

PASSIVELY OPERATED VAPOR-FED DIRECT METHANOL FUEL CELLS FOR PORTABLE APPLICATIONS

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Abstract: The impact of structural parameters and operating conditions has not been researched yet for vapor-fed operation of a DMFC at near-ambient conditions. Thus, a detailed parameter study that included reference cell measurements to assess anode and cathode losses separately was performed. Among other parameters like temperature or air stoichiometry, different opening ratios that controlled evaporation of methanol into the vapor chamber were examined. Water management was found to be a critical parameter for a vapor-fed DMFC. Depletion of water inside the anode catalyst layer, especially at higher current densities, decreased performance of the fuel cell substantially. Back diffusion of water from the cathode to the anode was examined. A micro-structured cathode electrode that increased water back diffusion due to a reduced mass transfer resistance was developed and investigated.

Key Words: DMFC, passive, vapor-fed, crossover, water management

1. INTRODUCTION

The power demand of portable electronics is increasing, as new features are being implemented into existing systems. This is especially true for devices in the low power range; supplements for battery technology are under investigation. Fuel cells are one potential candidate in this sector [1]. Their intrinsic property of separated fuel storage from the electrochemical conversion device offers a variety of customized applications. Gas storage, in particular hydrogen storage, is still a major drawback for low power systems. Thus liquid fuels like e.g. methanol or ethanol are an interesting alternative at the moment.

One hindrance of liquid fuels is the formation of gaseous CO₂ resulting in a two-phase system where immobile gas bubbles block fuel access to the catalyst sites and decrease the overall performance. Another drawback is a need for pumps, valves, heaters and fans that reduce durability and system efficiency.

The two-phase problem can be avoided if methanol is delivered to the anode as a vapor. Usually evaporators operated above the boiling point of methanol are used for vapor-fed direct methanol fuel cells (DMFC), reducing overall system efficiency [2-4]. The novel concept presented here will therefore focus on thermodynamically driven evaporation at ambient temperatures. Thus, membranes are used as phase

barriers between liquid and vapor methanol as shown in Fig. 1. Another benefit of the presented layout is the possibility to use pure methanol in the storage tank. Water for the methanol oxidation reaction at the anode diffuses back from the cathode where water is produced.

Experimentally, several structural parameters were studied along with varying operating conditions. Water supply to the anode electrode turned out to be one key issue.

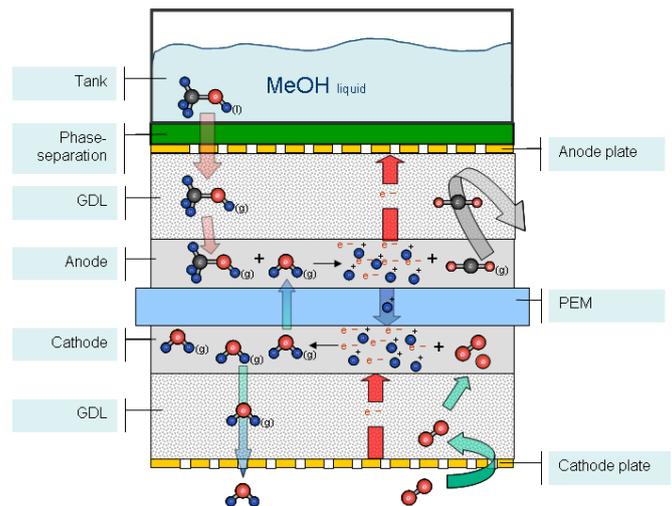


Fig. 1: Basic concept of a thermodynamically driven DMFC. The phase separation between liquid and gaseous methanol is guaranteed by a phase separation membrane.

2. EXPERIMENTAL

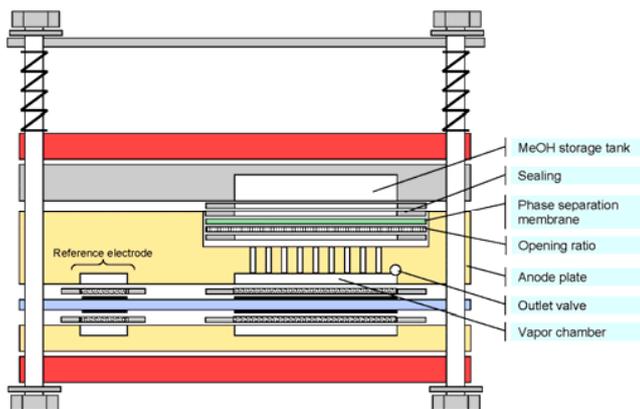


Fig. 2: Test cell used for experiments with the vapor-fed DMFC. Liquid MeOH is stored in the tank and is evaporated into the vapor chamber using the phase separation membrane. The vapor chamber has one outlet to release CO_2 into the atmosphere.

