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Short communication

Bifunctional activation of a direct methanol fuel cell

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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.

Keywords: DMFC; Crossover; Electrolysis; Performance recovery

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 × 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 × 1.5 cm were embedded into a polysulfone flow field. Contact area between each segment and electrode is about 0.5 cm × 0.3 cm.

The measuring system was designed to measure individual currents from each anode–cathode pair of segments while

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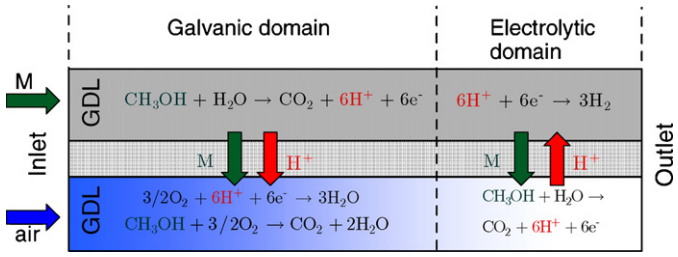

Fig. 1. Schematic of the processes in DMFC operating in the bifunctional regime.

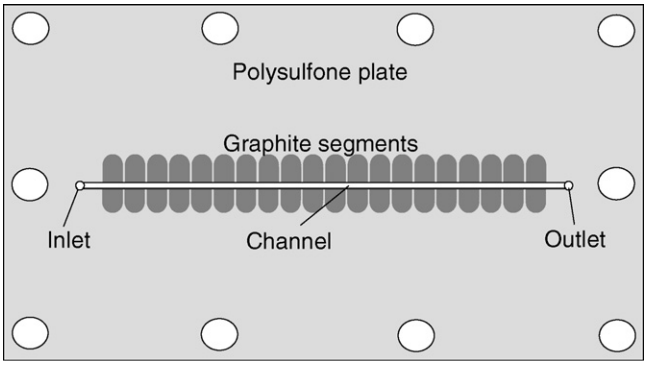

Fig. 2. Sketch of the segmented flow field. Twenty graphite segments are positioned along the 10-cm long single channel; channel cross-section is 1 mm × 1 mm. The flow field on the other side is a copy of the one shown. A MEA stripe of 3 mm width is clamped between the two flow fields.

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 °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 sub-critical 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,

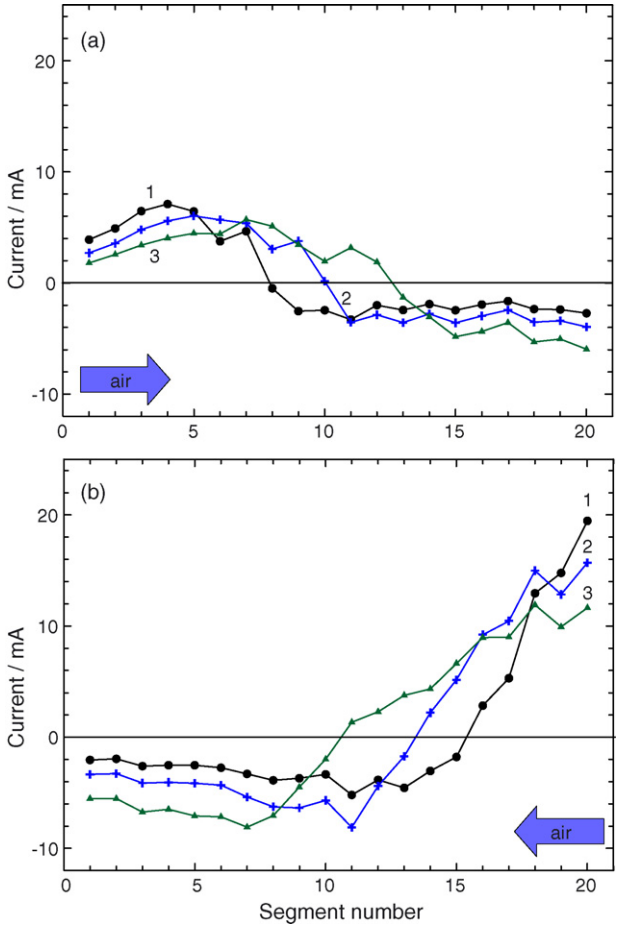

Fig. 3. Local current density along the channel. (a) Air inlet is connected to segment 1, "remote" segments operate in electrolysis mode (negative local current). (b) Air inlet is then switched to segment 20; better galvanic performance of the segments operated in electrolysis mode is clearly seen. Number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

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

[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].