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RESPONSE OF A PEFC

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SPATIAL DISTRIBUTION OF THE CO TRANSIENT RESPONSE OF A PEFC

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ABSTRACT

We report on the investigation of the current distribution of a PEFC under the influence of CO impurities in the hydrogen feed stream by application of the segmented cell system. Stepping the CO partial pressure of the anode feed stream from 0 to 100 ppm CO the current response of the cell was recorded for different stoichiometric flows. A poisoning time delay occurs along the flow path due to the anode flow rate. Also anode and cathode processes, e.g. CO turnover and oxygen mass transport limitation contribute to the time response of the cell.

INTRODUCTION

Practical PEM fuel cells based on perfluorinated ionomer membranes (e.g. Nafion) are likely to use reformed carbon based fuels as the primary source for the anode feed. Besides hydrogen, the reformat may contain trace amounts of carbon monoxide (CO, from a few to several hundred ppm) which would be detrimental to the cell performance. CO strongly adsorbs on the Pt catalyst surface, causing a decrease of the available active Pt surface area for H₂ electro-oxidation resulting in unacceptable losses in electrical current.

The overall current density obtained in a polymer electrolyte fuel cell (PEFC) is an average of widely varying local currents. Gradients of humidification, water generated at the cathode, hydrogen and oxygen partial pressures, and other factors impart a spatial dependence to current generation.

Similarly, time-dependent gradients of CO partial pressure influence the performance of a PEFC. To understand CO poisoning processes in a reformer operated fuel cell system in more detail and to design strategies for improving the overall CO tolerance, information on the current distribution of the fuel cell during CO transients is beneficial. Application of the sophisticated segmented cell approach, recently further developed at Los Alamos, reveals this information. The segmented cell system is capable of measuring current changes of ten individual segments in response to CO injected into the cell and moving downstream. It allows measurement of cell voltage and current of each segment as well as of the total cell with high resolution time. Thus, it can provide

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localized information about the rate of CO poisoning and the rate of CO recovery along the anode flow channel.

Here, we present a study with the segmented cell that examines the influence of CO on cell performance. Results will be shown for spatially resolved poisoning processes arising from different CO partial pressures and flow rates. Also, the discovery of trace amounts of CO oxidation to CO₂ will be discussed along with the influence of cathode processes onto the anode poisoning process.

EXPERIMENTAL

Measurement Setup

The most recent segmented cell hardware consists of a one-piece cathode and a segmented anode. The cathode has an active area of 104 cm² with the same outer dimensions as the segmented anode hardware. The anode is composed of 10 separate segments, each with an area of 7.71 cm² leading to a total active area of 77.1 cm². Segmentation of the anode catalyst layer, the anode gas diffusion backing, and the current collector was implemented to enable current and CO coverage distribution measurements. Individual current collector plates for the segments allow low contact resistance per segment and result in high measurement accuracy. The flow field is a six fold serpentine feeding the fuel to the segments in consecutive order.

Sample Preparation

Membrane Electrode Assemblies (MEAs) of the segmented cell system were prepared in a two-step process for improving homogeneity of the catalyst layers and durability of the MEAs. Using a machine driven doctor blade spreader the cathode catalyst layer was coated onto a Kapton decal medium, hot pressed, proton exchanged and dried as reported previously [1], [2]. The resulting half-cell was completed by spraying the anode catalyst onto the membrane using an automated spray system build in-house. Thus, geometric integrity of the cell and proper alignment within the setup was ensured.

Typical standard catalyst loadings of the MEAs were approximately 0.3 mg Pt/cm² on the cathode and 0.2 mg Pt/cm² on the anode with an average loading deviation of smaller than 3%. Both electrodes consisted of supported platinum catalyst (20 % Pt/C ETEK).

Prior to operation, the anode catalyst layer was activated using cyclic voltammetry. For this purpose N₂ was injected into the anode and H₂ into the cathode. The anode was used as the working electrode and the cathode as the reference and counter electrode. CV cycling was performed in the potential range from 0.1 – 1.4 V.

Reference and test measurements assured proper operation of the MEA before any transient measurements were executed.