2.1 Fuel Cell assembly

The design of the evaporator and the anode that were used throughout vapor-phase operation experiments is shown in Fig.2. Liquid MeOH was stored in a temperature-controlled storage tank and a needle valve was used to equalize the pressure between the tank and the surroundings. A plate of FR-4, a material used for making printed circuit boards, was used to change opening ratios. The opening ratio is defined as the open area versus the solid area of the plate. The plate and the phase separation membrane were attached between VITON sealing rings. The gold plated, stainless steel anode plate was used to give mechanical strength as well as to collect current. Vaporized MeOH diffused into the anodic vapor chamber and was oxidized at the anode catalyst layer (ACL). Atmospheric pressure was maintained through an outlet, where in particular CO_2 could leave the vapor chamber.

Cathode plates were constructed from SIGRACET[®] BMA5, a graphite compound material with both the working electrode flowfield and the isolated reference electrode flowfield milled into the material. Therefore, a serpentine flowfield with 1 mm wide channels was chosen. Connectors allowing direct measurement of the voltage without measuring at the current collectors were attached to the graphite material.

A thermo--couple was placed directly at the center of the working electrode on the back of each cathode. The working electrode had an area of 10 cm^2 . The reference electrode, which was offset 30 mm to one side of the working electrode, had an area of 1 cm^2 and a 1 mm serpentine flowfield. The large distance between the working electrode and the reference electrode was chosen to guarantee that no MeOH could diffuse in--plane between the working and the reference electrode. If MeOH diffuses from the working anode electrode to the reference electrode the reference potential of the normal hydrogen electrode (NHE) could change during operation, leading to additional errors in the measurement [5].

2.2 Measurement and Operation

In addition to an initial treatment of new MEAs, the fuel cell was preconditioned before each experiment. Therefore, the cell voltage was cycled four times from 0.6 V down to 0.05 V and up to 0.6 V again in 50 mV steps, each step lasting 10 s. This procedure was repeated if a strong hysteresis was detected between the third and fourth cycle.

Polarization measurements started at the OCV. The voltage was decreased in 25 mV-steps to short circuit or voltages slightly above short circuit with each step lasting 20 s. This measurement was repeated in order to study if hysteresis effects were present. The actual ohmic cell resistance was obtained using a Milliohmmeter which recorded the real part of the impedance at 1 kHz. It summarizes all ohmic losses R_{ohm} like flowfield resistances, contact resistances, membrane resistances etc. Therefore the anode losses η_{an} and cathode losses η_{ca} could be calculated using the potential between the attached NHE and the anode/cathode electrode.

3. RESULTS AND DISCUSSION

The impact of operating conditions and structural parameters on the performance as well as on polarization and concentration losses of a VDMFC was studied. The connected NHE was used to assess losses individually. A PDMS membrane at an opening ratio of 6.8 % was used to evaporate a 50 wt% solution of MeOH in deionized water into the vapor chamber. Dry air was supplied to the cathode flow channel. A minimum air flow rate of 40 sccm was set before

switching to a stoichiometry of 2. Hydrogen, which was humidified inside a washing bottle at ambient conditions, was fed to one electrode of the NHE. The other electrode of the NHE was flooded with deionized water to guarantee a stable reference potential. The temperature of the cell was kept constant at 50°C. A 31AA GDL was used on both the anode and the cathode side. For the CCM, Nafion 1135 being screenprinted with HiSPEC 6000 (3 mg/cm² Pt/Ru) at the anode and HiSPEC 11100 (1 mg/cm² Pt) at the cathode was used. The clamping force on the cell was set to 3450 N, which results in a pressure of 345 kPa on the GDL..

