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Polymer Electrolyte Fuel Cells: Potential Transportation And Stationary Applications

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(1)Introduction

The application of the polymer electrolyte fuel cell (PEFC) as a primary power source in electric vehicles has received increasing attention during the last few years. This increased attention is the result of a combination of significant technical advances in this fuel cell technology and 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 increase in industry's faith 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 a cost effective, highly performing PEFC stack and power system.

A related set of technical and cost challenges arises in the context of potential applications of PEFCs for stationary power applications, although there are clearly some differences in their nature, particularly to do with the different types of fuels to be employed for each of these applications. We describe in this contribution some recent results of work performed by the Core Research PEFC Program at Los Alamos National Laboratory, which has addressed materials, components and single cell testing of PEFCs. Also included are some recent observations and some insights regarding the potential of this fuel cell technology for stationary power generation.

The prerequisite for large scale applications of polymer electrolyte fuel cells (PEFCs) can be briefly summarized as a combination of high performance, high 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 a larger vehicle range, the PEFC operates on methanol reformate 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. However, at this point the Pt electrocatalyst does not seem any more a major cost or performance barrier in the PEFC. As shown in our recent work, optimized design of the catalyst layer and of its bonding to the membrane achieves a very significant enhancement of the effective catalytic activity from a given loading of Pt, and a significant lowering of mass transport barriers within the thin film catalyst layer (1,2). This has resulted in high performance of H_2/air PEFCs utilizing ultra low Pt loadings corresponding to about 0.[illegible] g/kW. [illegible] are fabricated by a process of good potential for effective scale-up (1-3). 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 (4-6). We report further in this presentation on aspects of anode catalyst poisoning in PEFCs which are of central importance for stationary power generation by PEFCs.

(2) Life Tests of Membrane/Electrode Assemblies with Ultra Low Pt Loadings

We report here on recent testing of activity and long-term performance stability of PEFCs with ultra-low Pt loadings. Our catalyzed membranes have been prepared by bonding composite thin films of 75%[20% Pt/C]+25% recast Nafion^R to the ionomeric membrane(1,2). We have employed most recently the thermoplastic, tetrabutylammonium (TBA) form of the ionomer for the preparation of the catalyst layer. The loadings employed in such PEFCs have been 0.12 mgPt/cm^2/electrode. Figure 1 gives an example of the performances obtained from PEFCs based on such catalyzed membranes, when operated as H_2/O_2 or as H_2/air cells, with external humidification of the inlet gas streams. The figure shows that the high frequency resistance of the cell is as low as 0.08 ohm cm^2, and does not increase significantly with cell current up to 3A/cm^2. The latter result means that the previously worrisome problem of water management in the PEFC is not too severe, particularly after thinner membranes of somewhat lower equivalent weight have become available. Figure 1b clearly demonstrates that the air cathode is an important source of performance limitation in the case of the H_2/air PEFC.

An important test of the viability of such PEFCs with ultra low Pt loadings, is their long-term performance stability. Life tests performed recently in our laboratory have demonstrated stable performance in tests lasting as many as 4000 hours. Results for one such cell are given in figure 2. It is clear from this figure that the high-frequency resistance of the cell has changed only slightly during cell life. This suggests good stability of the ionomeric membrane and no significant long-term effects of contaminants on it's protonic conductivity. A very gradual slight loss of current (10-20%), seen in most cases during the first 1000 hours of cell operation, was at first suspected to be caused by catalyst agglomeration. We have consequently measured Pt catalyst ripening in PEFCs which operated continuously for 2500 hours at a cell voltage of 0.5V, on pressurized hydrogen and air. 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 m^2/gr to 70 m^2/gr after 1000 hours and to 40 m^2/gr after 2500 hours. Such a surface area loss suggests that the cathode catalytic activity should decline by about 60% between the beginning and the end of the life test. However, in most cases, long-term current losses observed at 0.9V between beginning and end of the life test are negligible. A likely explanation is that the loss of Pt surface area is compensated by a higher specific activity per unit surface area of the larger catalyst particles. We conclude that the Pt catalyst ripening phenomenon does *not* contribute significantly to the long term performance losses observed in our PEFCs.

As tests of cells with 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*, caused by slow anode catalyst deactivation. We will describe in detail how this conclusion was reached. At this point, we have demonstrated 2000-4000 hours operation (at a constant voltage of 0.5V) for several PEFCs based on thin film catalysts of ultra low Pt loadings. In all cases a current loss of only 10% was measured from onset of the life test. We can thus conclude that the long term integrity of the thin film catalysts is very good, and, further, that a key component of a low cost, high performance/reliability PEFC technology has been established.

