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A Direct DME High Temperature PEM Fuel Cell

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Dimethyl ether (DME) has been identified as an alternative to methanol for use in direct fuel cells. It combines the advantages of hydrogen in terms of pumpless fuel delivery and high energy density like methanol, but without the toxicity of the latter. The performance of a direct dimethyl ether fuel cell suffers greatly from the very low DME-water miscibility. To cope with the problem polybenzimidazole (PBI) based membrane electrode assemblies (MEAs) have been made and tested in a vapor fed system. PtRu on carbon has been used as anode catalyst and air at ambient pressure was used as oxidant. A power density of 79 mW/cm² has been achieved at 200 °C.

Introduction

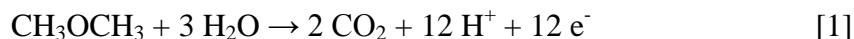
Direct oxidation polymer electrolyte membrane (PEM) based fuel cell has received a lot of attention as power source for small and medium sized applications, ranging from cell phones to small vehicles. Compared to hydrogen, organic liquid fuels have high energy density while having similar electromotive force for complete oxidation. Direct methanol fuel cells (DMFC) have been studied intensively over the last decade. Dimethyl ether (DME, CH₃OCH₃) has been identified as a suitable alternative for direct oxidation PEM fuel cells.

Dimethyl ether is the simplest ether with physical properties close to those of liquefied petroleum gasses (LPGs), i.e. butane. It is a clear gas at ambient temperature and pressure with a distinct sweet ether-like smell and thus does not require an odorant. DME can easily be liquefied by cooling down below -25 °C or compressing to 6 bar absolute. This is highly beneficial in terms of storage and transportation, as the already existing LPG infrastructure can be used.

As of mid 1990's DME has been promoted as a diesel substitute. It has a high cetane number, 55-60, compared to 55 for diesel. Lacking carbon-carbon bonds combustion of DME produces no soot, which is one of the major pollutants from diesel combustion engines. Using dimethyl ether instead of diesel also decreases NO_x, carbon monoxide and hydrocarbons emission. The only major challenge using DME as diesel substitute is its viscosity and lack of lubricating ability, which results in leakages and faster wearing of pumps and fuel injectors (1). Around the world there are a number of pilot projects where DME is used as diesel substitute, i.e. in Sweden, where Volvo has a fleet of trucks

running on DME, or in China, where DME is used to propel a fleet of busses. Moreover, DME is widely used as a cooking gas in China.

In fuel cells DME has several advantages over its main competitor methanol, including low toxicity and small fuel cross-over effect (2). In a conventional Nafion based fuel cells DME shows poor performance compared to methanol. This is due to lower electrochemical activity of DME at low temperatures, but also the low solubility of DME in water (3). From the overall anode reaction [1] for a direct dimethyl ether fuel cell it can be seen that for complete oxidation of DME three molecules of water are required, which corresponds to a water mixture with 46 wt% DME.



DME solubility in water is only 7.6 wt% at 20 °C or 1.65 M (3, 4) and even lower at 80 °C (3), which is the working temperature of the conventional Nafion based fuel cell. This results in phase separation, effectively reducing the performance of the cell. The solution to the issue could be to use a vapor fed fuel cell. The conventional Nafion based cells rely on liquid water for proton conductivity and cannot be used for this purpose. A phosphoric acid doped polybenzimidazole (PBI) based fuel cell (5) has operating temperature range of 120-200 °C and is thus suitable for vapor fed operation (3).

Experimental

The membrane electrode assemblies (MEAs) were prepared according to the following procedure. The anodes were made utilising commercial platinum-ruthenium on carbon (40 wt% Pt, 20 wt% Ru, Johnson Matthey). The catalyst ink consisting of catalyst powder, *ortho*-phosphoric acid (85 wt%, Sigma-Aldrich) and PBI (Celanese) dissolved in formic acid (98 wt%, Sigma -Aldrich) was mixed and placed in an ultrasonic bath overnight to obtain a homogeneous dispersion. The anodes were sprayed using an ultrasonic xyz spraying setup from SONO-TEC on 5x5 cm² pieces of non-woven carbon cloth (Freudenberg). The final catalyst metal loadings were calculated from the difference in electrode mass before and after spraying and drying.

The MEAs were made by hot pressing. An 8x8 cm² piece of 40 µm PBI membrane doped with phosphoric acid (Danish Power Systems) was sandwiched between the obtained anode and a cathode (Danish Power Systems) with 0.9 mg/cm² Pt loading utilizing a platinum on carbon catalyst. The area of the membrane not covered by electrode was covered with protective polysulfone film. The assembly was then hot pressed at 1 ton for 3 minutes at 200 °C.

