted to our model, are iR corrected. The high frequency resistance of the cell and its variation with external water supply and with cell current have been modeled by us before (6).

As stated above, it would be important to point first to clear qualitative indications from PEFC behavior which show that mass transport limitations in the cathode backing and/or in the cathode catalyst layer are indeed of substantial significance in determining cell characteristics. Figure 7 demonstrates clearly the effect of transport limitations in the backing of the air cathode. It shows that the effective limitation on the current in cathode,

operated on mixtures of oxygen and nitrogen is not set by the partial pressure of oxygen, which is very similar, if not identical, in all three cases of O₂/N₂ mixtures employed. Rather, at constant O₂ partial pressure, the current limitation is seen to drop with increased N₂ partial pressure. This points immediately to the significant effect of transport in the gas phase, rather than in any condensed domain of the system. The use of such diluted O₂ gas mixtures for fuel cell diagnostics has been suggested by Cutlip and coworkers (13). Other than demonstrate qualitatively the significance of mass transport limitation in the gaseous domain of the cathode, such polarization curves allow a quantitative evaluation of the key parameter of the backing, i.e., its effective porosity. The computer fitted curves in figure 7 have been obtained with a model for the cathode backing based on the Stefan-Maxwell, multi-component gas diffusion equations, yielding an effective porosity for the backing which drops linearly with current density from 0.22 at J=0 to 0.14 at J= 1.5 A/cm². This drop in effective porosity of the backing could be caused by a buildup of liquid water which increases with cell current.

Another diagnostic feature of PEFC characteristics observed at lower cell polarizations, is the ratio of the currents measured at the same (iR-corrected) potential with an O₂ and an air cathode of the same total pressure. As figure 7 shows, it is significantly smaller than 5:1. At such low cell polarizations the effect of the backing is small, and this deviation of the current ratio from 5:1 highlights the effects of the limited ionic conductivity and gas permeability within the catalyst layer (12).. Figure 7 demonstrates that computer-fitting of the O₂ and air (iR-corrected) performances of the same cell could be achieved by assuming a significant ionic resistivity for the composite layer of the catalyst, which contains only about 25% by volume of the ionomer (1-3).

(5) Conclusions

- (1) We have demonstrated performance stability in life tests lasting 4000 hours for H₂/air PEFCs based on ultra low platinum loadings (0.12 mg/cm²/electrode). An important ingredient for a low-cost, highly performing and reliable PEFC technology for transportation has thus been established.
- (2) Catalyst deactivation at the PEFC anode, caused by internally generated and/or feed stream trace impurities, brings about a slow loss of PEFC performance. This performance loss could be simply and effectively recovered after long-term cell operation by intermittent bleeding of low levels of oxygen, or air, into the fuel feed stream.
- (3) Significant catalyst agglomeration takes place in the Pt/C cathode catalyst of the PEFC, but apparently has no significant effect on cell performance.
- (4) Detailed diagnostic experimentation combined with comprehensive modeling for the PEFC shows that oxygen permeability losses in the cathode backing are very significant for operation on pressurized air, whereas effects of limited conductivity and gas transport within the thin film catalyst layer also contribute to the cell losses. The improvements required to achieve better performance for PEFC operation on low air pressures include enhanced mass transport in the cathode backing and minimized (ionic) resistive loss in the catalyst layer.

Acknowledgement:

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Figure 1a. Cell voltage, high frequency cell impedance and iR-corrected cell voltage as functions of cell current density for the case of pressurized oxygen/hydrogen. The cell is based on Membrane C (Chlorine Engineers) catalyzed by a thin film catalyst layer of 0.12 mgPt/cm²/electrode.

Figure 1b. Same cell and measurements as in figure 1a, for the cases of pressurized air/hydrogen and of 1 atm air/hydrogen.

Figure 2. Comparison of the long-term stability of cell performance for cells with 0.12 mgPt/cm², where the thin-film catalyst layer was prepared with the ionomer in either the Na⁺ or the thermoplastic, TBA form.

Figure 3. Variations in size distribution of carbon-supported Pt particles as a result of continuous life testing at cell voltage of 0.5V. Cell temperature was kept at 80°C and gas pressures were 5 atm air, 3 atm H₂. (Both gas streams were humidified).

