Short communication

Bifunctional activation of a direct methanol fuel cell

A.A. Kulikovsky [a,*], H. Schmitz [a], K. Wippermann [a], J. Mergel [a],
B. Fricke [b], T. Sanders [b], D.U. Sauer [b]

[a] *Institute of Energy Research, Fuel Cells (IEF-3), Research Center "Jülich", D-52425 Jülich, Germany*
[b] *Institute for Power Electronics and Electrical Drives, RWTH Aachen University, Jaegerstr. 17-19, 52066 Aachen, Germany*

Abstract

We report a novel method for performance recovery of direct methanol fuel cells. Lowering of air flow rate below a critical value turns the cell into bifunctional regime, when the oxygen-rich part of the cell generates current while the rest part works in electrolysis mode (electrolytic domain). Upon restoring the normal (super-critical) air flow rate, the galvanic performance of the electrolytic domain increases. This recovery effect is presumably attributed to Pt surface cleaning on the cathode with the simultaneous increase in catalyst utilization on the anode.
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1. Introduction

At low air flow rates direct methanol fuel cells (DMFCs) turn into bifunctional (BF) regime [1–3]. In this regime the cell active area splits up into two domains. The domain close to the inlet of the oxygen channel generates current in a normal DMFC mode (galvanic domain, GD), while the rest part of the cell consumes current to produce hydrogen (electrolytic domain, ED).

BF regime arises due to methanol crossover. Close to the outlet of the oxygen channel no oxygen is left for burning methanol permeated through the membrane. In this region methanol is electrochemically oxidized on the cathode side to protons and electrons. Protons move to the anode, where they recombine with electrons to yield hydrogen. The electrolytic domain thus operates as an electrolytic cell described by Ren et al. [4]. Direct observation of hydrogen on the anode side of DMFC in this regime was performed in ref. [1]. Sketch of the processes in the cell is depicted in Fig. 1.

To study the BF regime in detail we have designed a cell with single straight channels and segmented electrodes [2] (see also below). Measurements of local current in such a cell unexpectedly showed that short (1–30 s) operation in electrolytic mode improves galvanic performance of the segment.

It is thus beneficial to periodically switch the cell to electrolytic mode. Thanks to BF regime this can be done without an external power supply: one simply has to lower air flow rate below the critical value. Here we report the details of such *bifunctional activation*.

2. Experimental

For the MEA we prepared electrode stripes with a geometrical area of $3 \, cm^2$ ($0.3 \, cm \times 10 \, cm$). As anode and cathode catalysts we used PtRu(60%)/C (Johnson Matthey 'HiSpec10000') and Pt(60%)/C (Johnson Matthey 'HiSpec9000'), respectively, with PtRu and Pt loadings of $2 \, mg \, cm^{-2}$. The electrodes were hot-pressed onto a Nafion 117 membrane. Further details concerning the preparation conditions can be found in ref. [2].

The segmented cell consisted of two single channel flow fields, two endplates made of steel and printed circuit board on the anode side. The latter was inserted between the flow field and the endplate (the sketch of the flow field is shown in Fig. 2). Twenty graphite segments with the dimension $0.5 \, cm \times 1.5 \, cm$ were embedded into a polysulfone flow field. Contact area between each segment and electrode is about $0.5 \, cm \times 0.3 \, cm$.

The measuring system was designed to measure individual currents from each anode–cathode pair of segments while
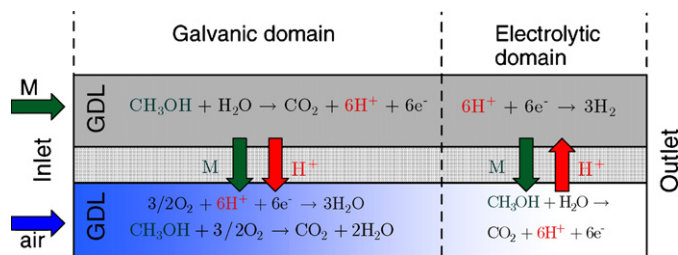
Fig. 1. Schematic of the processes in DMFC operating in the bifunctional regime.
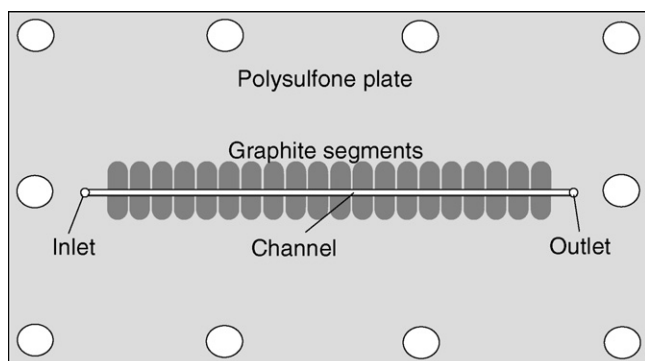