(3) PEFC Modeling and Diagnostics

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 limited ionic conductivity and/or gas permeability within the catalyst layer. Mathematical treatments of these two aspects were described in previous contributions (7). All of the experimental polarization curves shown here, and fitted to our model, are iR-corrected. The high frequency resistance of the PEFC and its variation with external water supply and with cell current have been modeled by us before (8). Figure 4 demonstrates the quality of the fit obtained to our comprehensive PEFC cathode model, which considers losses caused by limited electrocatalytic activity and by transport limitations within the catalyst layer and backing layer. The figure demonstrates a simultaneous fit to four, iR-corrected polarization curves, obtained with a range of cathode inlet compositions and total pressures. The use of diluted oxygen gas mixtures for diagnostics has been suggested by Cutlip, Stonehart and coworkers (9), and turned out to be a very effective diagnostic for the PEFC. The experimental results highlight the effect of transport limitations in the backing of the air cathode. At very similar O_2 partial pressures (two lowest plots in figure 4), the current limitation is seen to become more severe with increased N_2 partial pressure. This points immediately to the significant effect of oxygen transport in the gas phase, rather than in any condensed domain of the system. Such a family of polarization curves has enabled quantitative evaluation of the key parameter of the cathode backing, i.e., the effective porosity and its possible dependence on cell current (through the generation of liquid water). The computer-fitted curves in figure 4 have shown 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/cm^2. The effect of the ionic resistivity within the catalyst layer can be seen from the low "oxygen advantage" around a cathode potential of 0.8V, which can be explained only by such an ionic resistance effect in the layer containing the catalyst (7). According to the model fit, the effective ionic conductivity in the composite, Pt/C//recast ionomer layer, is as low as .007S/cm (compared with .1S/cm for the neat recast ionomer).

(4) The Potential of Stationary Power Generation by PEFCs

Stable PEFC anode operation on a feed stream of, e.g., natural gas reformate, is a challenge that has to be met in order to enable utilization of PEFCs for stationary power generation. This challenge is considered more serious in the case of the PEFC because of the low temperature of operation (80^{0}C). To the best of our knowledge, no demonstration of a system consisting of a natural gas reformer and a PEFC stack has been reported as yet. However, some of the problems associated with the operation of PEFCs on realistic fuel feed streams have been addressed recently in the context of operation of PEFCs on methanol reformate. In the latter case, it has been demonstrated that a significant lowering of the level of CO, from 1% at the reformer outlet down to about 10 ppm, can be achieved in a selective oxidation stage based on a Pt/Alumina catalyst (10). We have shown that the sensitivity of the PEFC to such residual levels of CO (10 ppm) is still very significant. We have demonstrated, however, the ability to remediate effects of residual CO in the fuel feed stream by bleeding of small levels of O_2, or air, into the anode compartment of the fuel cell (4-6). This approach is demonstrated in figures 5 and 6. There have been some recent indications on the success of implementing this approach in PEFC stacks. We have tested the oxygen bleeding approach recently for prolonged periods of time as part of our single cell testing activity and found no problem associated with its extended application. One can thus conclude that stable anode performance in PEFCs operated on natural gas reformate can probably be achieved with a combination of (i) a CO level limited to 1% in the reformer outlet stream, (ii) a selective oxidation stage upstream the fuel cell to lower the CO down to the 1-10ppm level, and (iii) in situ oxygen bleeding into the anode compartment to remove effects of residual CO. To the extent that levels of CO higher than 1% are generated in natural gas reforming, a water shift stage following the reformer and operating at a lower temperature should solve this problem, and enable minimization of oxidative treatment required down stream. The overall loss of fuel caused by oxidative treatments of this type should not exceed 4%, provided the CO level in the reformer outlet stream is lowered to 1%.

A further very important point in this context arises from the different conditions of operation of a PEFC stack and a selective oxidizer in the power generation vs. the transportation mode. For example, a large part of the effort devoted to the in situ oxidative removal of CO (4-6) had to do with the higher power requirements from the PEFC in transportation applications. In the case of stationary power generation, where energy conversion efficiency is of highest concern and the cell would operate at a constant working point of somewhat lower power, some of the problems caused by residual CO within the anode can be totally solved by appropriate anode catalysts of sufficient CO electro oxidative activity, e.g. Pt-Ru/C. Our recent work with a Pt-Ru/C PEFC anode catalyst, prepared and bonded to the membrane in the same way employed for Pt/C catalysts (1,2), gives reason for some optimism. The benefit of stationary operation of the selective oxidizer could be even more dramatic because the fundamental requirement of accurate temperature control in this stage can be implemented much more easily under such simpler operation conditions.

The obvious remaining question is what are the advantages to be gained by solving the problem of stable anode performance in a PEFC stack operating on natural gas reformate. The answer is that the PEFC may have some rather attractive features for this application, particularly when compared with alternative fuel cell technologies for stationary power generation. The PEFC is a low temperatere system employing very benign materials, and a pseudo solid state structure. Compared with other low-temperature fuel cells it has the advantages of employing distilled water rather than corrosive electrolytes, and to have a structure that easily enables pressurization, including differential pressurization. Pressurization, up to an optimized level dictated by overall energy efficiency considerations, can bring about significant enhancement of air cathode efficiency. Also, the power density obtained at an optimized working point for stationary power generation (about 0.7V) would be 2-3 times higher than that of the phosphoric acid fuel cell, and thus the foot print of a PEFC stack will be significantly smaller. Compared with high temperature cells such as MCFC or SOFC, the major advantages are associated with the much less severe materials problems, and much easier access and maintenance associated with the lower temperature of the PEFC stack. Also, much easier start-up/shut down will be possible, enabling surge power applications without the need to keep the stack continuously at a high temperature to be ready for use.