Figure 4. Gradual losses and performance recovery in a PEFC operated at constant voltage of 0.5V on 5 atm air/3 atm H₂ at 80°C. Performance recovery after 3000 hours was achieved following intermittent bleeding of low levels of air into the fuel feed stream.

Figure 5. Polarization curves, recorded for diagnostics with an O₂ cathode, at different times in the life of the cell discussed in figure 4. Anode catalyst cleansing was performed at t=3000 hours.

Figure 6. Same as figure 5, for cell operation on air/H₂.

Figure 7. Experimental (iR-corrected) results and the model fit performed simultaneously for all four cases shown, consisting of cathodes of the same cell operated on (top to bottom): 5 atm O₂, 5 atm air, 13% O₂ in an O₂+N₂ mixture with P_{total}= 2 atm, 5% O₂ in an O₂+N₂ mixture with P_{total}= 5 atm. The best fit was obtained with the following parameters: Cathode backing thickness - 300 μ m with an effective porosity varying linearly between 22% at zero current and 14% at

I = 1.5 A/cm², and cathode catalyst layer thickness 7.5 μ m with an effective protonic conductivity 0.074 S/cm and effective oxygen diffusion coefficient 5.4x10⁻⁴ cm²/sec.

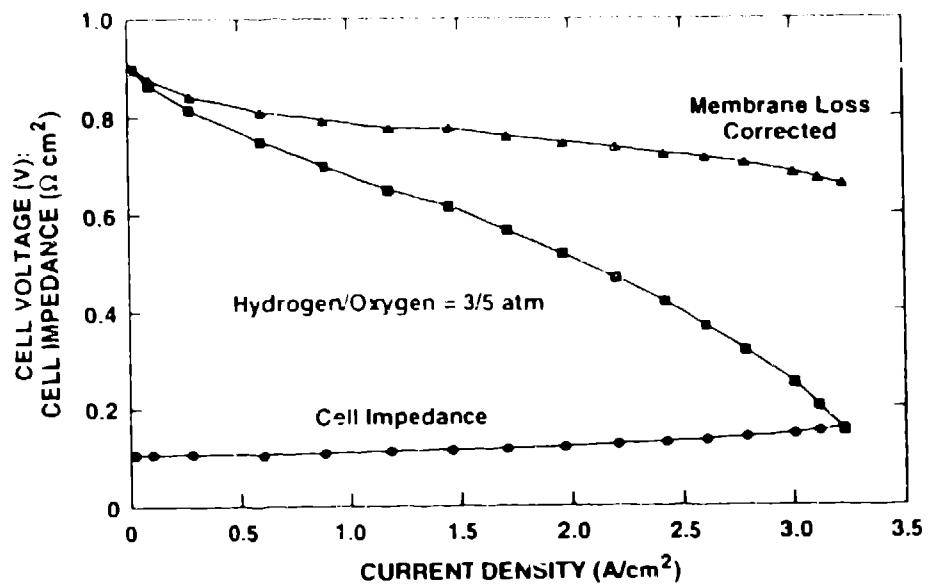


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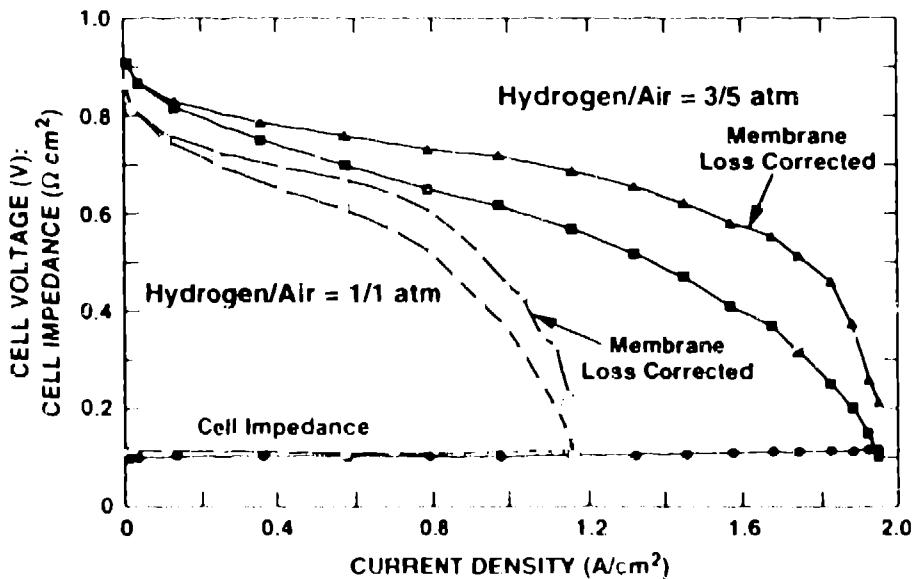