The MEAs were placed between two graphite flow plates with PTFE gaskets for gas sealing. Gilded copper current collector plates were placed between the flow plates and the aluminum end plates. The fuel cell operation was performed in an in-house build test rig. See Figure 1 for a schematic flow diagram. The evaporator unit consisted of an electrically heated steel tube filled with steel balls to facilitate better heat distribution. Hydrogen and DME gas and air/oxygen were supplied by means of mass flow controllers while water and methanol-water mixture were supplied by a calibrated peristaltic pump. The tubing connecting the evaporator and the fuel cell was insulated and electrically

heated to prevent condensation of water. For DME experiments the fuel gas and water were supplied into the evaporator via separate inlets. For the experiments with methanol a stoichiometric methanol-water solution instead of pure water was fed through the water inlet.

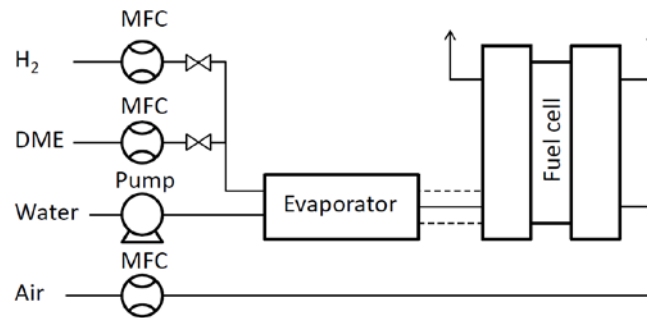


Figure 1: Schematic drawing of direct DME fuel cell setup. MFC – mass flow controller.