The conclusion seems to be that consideration of PEFC stacks for power generation is very worthwhile, and, once stable anode performance has been demonstrated in conjunction with a natural gas reformer, as seems feasible from the discussion above, the advantages of the high power density, reliable, pressurizable, and easily maintainable fuel cell stack associated with minimized materials stability problems, will clearly emerge.

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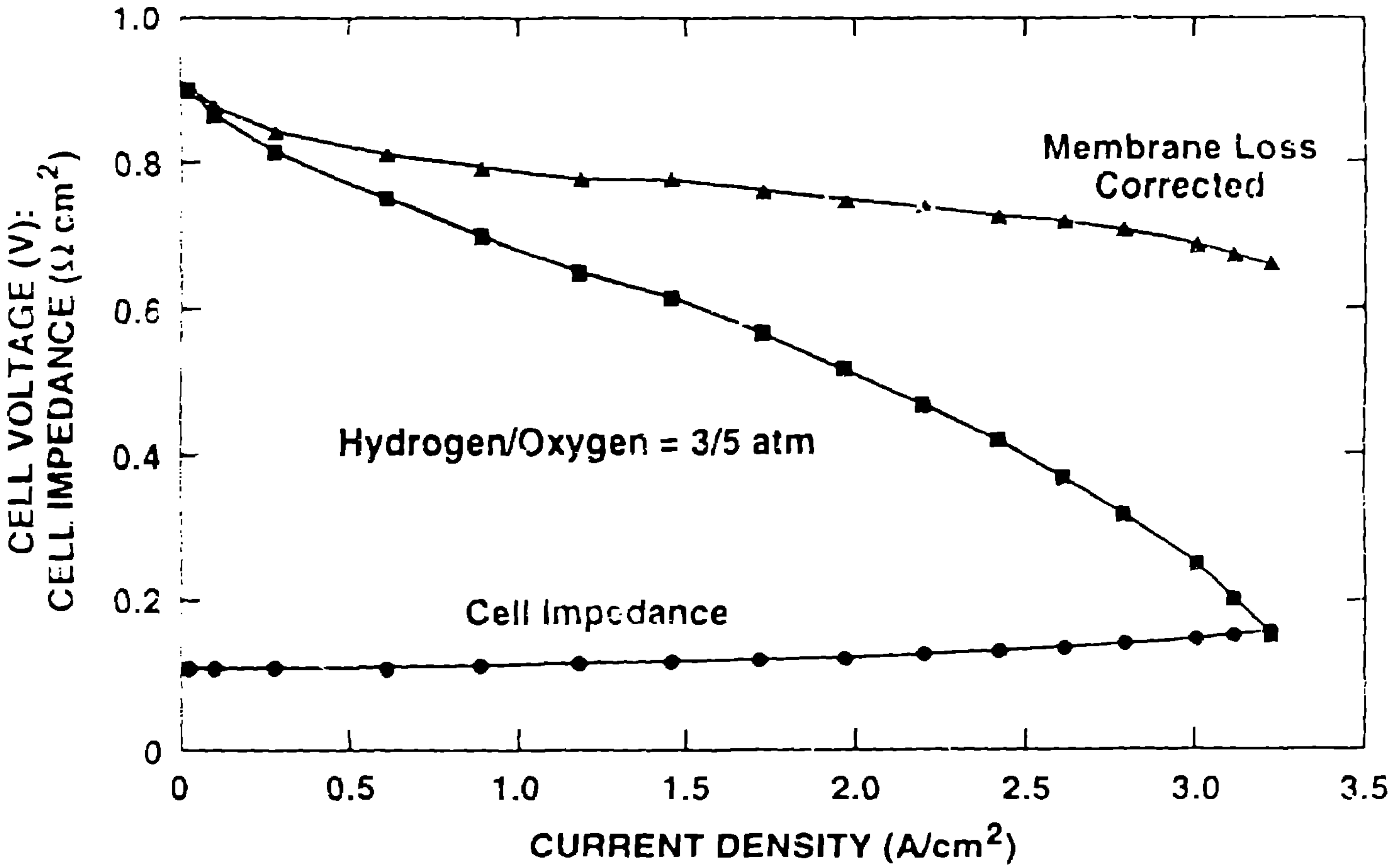
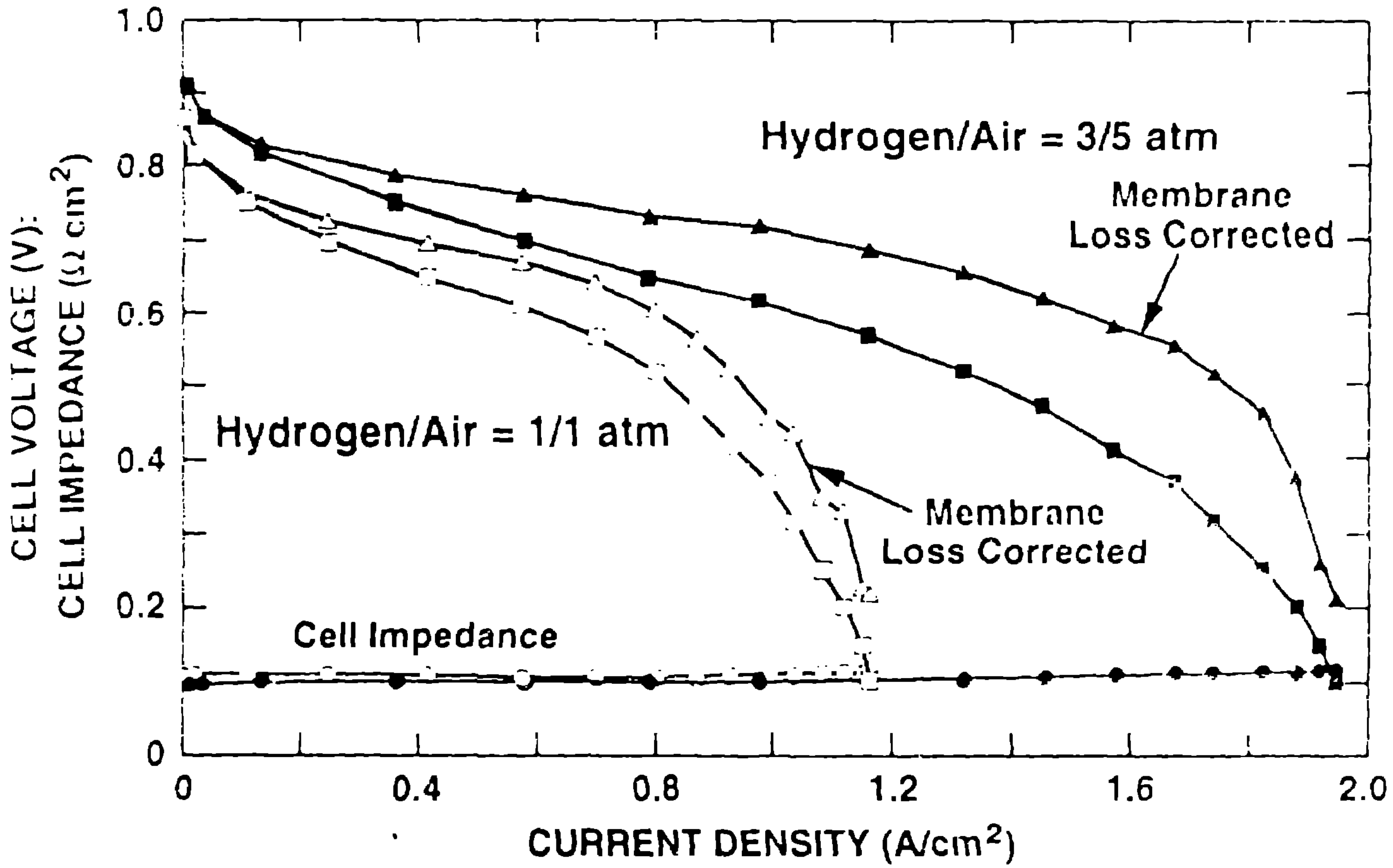