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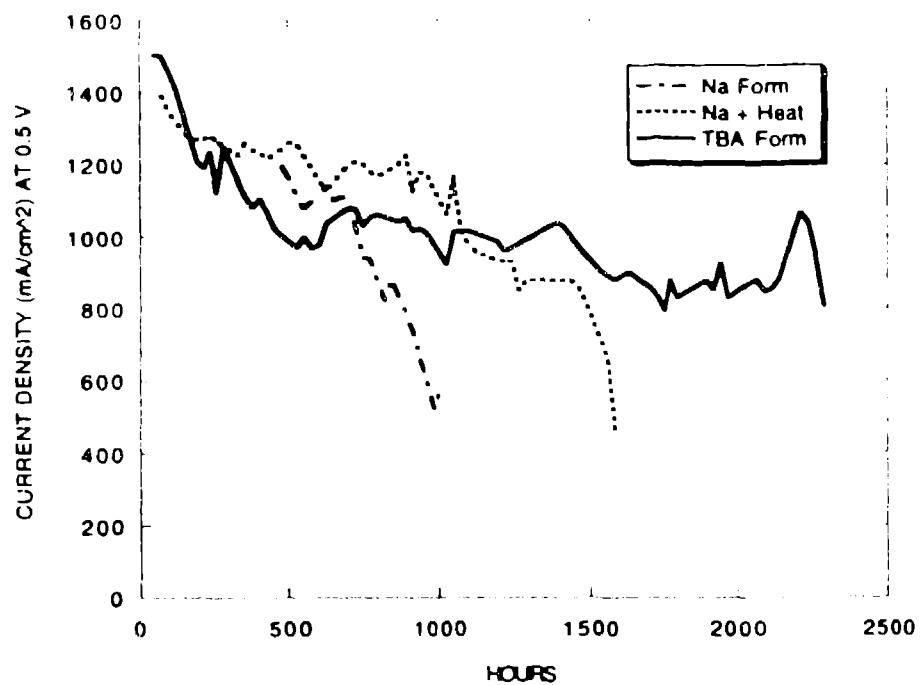


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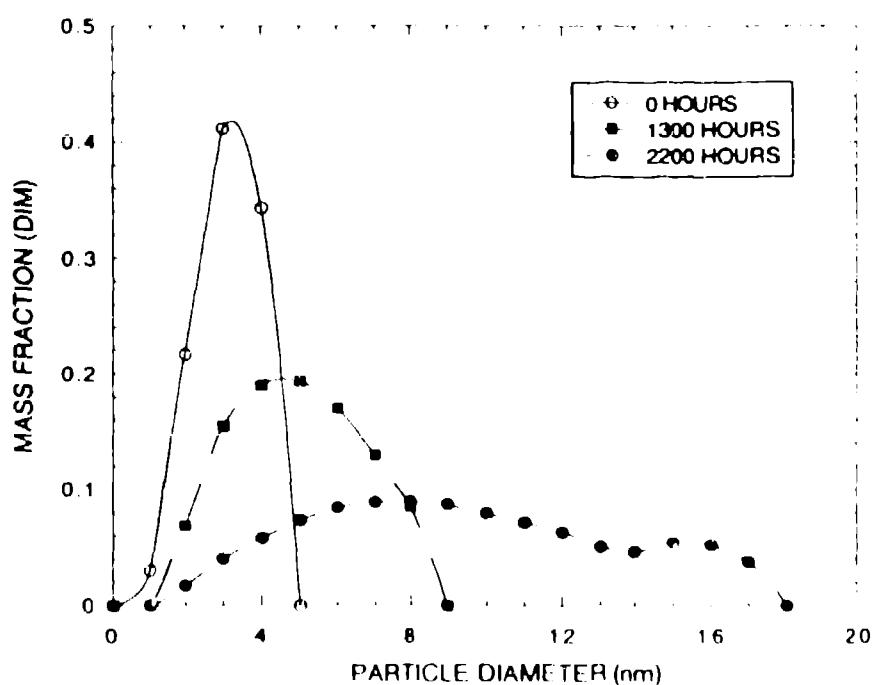


Figure 3. Variations in size distribution of carbon-supported Pt particles as a result of continuous life testing at cell voltage of 0.5V. Cell temperature was kept at 80°C and gas pressures were 5 atm air, 3 atm H₂. (Both gas streams were humidified).