Operating Conditions

Unless mentioned, the cell was operated under the following conditions, which we entitle as standard conditions. The humidifier temperature for the anode and the cathode were 105 °C and 80 °C respectively. The gas humidification levels were below 100% saturation, especially at high gas flow rates as a result of limited residence time in the humidifier liquid [3]. The temperature of the cell was 80 °C. Operating back pressure for both the anode and the cathode was 30 psig. Gas flows were controlled by electronic mass flow controllers (MKS, RS 485), calibrated with a digital flow meter (Fisher Scientific, Model 650) adjusted for the atmospheric pressure and the temperature in the laboratory. The gases flowed in parallel fashion from cell inlets to cell outlets through six channel serpentine flow fields.

The anode was operated on hydrogen at a fixed stoichiometric gas flow of 1.1, 1.5 or 2.0, calculated for a total cell current of 60 A at a cell voltage of 0.6 V. The cathode was typically operated with a fixed air flow of 4000 sccm, corresponding to a cathodic stoichiometric flow of around 4.

Measurements & Setup

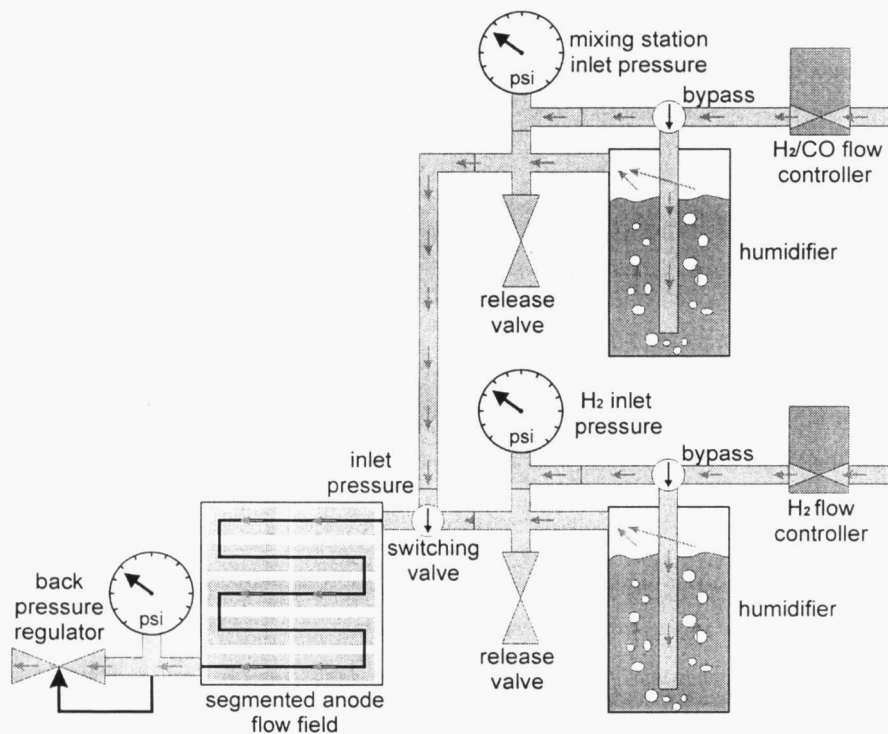


Figure 1: Schematic of CO transient measurements setup for fixed CO partial pressures.

Figure 1 shows a schematic of the transient measurement setup. The inlet consisted of two individual gas feeds, one for the pure hydrogen gas, the other for hydrogen contaminated with CO (H₂/CO). The system included computer controlled mass flow controllers, temperature controlled gas humidifiers, inlet pressure gauges, and pressure release valves.

At the beginning of each measurement, the cell was operated with humidified pure hydrogen for 1 minute. In the meantime, the H₂/CO line was first purged, and then pressurized to the hydrogen inlet pressure. Poisoning of the cell was initiated by switching the gas source from the H₂ line to the H₂/CO line. The release valves helped to avoid over-pressurization of the inlet lines and allowed to switch back to pure hydrogen in the same manner, for testing cell recovery with neat H₂. Substitution of the three-way valve with a T-intersection and a two-way valve, allowed mixing of the two source gases and thus injection of variable concentrations of CO.

The current response of the cell was measured with a Hall sensor setup built in-house, along with three data acquisition cards, and a PC. In house written LabVIEW programs controlled and recorded up to 18 data points per second. Cell voltage, total cell current, single segment voltages and single segment currents were recorded, resulting in twenty-two parallel high speed input channels.

Additionally, four-way valves allowed experiments involving counter-flow of reagents and using gas chromatography.