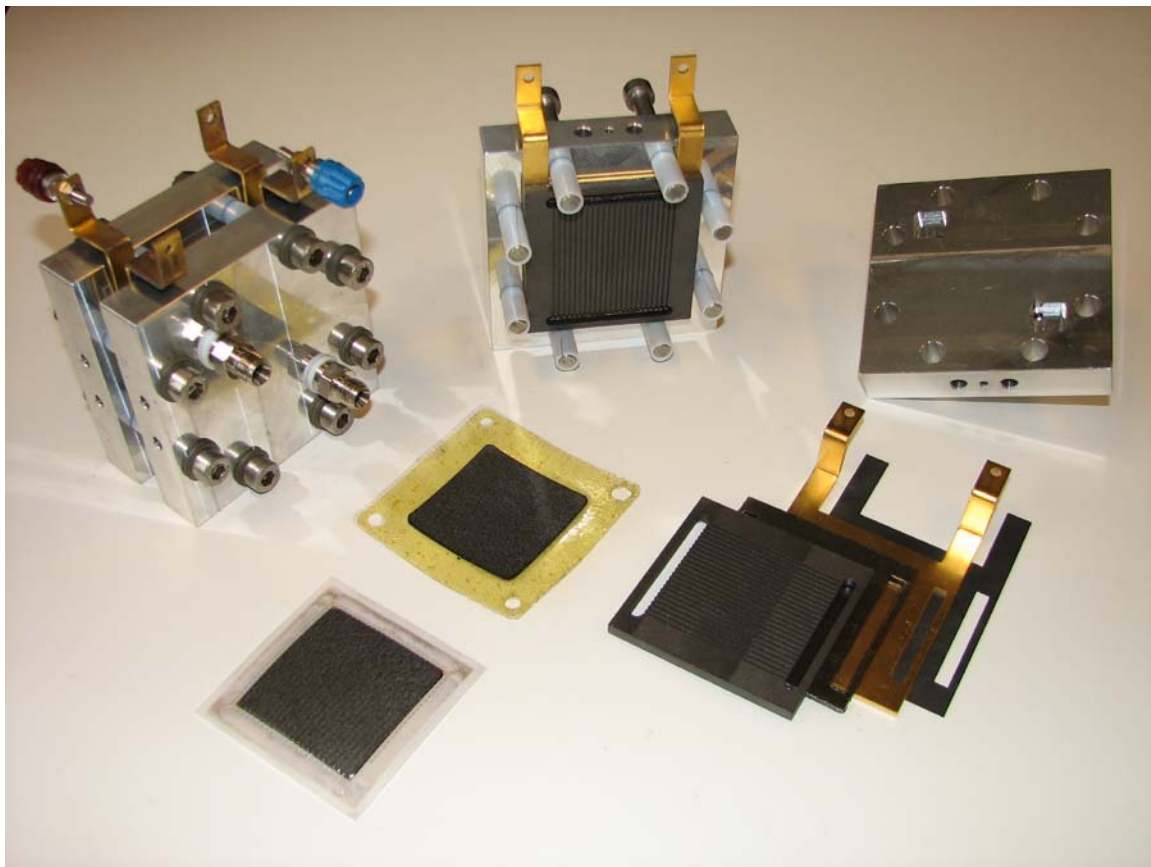


Figure 2: Single cell, MEAs and cell housing. Front row from left to right - used MEA with Teflon gasket, fresh MEA, graphite flow plate, Papyex sealing, gilded current collector and Viton gasket. Upper row from right to left – aluminum end plate, half-assembled single cell and complete cell.

The cell was heated to 150 °C for 4 hours prior to the measurements with 195 mL/min H₂ gas at 200 mA/cm² on the anode side. The cathode was fed with 905 mL/min air at ambient pressure without preheating of the incoming gas. The cell was then heated

to 200 °C and fuel switched to DME gas. The anode was vapor fed from the evaporator supplied with 32 mL/min DME gas and 0.07 mL/min liquid water (3:1 molar ratio) at ambient pressure. For the methanol experiments the methanol-water mixture (1:1 molar ratio) was supplied at 0.23 mL/min flow rate. The i-V curves were obtained after one hour of stabilization time at 200 mA/cm² using a ZVL eLoad (American Reliance) controlled by a computer.

Results and discussion

A series of MEAs were made and tested at ambient pressure with air as oxidant. The performance of a single cell utilizing an anode with 4.2 mg_{Pt-Ru}/cm² metal loading, 1.0 mg_{Pt}/cm² cathode and a 40 μm thick (before doping with H₃PO₄) PBI membrane at 200 °C is shown in Figure 3. The obtained peak performance was 79 mW/cm², which is almost twice that reported for direct DME in a polymer fuel cell at ambient pressure (6-8). It is also higher than the 67 mW/cm² recently reported by our group (3). The open circuit voltage of 0.75 V suggests some fuel crossover. It is common practice to use diluted methanol as fuel in order to reduce the fuel crossover loss in direct methanol fuel cells. In this study, however, the DME-water ratio was stoichiometric, i.e. a molar ratio of 1:3 was used. The recorded open circuit voltage depression was less than reported for DMFC with diluted methanol nonetheless. This observation supports the assumption that permeability of DME molecules through PBI membrane is smaller than that of methanol. For a comparison, good hydrogen fuelled PBI based cells have open circuit voltages often around 0.9 V.