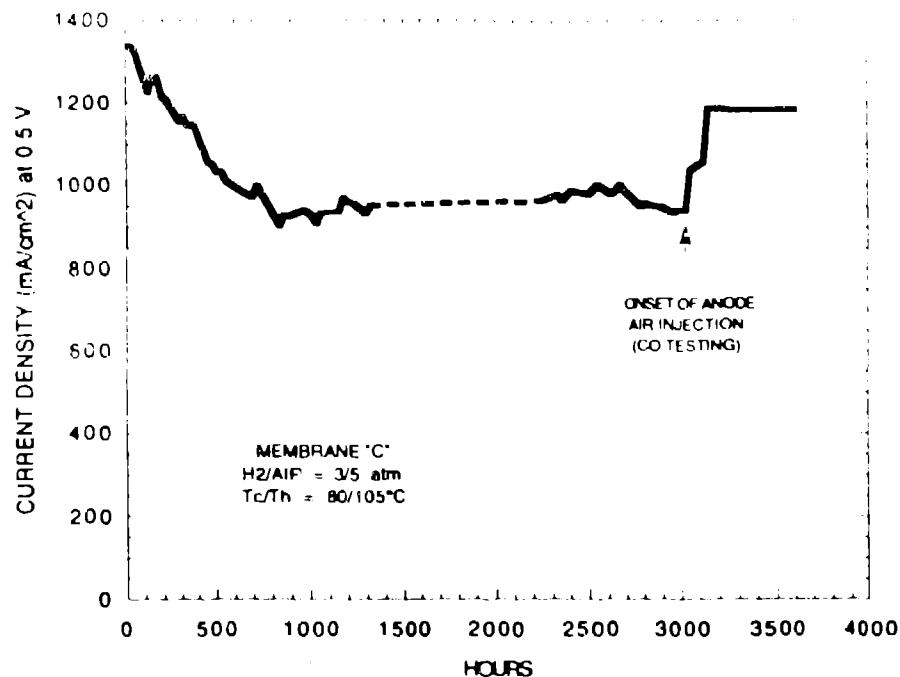


Figure 4. Gradual losses and performance recovery in a PEFC operated at constant voltage of 0.5V on 5atm air/3atm H₂ at 80°C. Performance recovery after 3000 hours was achieved following intermittent bleeding of low levels of air into the fuel feed stream.