Fig. 2. Sketch of the segmented flow field. Twenty graphite segments are positioned along the 10-cm long single channel; channel cross-section is $1\,mm \times 1\,mm$. The flow field on the other side is a copy of the one shown. A MEA stripe of 3 mm width is clamped between the two flow fields.

Fig. 3. Local current density along the channel. (a) Air inlet is connected to segment 1, "remote" segments operate in electrolysis mode (negative local current). (b) Air inlet is then switched to segment 20; better galvanic performance of the segments operated in electrolysis mode is clearly seen. Number at the curve indicates air flow rate (ml min^{-1}).

keeping potentials of all anodic segments constant. On the cathode plate equipotentiality of segments was provided by highly conductive endplate.

All measurements were carried out at a temperature of $80\,^\circ$C under ambient pressure. The anode was always fed by 1 M methanol solution with the flow rate of 0.1 or 0.31 ml min^{-1}. The respective stoichiometry of methanol λ^a varies in the range 6–300, depending on the current. The air flow rate at the cathode was varied; the respective value is indicated in the figures below. For further experimental details please see ref. [2].

3. Results and discussion

Fig. 3a shows the distribution of local current density along the cell when air inlet is at the segment 1. Numbers indicate air flow rate f_{air} (ml min^{-1}); all three curves correspond to subcritical flow rates, when the cell operates in a BF regime.[1] With the growth of f_{air} the length of the GD increases while the length of the ED decreases (Fig. 3a); at the critical f_{air} the length of the ED is zero.

In this experiment f_{air} was increased in steps from 1 to 2 and then to 3 ml min^{-1}. Each curve corresponds to a steady-state regime of cell operation, i.e. the curves were registered when the transient effects vanished. Typically, the steady-state distribution of local current establishes in 2–3 min of cell operation. Thus,

in the course of measurements every segment in the range 9–20 has several minutes operated in electrolytic mode.

Then the cell was stopped and air supply was connected to segment 20, i.e. air inlet and outlet were interchanged (Fig. 3a). The curves in Fig. 3b correspond to the same three values of air flow rate of 1, 2 and 3 ml min^{-1}. Now peak current in all cases exceeds 10 mA; for $f_{air} = 1$ ml min^{-1} it reaches 20 mA (segment 20; Fig. 3b). This suggests that the segments operated in electrolytic mode exhibit then better galvanic performance.

To verify this result we run the cell in normal DMFC mode providing super-critical air flow at a current in the external load of 150 mA . In this (base-case) regime all segments operate in galvanic mode. Every 30–40 min we performed an "activation": air flow was reduced to a sub-critical value of 3 ml min^{-1} and the current in the load was decreased to 10 mA. In this regime nearly half of the segments turn into electrolysis mode. The cell was kept in this activation regime for 30 s and then returned to the base-case state.

Cell voltage versus time is shown in Fig. 4. In this experiment activation improves the galvanic performance of the DMFC by