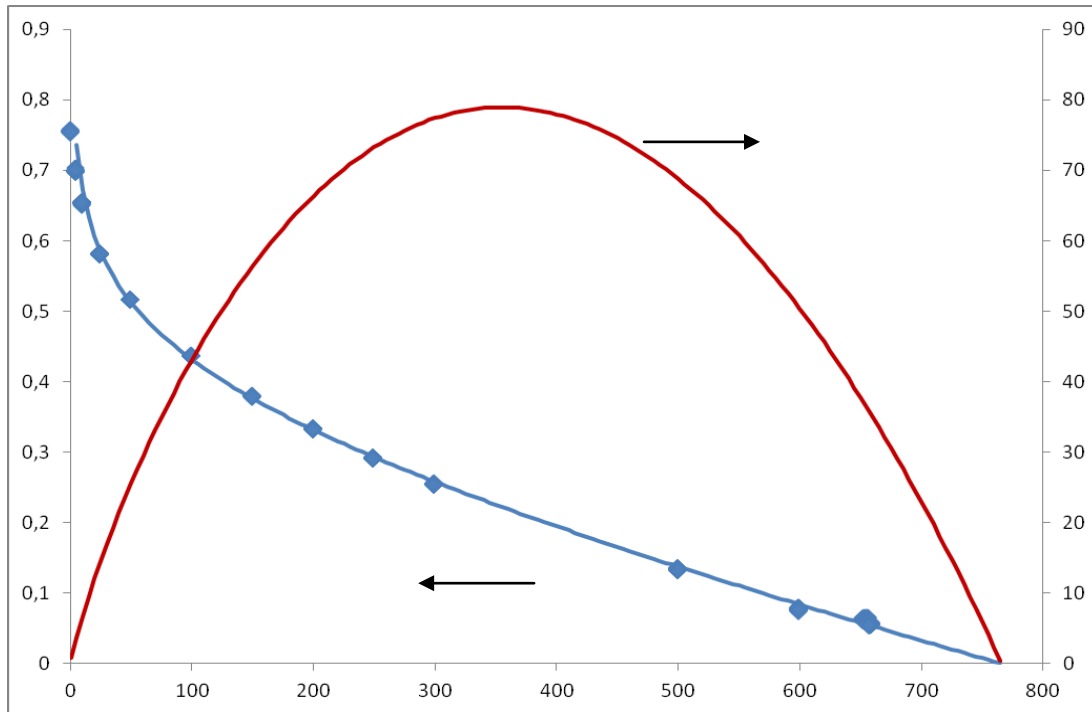


Figure 3: Performance curve of vapor fed direct DME fuel cell at 200 °C, ambient pressure and air as oxidant. Markers indicate voltage measurements. The solid lines represent the models for i-V and power density curves. Anode – 4.2 mg_{PtRu}/cm², cathode – 1.0 mg_{Pt}/cm², membrane thickness 40 μm before doping.

Direct DME and methanol vapor fed fuel cell performance

Another cell was operated with DME and methanol in sequence. The performance with methanol as fuel was higher than that of DME, but the difference was remarkably small. Performance curves with both DME and methanol as fuels at 150 and 200 °C of the same cell can be seen on Figure 4. The peak power for DME at 200 °C is app. 80% of that of methanol. The open circuit voltage of DME is higher than that of methanol at both temperatures, confirming the lower fuel crossover. It is also interesting to note that by increasing the temperature, the performance of DME is more than tripled, while methanol performance is only doubled. The i-V curve of DME at 150 °C shows a very large activation loss, barely reaching into the linear region. By increasing the temperature the kinetics of oxidation are greatly improved and DME becomes competitive with methanol. Previous results when a cell was fuelled with DME and methanol respectively have shown that the ratio between the DME and the methanol performance was of a similar magnitude at both 150 and 200 °C (3). This apparent inconsistency indicates that the reproducibility can be improved.