1.0
0.8
0.6
0.4
0.2
0
CELL VOLTAGE (V):
CELL IMPEDANCE (Ω cm²)
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
CURRENT DENSITY (A/cm²)
Membrane Loss Corrected
Hydrogen/Oxygen = 3/5 atm
Cell Impedance

Fig 1a



1.0
0.8
0.6
0.4
0.2
0
CELL VOLTAGE (V);
CELL IMPEDANCE (Ω cm^2)
0
0.4
0.8
1.2
1.6
2.0
CURRENT DENSITY (A/cm^2)
Hydrogen/Air = 3/5 atm
Membrane
Loss Corrected
Hydrogen/Air = 1/1 atm
Membrane
Loss Corrected
Cell Impedance

Fig 1b

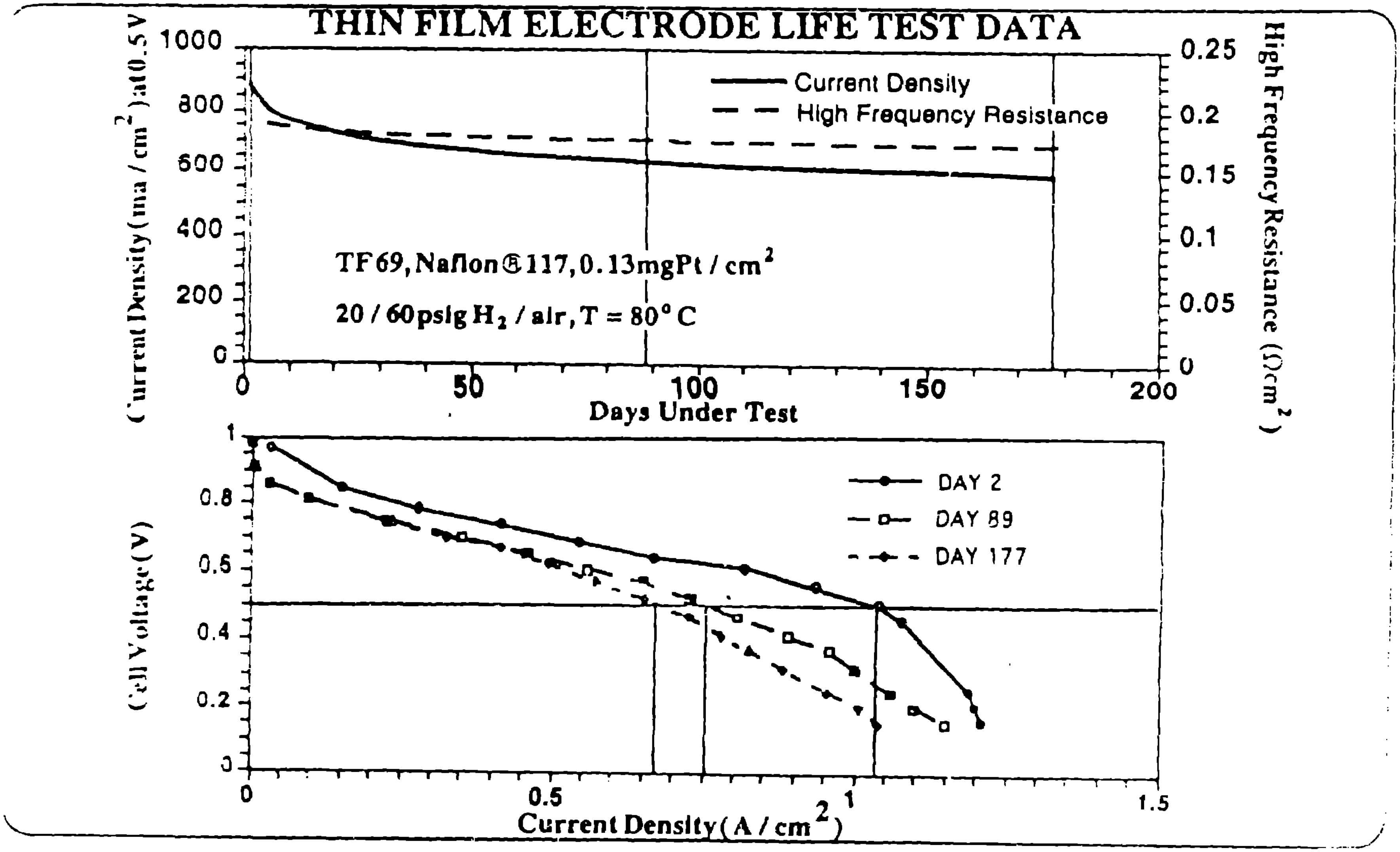

THIN FILM ELECTRODE LIFE TEST DATA
Current Density(ma / cm²)at0.5V
1000
800
600
400
200
0
Current Density
High Frequency Resistance
TF69, Nafion®117, 0.13mgPt / cm²
20 / 60psig H₂ / air, T = 80° C
0
50
100
150
200
Days Under Test
High Frequency Resistance (Ωcm²)
0.25
0.2
0.15
0.1
0.05
0
Cell Voltage (V)
1
0.8
0.6
0.4
0.2
0
DAY 2
DAY 89
DAY 177
0
0.5
1
1.5
Current Density(A / cm²)