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[1] The critical flow rate is approximately 7 ml min^{-1}; by the definition it corresponds to zero current in the last segment. It is worth mentioning that this rate does not depend on cell current [2,5].
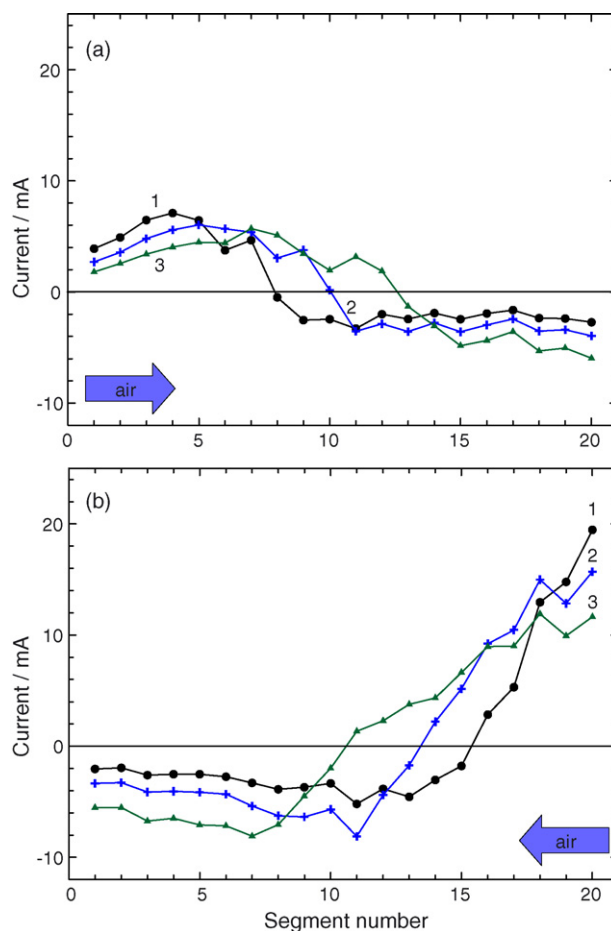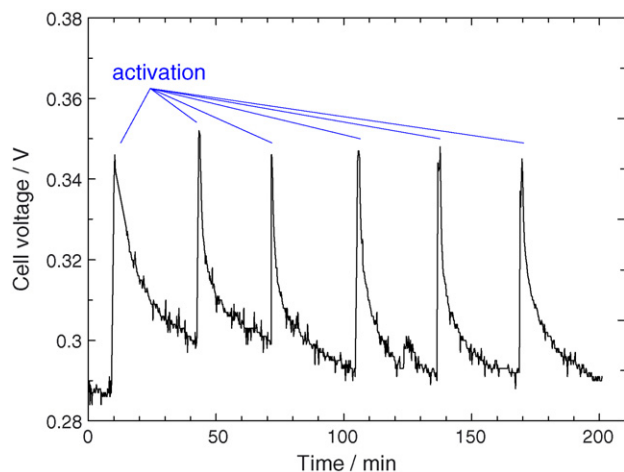
Fig. 4. The effect of periodical bifunctional activation on cell voltage. The cell is run in normal DMFC mode at 150 mA in the load and super-critical air flow rate of 11 ml min^{-1} ($\lambda^c \simeq 5$). Each 30–40 min the cell is activated: for 30 s air flow is decreased down to a sub-critical value of 3 ml min^{-1} and current in the load is decreased to 10 mA. Note that no external power supply is used.

3–7%.[2] Note that the actual value of performance improvement varies from cycle to cycle. This may be caused by the variation in a number of segments which turn into electrolysis mode. As discussed above, in the BF regime multiple states of the cell correspond to the same current in the load; thus fixing I_{load} does not guarantee the reproducibility of the ED length. Note that only half of the segments were periodically activated; we thus may expect that activation of all segments would give even better results. This, however, would require a more sophisticated procedure, including reverse of air flow direction as in Fig. 3.

Similar effect of DMFC performance improvement at periodical full break of air supply was reported in ref. [6]. Following [6], full break of oxygen supply decreases the cathode potential to the value required for "cleaning" of Pt surface from oxides, which poison the cathode catalyst during normal DMFC operation.

Above we have shown that *lowering* of air flow rate below a critical value turns the cell into the BF regime; operation in this regime partially recovers cell performance. It is, therefore, important to understand the difference between our method of cell recovery and the method proposed in ref. [6].

The experiments [6] were performed with a 100 cm^2 DMFC.[3] The cell was not segmented and thus no local measurements

of current distribution were performed. During the air-breaking interval current in the cell was kept constant with the aid of external power supply and special electronic equipment. No hydrogen evolution on the anode side was reported. This suggests that at the time of air break an electrolytic domain was not formed in the cell.

In our experiments, however, lowering of air flow creates steady-state electrolytic domain in the cell. This reverses the sign of the cathode overpotential in the ED and induces hydrogen evolution on the anode side there. In the galvanic domain the cathode and the anode half-cell potentials remain unchanged.

Thanks to the detailed study [6] we may assume that negative polarization induces Pt cleaning on the cathode side. Oxide film growth on Pt surface is exponential in time and it reaches saturation in about 50 min (Fig. 7 of ref. [6]). This correlates with the exponential-like shape of voltage relaxation after activation in Fig. 4. Moreover, the characteristic time of this relaxation (30–50 min) correlates with the time of saturation of oxide film growth [6].