3.1 Methanol Concentration

Experiments with different MeOH solutions in deionized water at 25, 50 and 75 wt% and pure MeOH were conducted to study the impact of the MeOH concentration on a VDMFC. All other

operational and structural parameters were kept constant.

The IV characteristics and the electrode losses are depicted in Fig. 3. It should be mentioned that these results are valid only for an opening ratio of the evaporator of 6.8 % and will change when the opening ratio is varied. Optimal performance for the given conditions was achieved by having a 50 wt% solution of MeOH; it decreased for higher and lower concentrations. Two opposing effects could be studied on the anode and the cathode. Crossover increased with MeOH concentration and consequently cathode losses increased as shown. The great difference between pure MeOH and the three solutions indicated a much higher crossover, probably combined with partial flooding of the cathode.

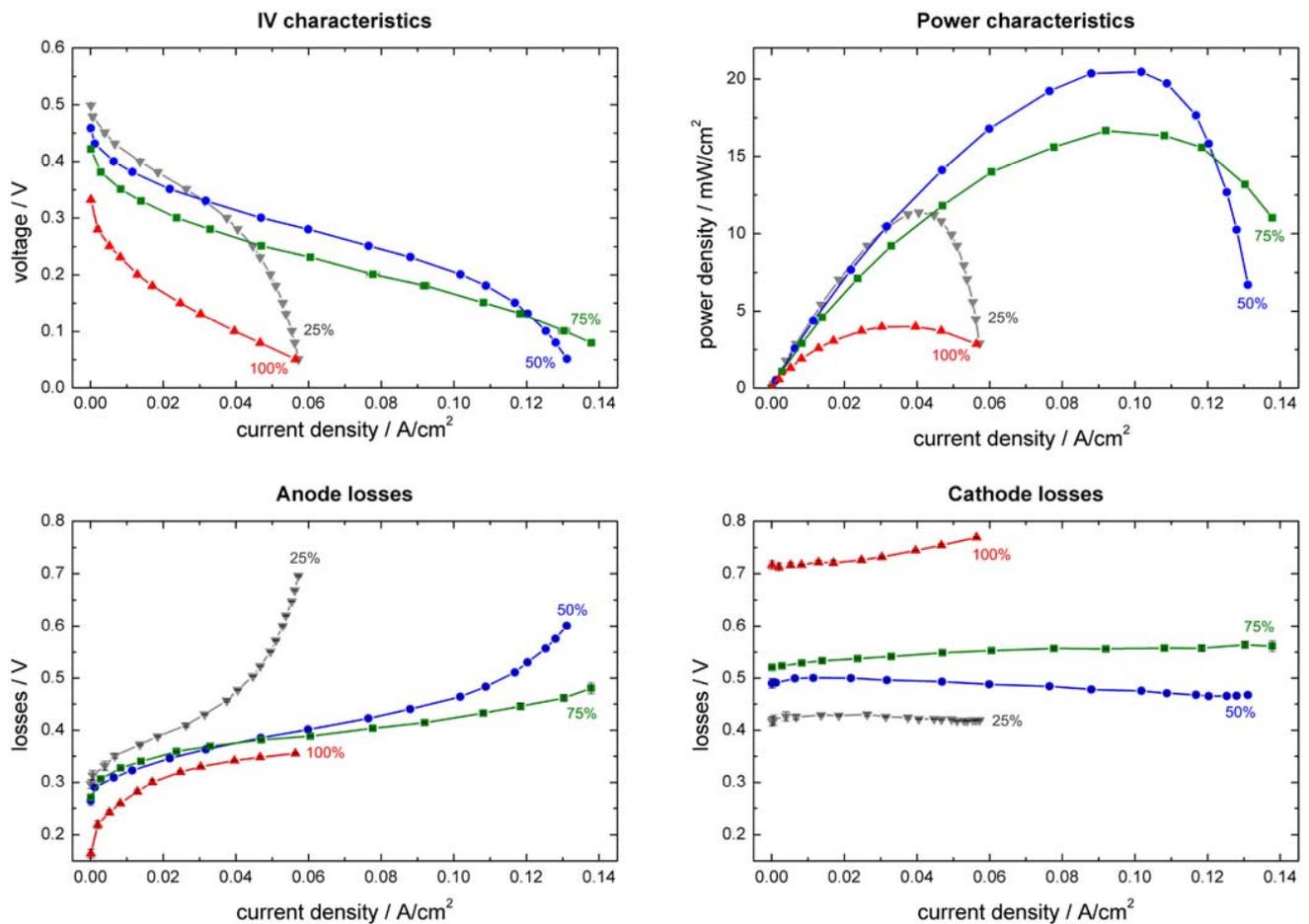


Fig. 3: Electric properties of a VDMFC for different MeOH concentrations. Anode and cathode polarization losses were calculated using a connected reference NHE. The temperature was 50°C, the cathode air stream 40 sccm/λ 2 and the evaporator opening ratio 6.8 %.