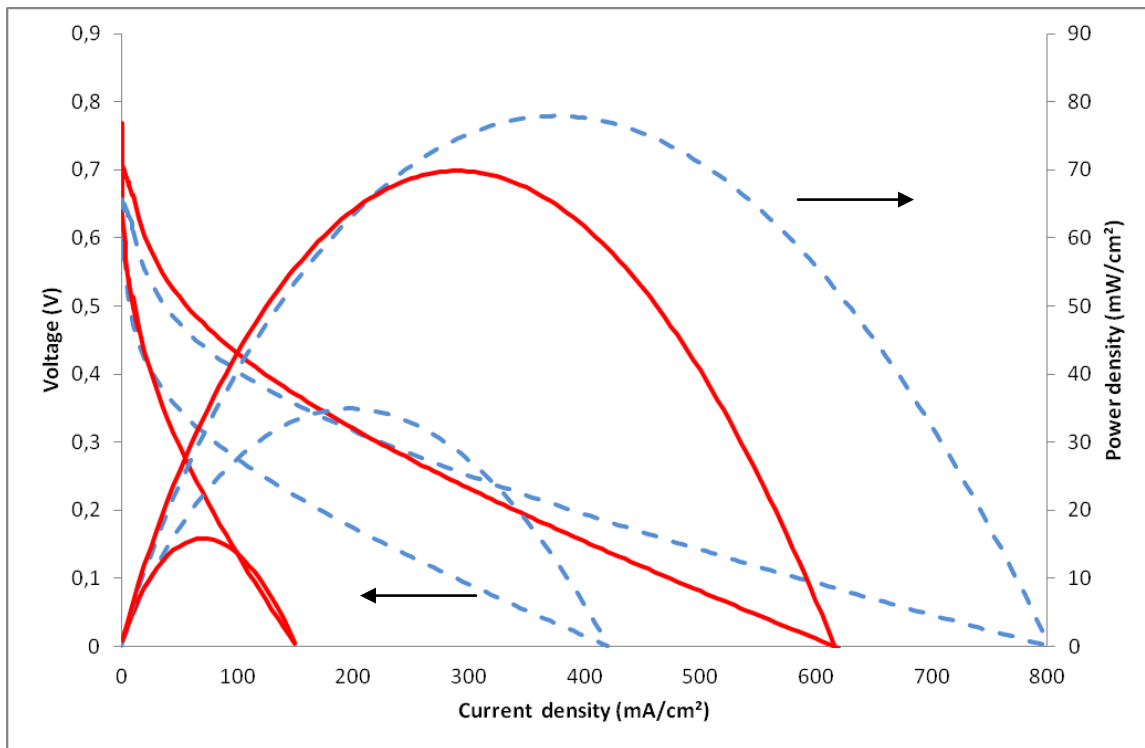


Figure 4: Performance curves of a single cell vapor fed with DME (full lines) and methanol (dashed lines) at 150 °C (lower) or 200 °C (upper), ambient pressure and air as oxidant. Anode – 4.0 mg_{PtRu}/cm², cathode – 0.6 mg_{Pt}/cm², membrane thickness 43 μm before doping.

Oxygen vs. air as oxidant.

Many reports made on direct methanol fuel cells are done using pure oxygen at the cathode. This always boosts the performance compared to a cell operated on air by a hundred mV or even more at moderate and high current loads with hydrogen as fuel. In order to investigate the effect of oxygen on the direct DME cell, the cathode of a single

cell was fed with 190 mL/min O₂. The performance curves of a single cell with 4.0 mg_{PtRu}/cm² anode loading, 0.6 mg_{Pt}/cm² cathode loading and membrane thickness of 43 μm before doping with H₃PO₄ with direct DME and direct MeOH operation can be seen on Figure 5 and Figure 6 respectively.

The performance of the MEA with hydrogen as fuel and pure oxygen on the cathode side did indeed show an increase in open circuit voltage from 0.90 to 0.94 V and in power density from 300 to 400 mW/cm² at 800 mA/cm² (not shown). The effect of oxygen on both DME and methanol was not so pronounced, as seen in the figures. The effect of pure oxygen is primarily on the cathode side so it is not expected to depend much on which fuel is converted at the anode. Nevertheless, since crossover plays a role in all PEM fuel cells the explanation might be more complicated.

Fuel cells containing phosphoric acid in the electrolyte all suffer from the fact that phosphate adsorbs strongly on the noble metal catalyst. This is the reason why high temperature PEMFC do not show higher power density than conventional sulphonic acid based fuel cells at 80 °C. Instead it is lower and that is despite the much higher temperature from which one would expect faster kinetics and higher electrolyte conductivity.