RESULTS & DISCUSSION

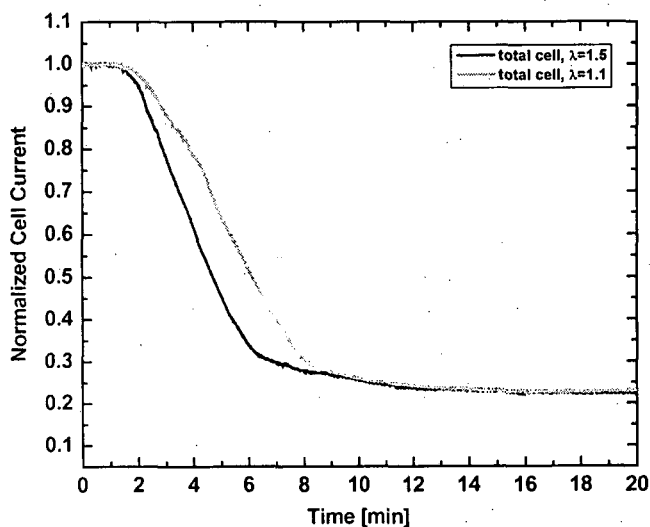


Figure 2: Transient response of a 80 cm² PEFC to an increase in CO partial pressure from 0-100 ppm CO at 1 minute operation time. Increasing gas flow rates result in faster degradation of the cell performance. Steady state currents remain constant at both flow rates.

Figure 2 shows the transient response of the normalized total cell current of the segmented cell for stoichiometric hydrogen flows of 1.1 and 1.5, hereafter referred to as 1.1 or 1.5 stoich. Cell currents and segment currents operating on pure hydrogen were measured and averaged during the first minute of operation. Subsequently, the measured currents were divided by this value, generating a normalized current value. At 1 minute operation time the anode was exposed to 100 ppm CO which causes the cell current to drop, due to CO poisoning. Steady state conditions were reached after saturation of the catalyst layer with CO. As in previous studies by Bauman et. al. [4], the saturation time of a platinum electrode was dependent on the anode inlet flux and the CO mole fraction, while the current at steady state conditions was only dependent on the CO mole fraction. Both these effects are visible in the measurement of the total cell transients shown in

Figure 2. With 1.1 stoich, the saturation time was about 10 minutes and with 1.5 stoich about 7 minutes. In both cases the cell eventually reached the same steady state current of about 23% of the initial cell currents. The higher flow rate resulted in a faster decay of cell performance, but the same steady state current.

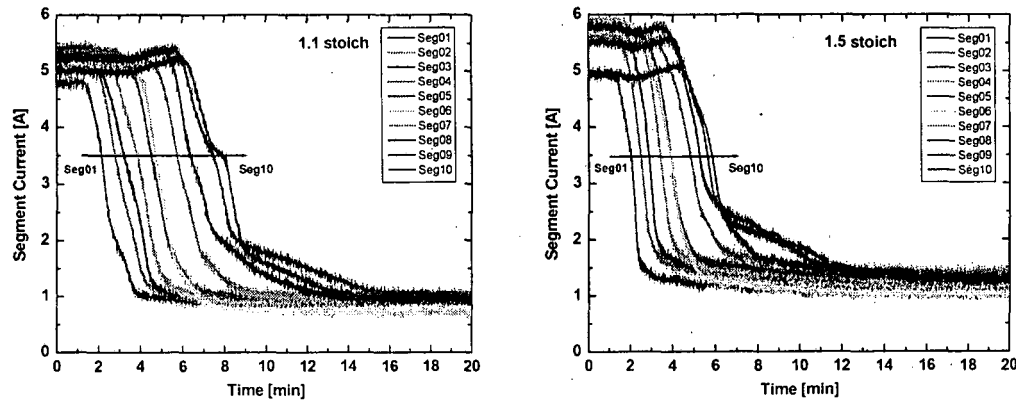


Figure 3: Single segment current distribution for stoichiometric flows of 1.1, and 1.5. The poisoning of the cell is strongly dependent on the position of the segment at a given flow.

Figure 3 shows the distribution of single segment currents of the measurements shown in Figure 2. A strong spatial dependence of the poisoning process occurs for both flow rates. In both cases the poisoning patterns are identical. Current at Seg01, the segment located closest to the inlet, dropped first. Current drops in all of the other segments followed in consecutive order downstream.