Fig 2

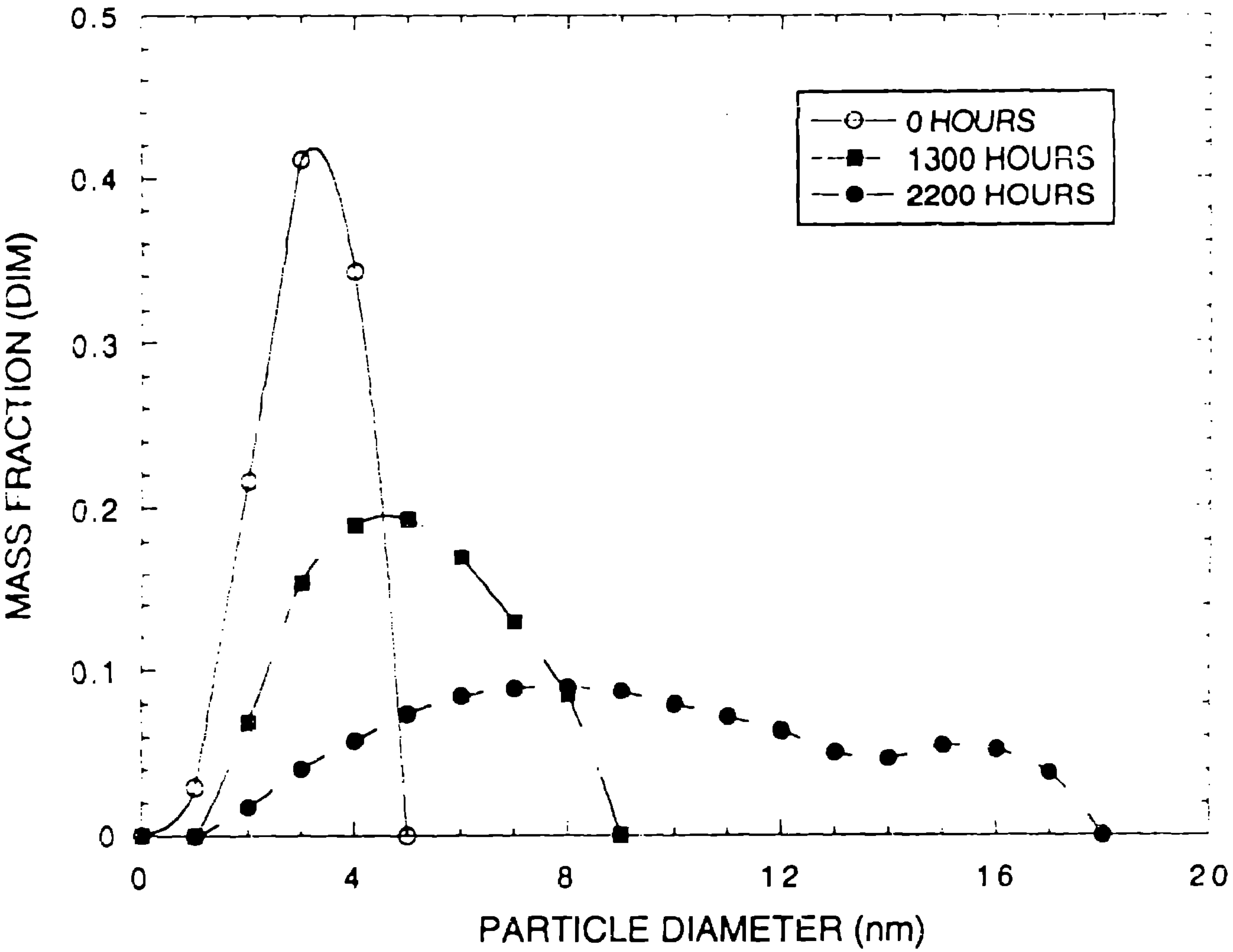

0 HOURS
1300 HOURS
2200 HOURS
MASS FRACTION (DIM)
0.5
0.4
0.3
0.2
0.1
0
0
4
8
12
16
20
PARTICLE DIAMETER (nm)

Fig 3

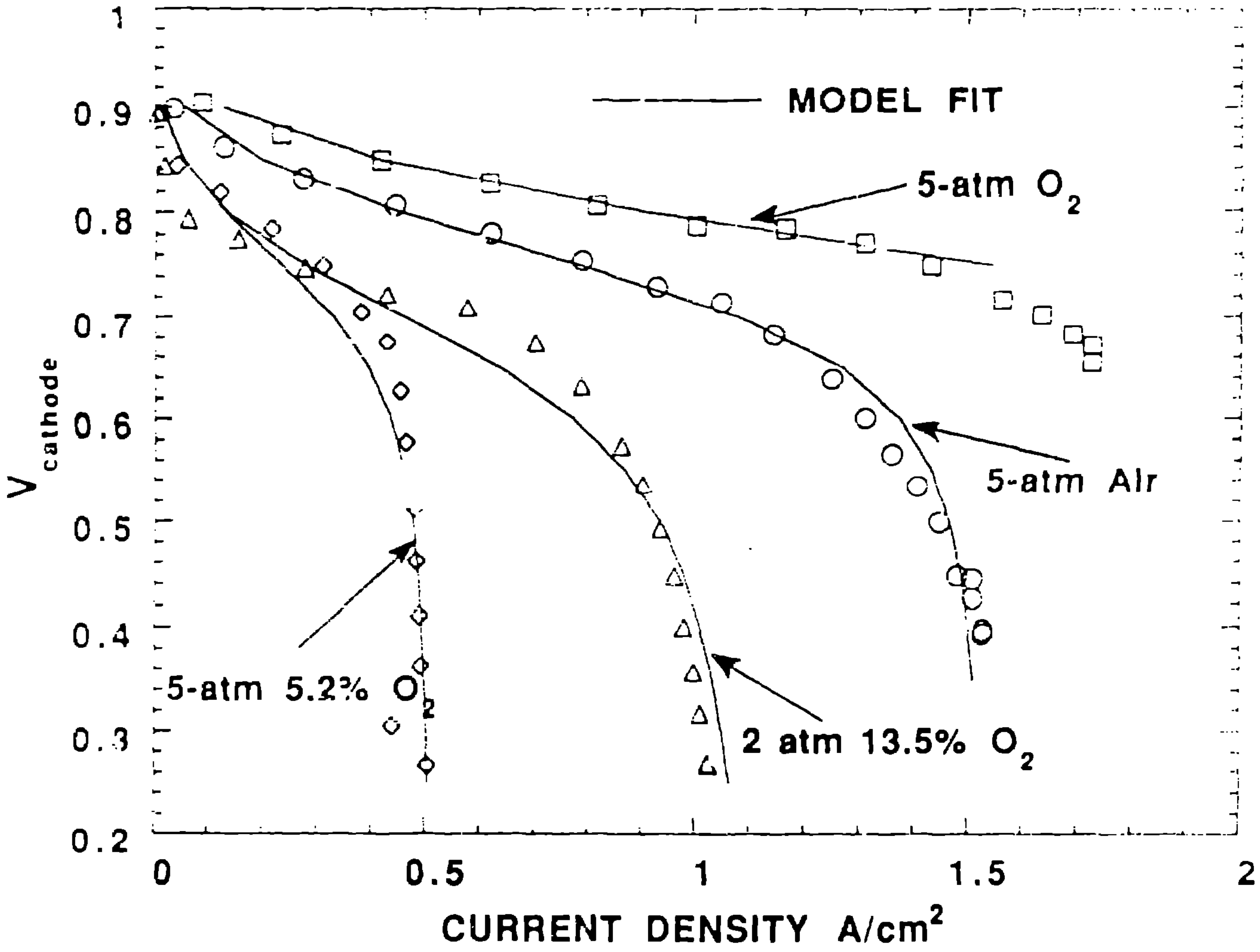