Furthermore, hydrogen evolution on the anode side also contributes to cell recovery [7]. Following [7], running the DMFC anode in hydrogen evolution mode increases the number of Pt sites connected to feed transport system, i.e. the number of electrochemically active sites on the anode. Note that in ref. [7] the DMFC anode was turned into hydrogen evolution mode using the external power supply.

Another possible mechanism of anode recovery is improvement of anode transport properties during hydrogen evolution. In our laboratory we got evidences that intense formation of CO_2 bubbles at high current densities improves performance of DMFC anode. In other words, gas "bubbling" improves transport properties of the anode porous layers.

We, therefore, may assume that our method of DMFC activation simultaneously utilizes recovery mechanisms of the cathode [6] and the anode [7]. The advantage of this method is that it does not require external power source: the galvanic domain serves as a power supply for the electrolytic domain [2].

To prove that the effect of activation is due to formation of electrolytic domain we have performed the following measurements. The cell was run in normal DMFC mode and periodically switched to electrolysis mode using the external power supply. More specifically, for 30 s air flow was replaced with nitrogen flow and simultaneously current in the load was reversed to $I_{load} = -100$ mA. This procedure turns the whole cell to electrolysis mode.

The result is shown in Fig. 5; the effect of activation is clearly seen. Moreover, the characteristic time of cell voltage relaxation in each cycle is roughly the same as in Fig. 4. This suggests that the mechanisms of activation in both these methods are the same.[4]

So far we did not see any signs of electrode or membrane degradation due to the activation. However, more experi-

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[2] This estimate stems from the following arguments. The energy delivered in the load without activation is $E = V I_{load} \Delta t$, where V is the "undisturbed" cell voltage and Δt is the time interval between two subsequent activations. Approximating voltage decay after activation roughly with the linear function and neglecting the time of activation as compared to Δt, we get total energy delivered after the activation: $E_{act} = E + (1/2)(V_{peak} - V) I_{load} \Delta t$, where V_{peak} is the peak voltage. The ratio E_{act}/E is

$$\frac{E_{act}}{E} = 1 + \frac{1}{2}\left(\frac{V_{peak}}{V} - 1\right)$$

For the estimate we take two pairs of V_{peak}, V: (0.34, 0.3) and (0.31, 0.29) (Fig. 4).

[3] Unfortunately, no details of the cell and flow field geometry were reported.

[4] Note that the gain in cell power in Fig. 5 is higher, than in Fig. 4, since cell voltage now relaxes to the higher level. At present we have no explanation of this effect.
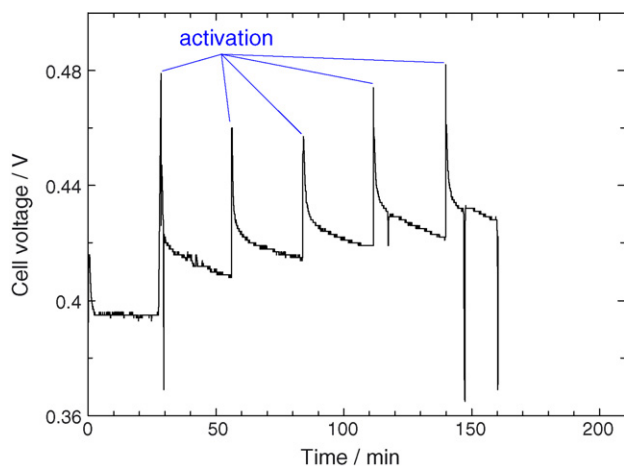
Fig. 5. The effect of periodical activation with external power supply on cell voltage. The cell is run in normal DMFC mode at 468 mA in the load; air flow rate is 100 ml min^{-1} ($\lambda^c \simeq 15$). Each $\simeq$30 min the cell is activated: for 30 s air is replaced with nitrogen at the same flow rate and simultaneously current in the load is reversed to $I_{load} = -100$ mA using the external power supply.

ments are needed to clarify the long-term effect of the activation.

4. Conclusions

Measurements of local current distribution in a cell with straight channels and segmented electrodes reveal the following

effect. The decrease in air flow rate below a critical value turns part of the DMFC into electrolysis mode. Restoring then normal (super-critical) air flow rate returns the electrolytic domain to galvanic mode with increased galvanic performance. This *bifunctional activation* is presumably attributed to cleaning of the Pt surface on the cathode side from oxides and to increase in the number of electrochemically active sites on the anode side.

Periodical lowering of air flow rate below the critical value thus recovers cell performance. This method of performance recovery does not require an external power source; at the time of activation galvanic domain plays the role of the power supply.

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