The CO injected into the fuel stream gradually poisoned the segments while moving downstream. CO saturation time of each segment depended on catalyst loading, CO mole fraction, anode flow, and position in the cell. A decrease in anode flow from 1.5 stoich to 1.1 stoich lengthened the time an individual segment is saturated with CO, due to an increased residence time at the individual segments. Consequently, the poisoning delay time between the segments increased. The time for the last segments to become saturated with CO under the given operating conditions, was 12 minutes for 1.5 stoich and 16 minutes for 1.1 stoich respectively.

At the beginning of the poisoning process, downstream segments, e.g. Seg08, Seg09, Seg10, showed a small increase in performance. This effect was stronger at lower anode flow rates. CO adsorption at the cell inlet decreased hydrogen and oxygen utilization causing the concentrations closer to the cell outlet to increase. Also, less water was transported through the MEA at the upstream segments and, due to the smaller currents, less water was produced at the cathode. Consequently, oxygen transport to the reaction sites of the cathode was facilitated. To determine which electrode had a stronger effect on the results, further investigations were carried out in that matter and are described below.

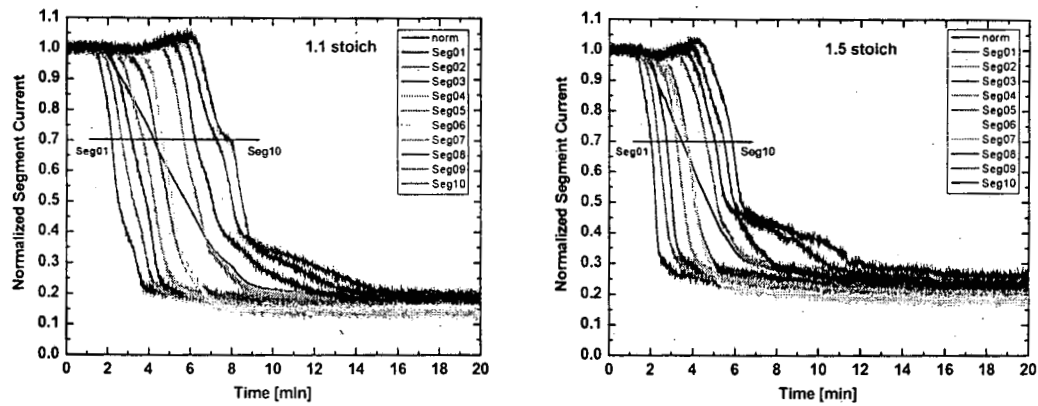


Figure 4: Current distribution of the normalized transient response for stoichiometric flows of 1.1 and 1.5.

The data of the CO transient measurement in normalized form is shown in Figure 4. The features discussed above are more apparent in this format. The poisoning time delay is clearly visible, as well as the small performance increase of the segments near the outlet.

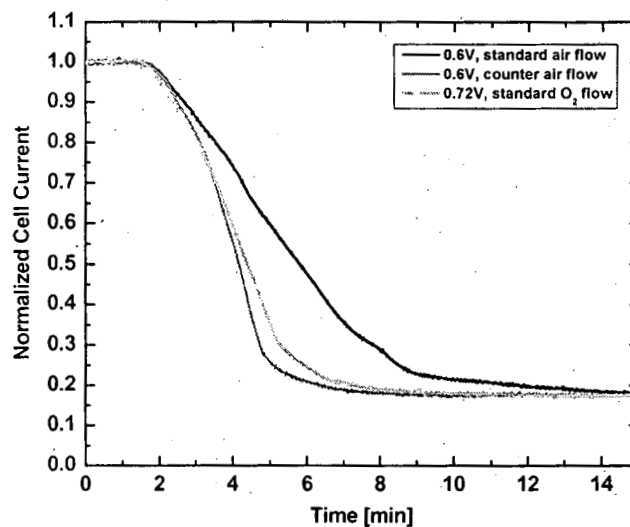


Figure 5: Transient response of PEFC operated at standard air flow, counter air flow and standard oxygen. The cell was operating at a fixed flow of 1.1 stoich before poisoning with 100 ppm CO. Cell voltage varies from 0.6 V for both air flows, to 0.72 V for oxygen operation, to keep the generation of water identical for all measurements.

Figure 5 shows transient measurements of the total cell operating with standard air flow, with counter air flow, and with standard oxygen flow. The cell was operated at the same total cell current before poisoning with 100 ppm CO. Cell operation with O₂ was carried out at 0.72 V, in order to have the same initial current as during operation with air. This adjusted the initial amount of water generated at the cathode to be identical in all of the experiments.