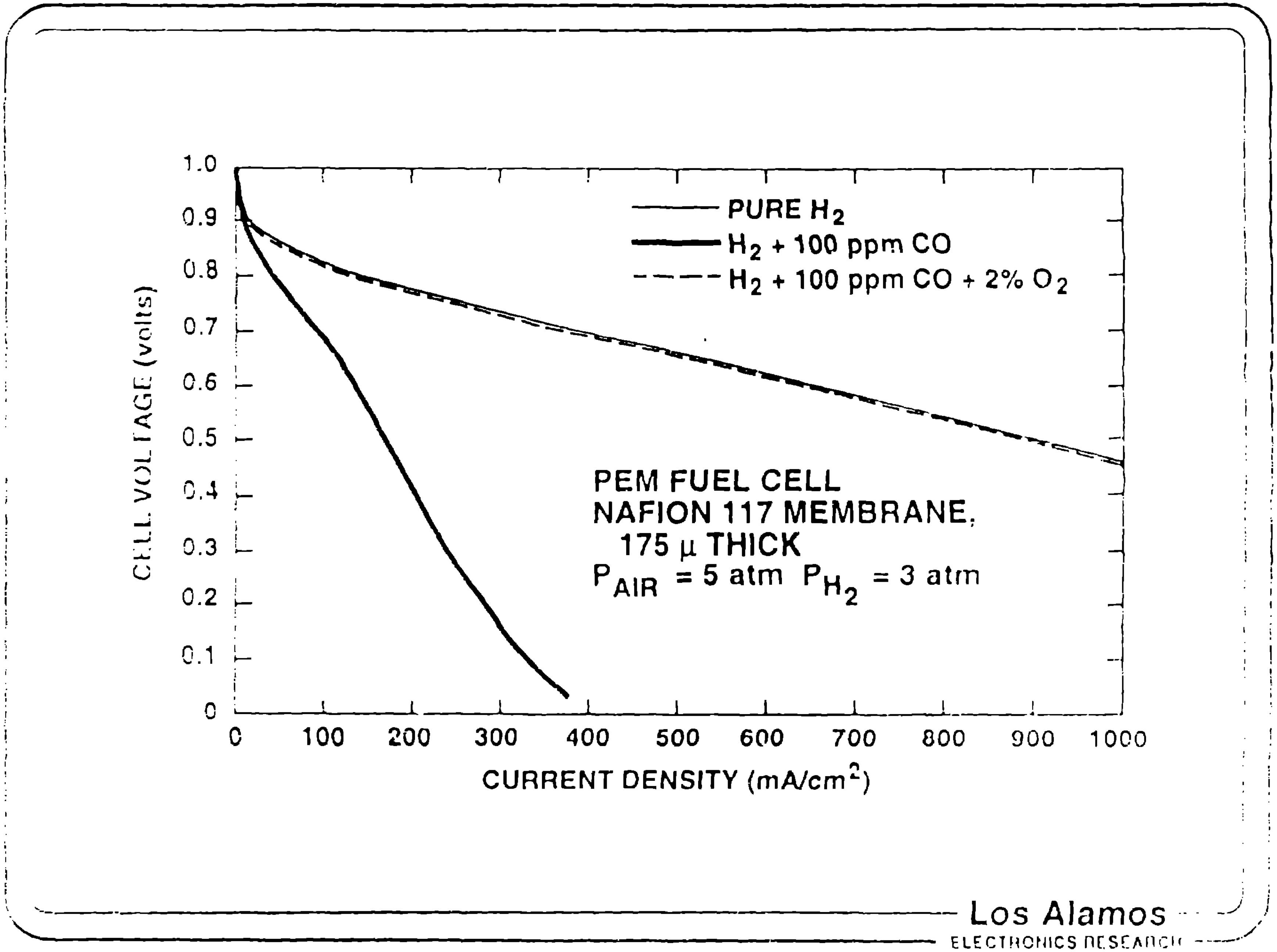

MODEL FIT
5-atm O_2
5-atm Air
5-atm 5.2% O_2
2 atm 13.5% O_2
$V_{cathode}$
CURRENT DENSITY A/cm^2
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0
0.5
1
1.5
2