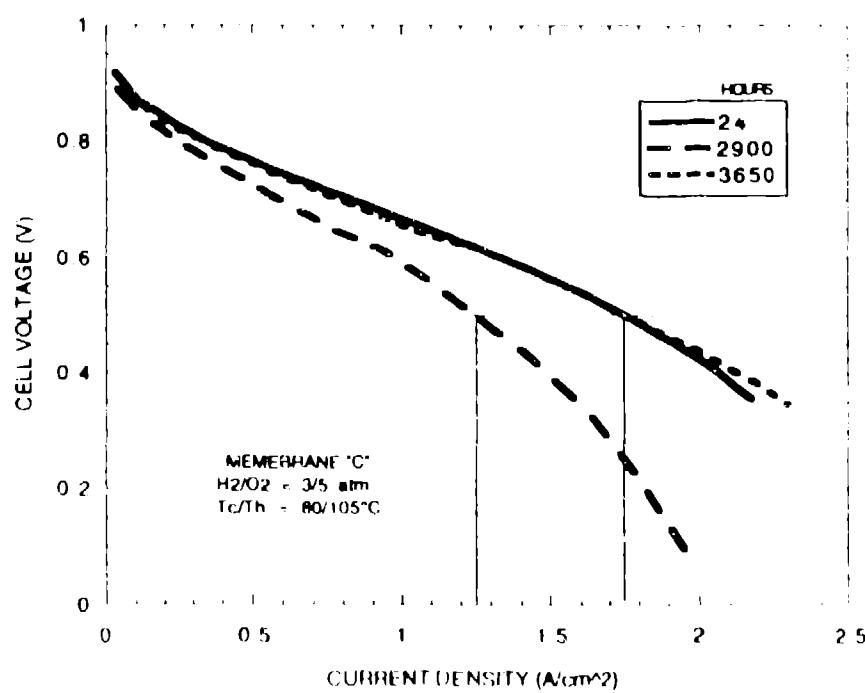


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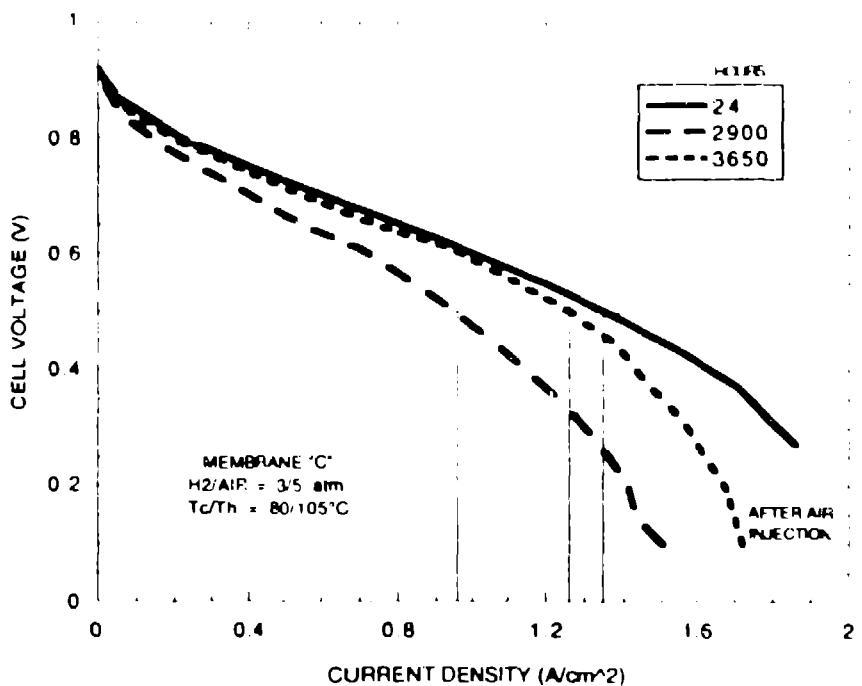


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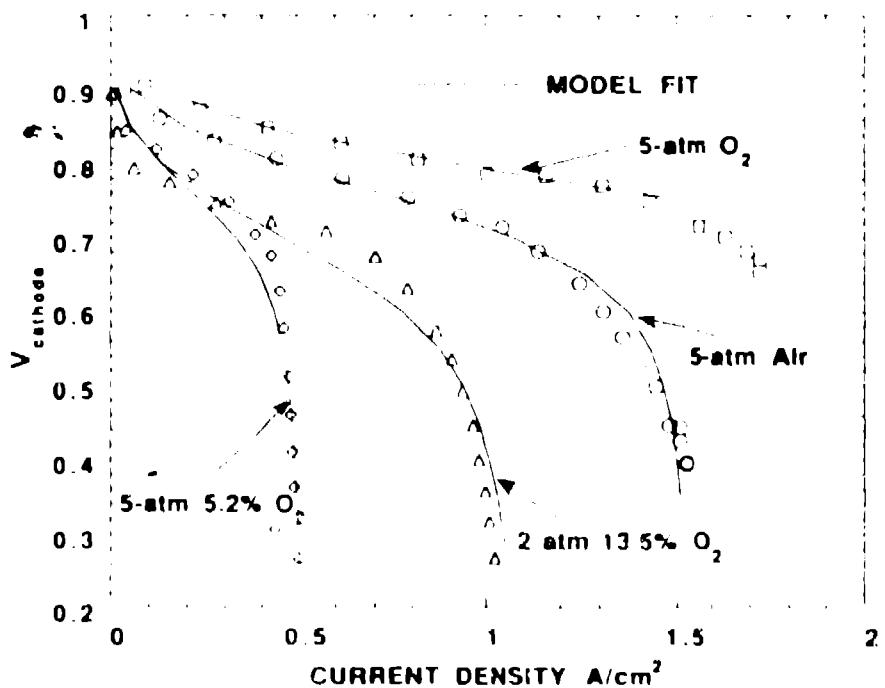


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