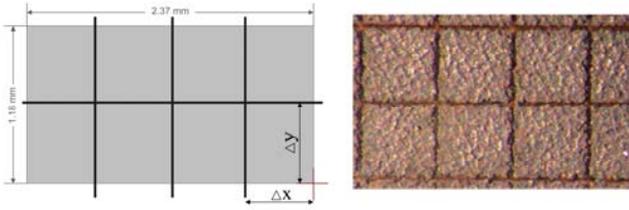


Fig. 4: Laser segmentation of the cathode catalyst layer to increase water back diffusion from cathode to anode. Schematic drawing of the path of the laser beam and magnification of an ablated catalyst layer.

Anode losses decreased as expected with increasing MeOH concentration. Besides having higher partial pressures of MeOH at the anode electrode, resulting in higher anodic current densities, the water concentration at the anode also greatly influenced the electrode losses. According to the Antoine equation with parameters for MeOH and water, the amount of evaporated water is only a fraction of the evaporated MeOH, depending on the MeOH concentration. Because one mole of water is needed to oxidize one mole of MeOH, the lack of water is slowing down the MOR.

3.1 Water Management

Micro-segmentation of the cathode electrode by a laser ablation process, as shown in Fig. 4, drastically increased the water back diffusion. Anode polarization losses of a vapor-fed DMFC with and without a segmented cathode catalyst

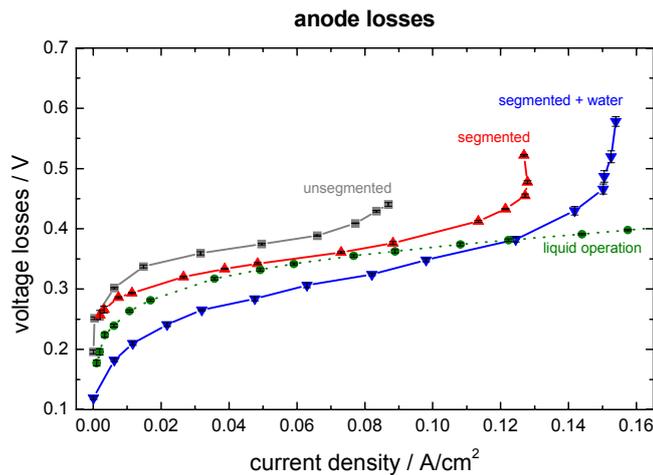


Fig. 5: Polarization losses at the anode electrode of a vapor-fed DMFC with and without a segmented cathode catalyst layer versus standard liquid operation. Additional 0.5 ml of water was injected into the cathode air stream for "segmented + water"..

layer can be seen in Fig. 5 and are compared to anode polarization losses of a liquid-fed DMFC.

Performance between the unsegmented and the segmented cathode increased significantly and the limiting current density nearly doubled. It can be seen that anode losses of the unsegmented and the segmented cathode differ by 50mV, a fact caused by higher water concentrations within the anode. This conclusion was verified when additional 0.5 ml of water was injected into the segmented cathode and anode losses dropped further. Vapor operation under these conditions exhibited superior performance compared to conventional liquid-fed DMFCs.

4. CONCLUSION

Complete passive vapor operation of a DMFC for portable applications without any need for active components like pumps, fans etc. is demonstrated. Water concentration at the anode electrode was found to be a major factor that influenced performance of the vapor-fed direct methanol fuel cell significantly. Back diffusion of cathodic product water was enhanced by introducing hydrophobic layers at the cathode side and by partial ablation of the cathode catalyst layer. This new technological approach will increase reliability as well as overall efficiency and decrease the complexity of a DMFC.

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