Both variations of the cathode flow with respect to the standard flow, e.g. changing to air counter flow or changing to oxygen flow, show the same effect on the transient measurement of the cell. The cell responds to cell poisoning substantially faster than operating at standard conditions. In both cases steady state conditions are reached at about 8 minutes operation time, compared to about 10-15 minutes of the standard cathode operation mode. This result is very surprising, since the anode flow conditions, including the CO partial pressure were identical.

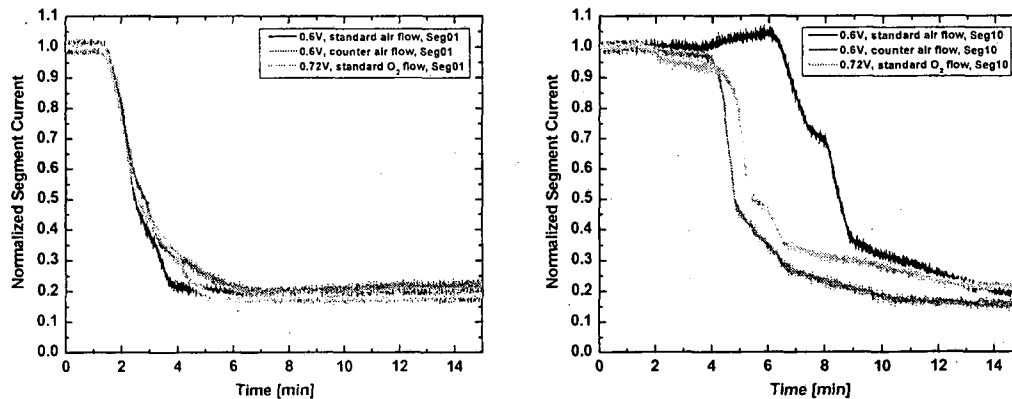


Figure 6: A comparison of the transient response from Seg01 and Seg10 operated at standard air flow, counter air flow, and standard oxygen flow. The poisoning process of Seg01 is identical, proofing identical prepoisoning conditions of the cell. Poisoning varies with oxygen access within the cell. Presence of liquid water and oxygen supply and demand of the cathode influence the poisoning process of the fuel cell.

Figure 6 shows the transient response of Seg01 and Seg10 for the three cases introduced in Figure 5. The transient response of Seg01 is fairly identical. The measurements show identical segment current drops. They reach the same steady state currents of about 20% after 6 minutes operation time. This indicates identical poisoning conditions, identical flow rates, and identical CO partial pressures.

At the cell outlet, the transient response of Seg10 varies for the three measurements. The poisoning process for the standard case is significantly delayed and slower. Instead of observing a starting decay of the cell current at 4 minutes, as in the air counter flow or oxygen case, the segment current increases instead. It starts dropping at about 6 minutes operation time, a poisoning delay of about 2 minutes. Furthermore, the rate of current decay is significantly slower.

How can the cathode flow have a possible influence on anode poisoning processes? Although the cell voltage is kept constant during the measurements, different current densities occur at the various segments due to mass transport limitations and fuel/oxidant concentrations. Consequently different anode and cathode potentials adjust throughout the cell. Since anode and cathode potential is linked together through the electrochemical system, potential changes on one electrode influence the potential situation on the other electrode. The poisoning process is dominated by the potential situation at the anode, but influence of the cathode potential is inevitable. For example increasing oxygen partial pressure will increase the cathode potential, i.e. will decrease the cathode overpotential. Hence, the anode overpotential increases together with the current density of the cell. The increase of the anode potential counteracts CO poisoning

and slows the poisoning process. Thus changing the oxygen concentration at the cathode indirectly influences the CO poisoning at the anode.

CONCLUSIONS

We have employed a segmented fuel cell system to investigate CO poisoning processes in a PEFC. Spatial dependence of CO poisoning occurs along the anode feed stream of the cell. During the CO adsorption process, spatial operation conditions within the cell are changing. These occurring processes have an influence on spatial and total cell poisoning delays. Also cathode operation conditions contribute to the poisoning response of the cell, offering new strategies for CO tolerance improvements.

Current research efforts include enhancing our understanding of the interaction between anode and cathode processes with and without CO in the hydrogen feed stream. Furthermore, modeling of the observed effects should help to develop strategies to improve CO tolerance in fuel cell systems.

ACKNOWLEDGEMENTS

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