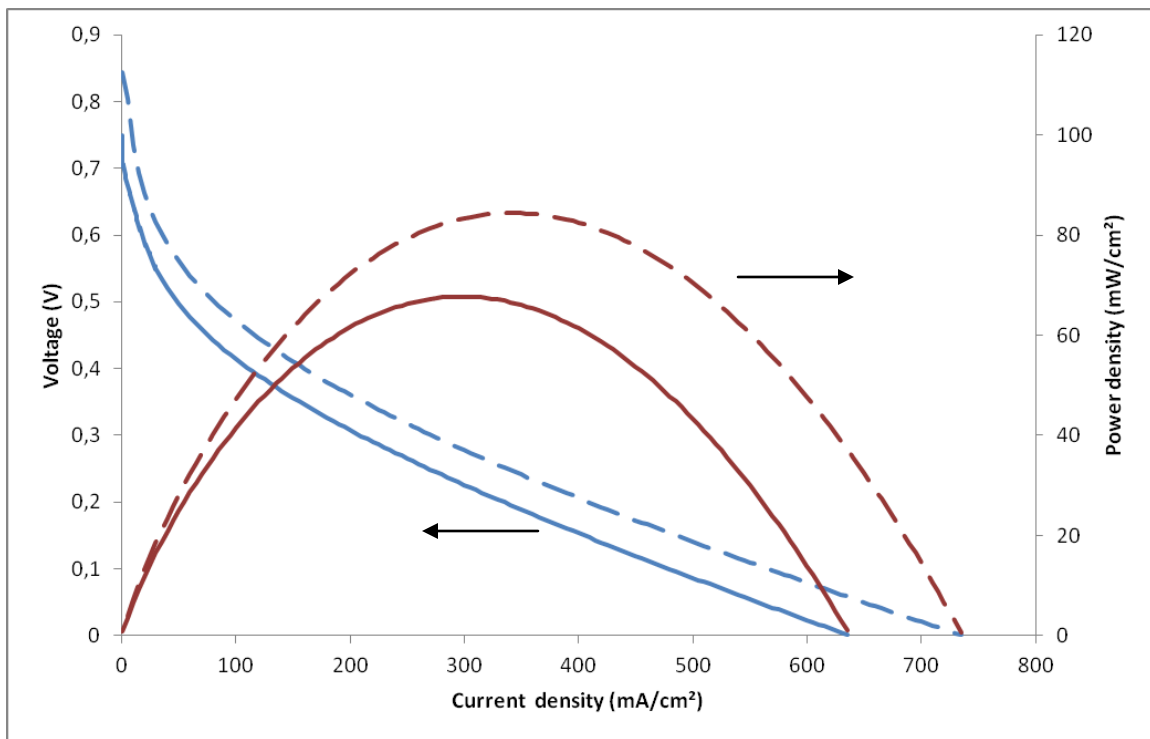


Figure 5: Performance curves of a single cell operated at 200 °C with DME as fuel. Solid line – with air as oxidant, dashed line – with O₂ as oxidant.

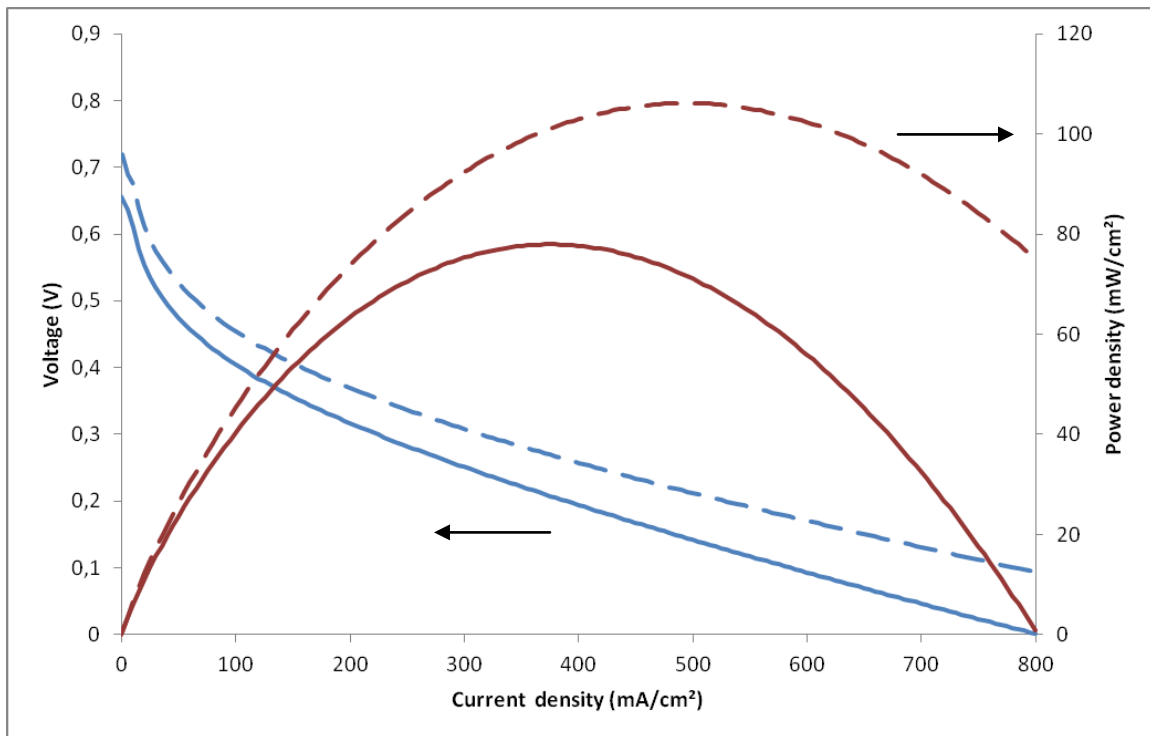


Figure 6: Performance curves of a single cell operated at 200 °C with methanol as fuel. Solid line – with air as oxidant, dashed line – with O₂ as oxidant.

Conclusion

A direct DME fuel cell of the high temperature PEMFC system was operated at 150-200 °C and a peak performance of up to 79 mW/cm² was demonstrated at 200 °C with air as oxidant and without pressurization. This is an improvement compared to previous work with a peak power of 67 mW/cm². Comparison with direct methanol fuelling was performed under similar conditions and the result was that the peak performance was only slightly higher when the cell was powered by methanol instead of DME at 200 °C. At 150 °C the measured relative difference was larger which is in disagreement with previous studies. Finally a cell was operated on air and later on pure oxygen. The voltage gain by switching to pure oxygen was only ca. 50 mV at moderate load for both DME and methanol.

Acknowledgments

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