Fig 4


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
CELL VOLTAGE (volts)
0
100
200
300
400
500
600
700
800
900
1000
CURRENT DENSITY (mA/cm^2)
PURE H_2
H_2 + 100 ppm CO
H_2 + 100 ppm CO + 2% O_2
PEM FUEL CELL
NAFION 117 MEMBRANE,
175 μ THICK
P_{AIR} = 5 atm P_{H_2} = 3 atm
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ELECTRONICS RESEARCH

Fig 5

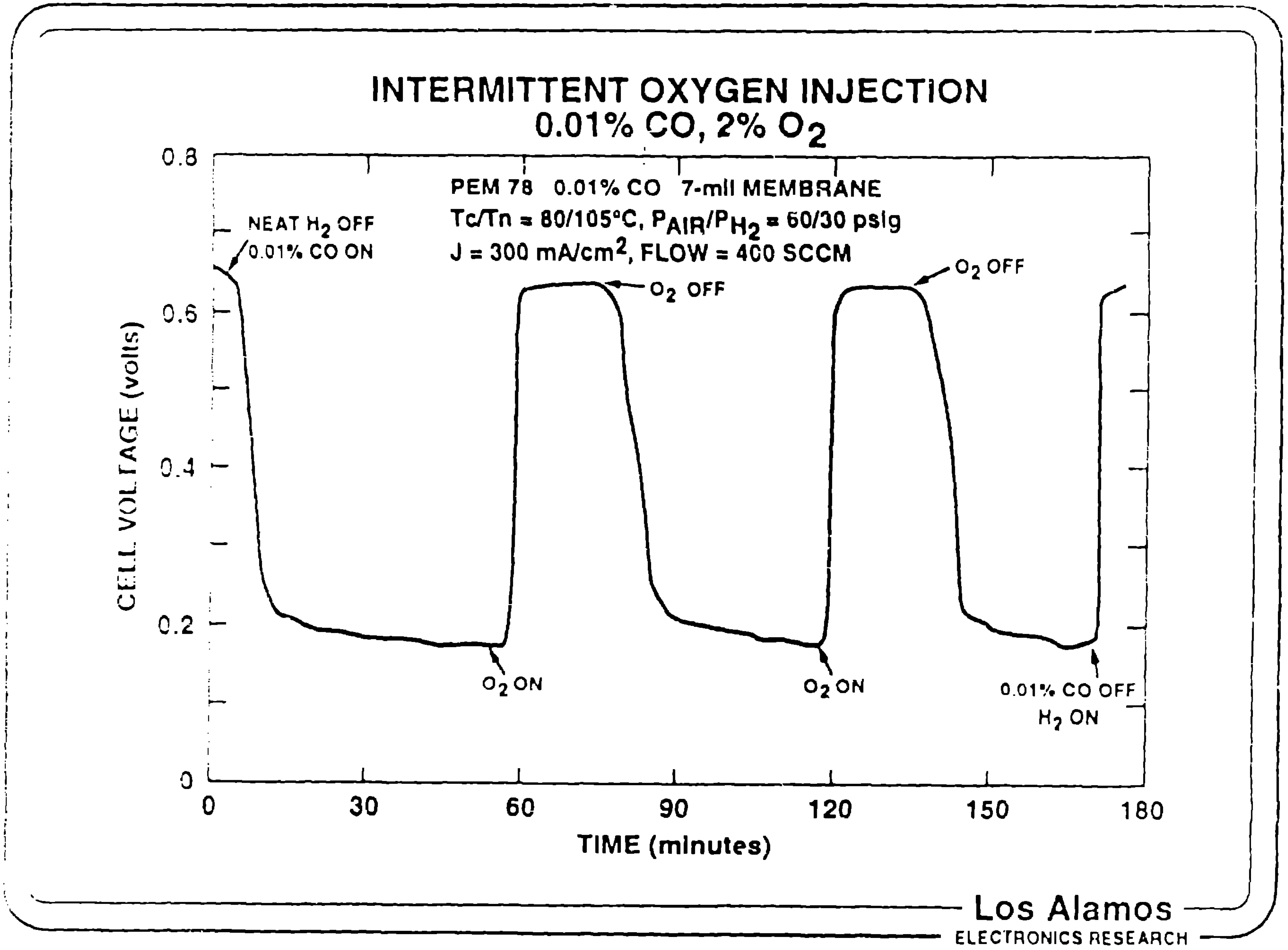
INTERMITTENT OXYGEN INJECTION
0.01% CO, 2% O_2
PEM 78 0.01% CO 7-mil MEMBRANE
Tc/Tn = 80/105°C, P_{AIR}/P_{H_2} = 60/30 psig
J = 300 mA/cm^2, FLOW = 400 SCCM
NEAT H_2 OFF
0.01% CO ON
O_2 OFF
O_2 OFF
O_2 ON
O_2 ON
0.01% CO OFF
H_2 ON
CELL VOLTAGE (volts)
0.8
0.6
0.4
0.2
0
0
30
60
90
120
150
180
TIME (minutes)
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Fig 6