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Short communication

Effect of cathode structure on planar free-breathing PEMFC

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Abstract

The effect of cathode structure on the performance of planar free-breathing fuel cell is studied. Three different types of gas diffusion backings and current collector plates on the cathode were used. The gas diffusion backings used were thick carbon sheet, titanium sinter, and carbon paper. Difference between current collector plates was the size of the openings between current collecting ribs. Results showed that with thicker gas diffusion backings the structure of the current collector had only some effect on the cell performance but with thin carbon paper the effect was significant. Very high power densities for free-breathing fuel cell were achieved with thin gas diffusion backing with the record of approximately 360 mW cm^{-2}. However, the cell was also vulnerable for flooding as there was liquid water observed on the cathode surface. Despite the liquid water saturation it seems that this kind of cell design may be suitable especially for portable applications.

Keywords: PEMFC; Planar design; Free-breathing; Cathode structure; Liquid water saturation

1. Introduction

The interest in small-scale fuel cell applications has significantly increased in the last few years. It is believed that small-scale fuel cells may have potential in replacing batteries in portable applications [1,2]. The fuel cell running a small-scale application should be compact and have high power density. In order to have small fuel cell system, the operation of the cell should be highly passive, i.e. the number and power consumption of auxiliary devices should be minimized. The power density of the cell itself is usually decreased with passive methods of operation, but the effect on the whole system is very much dependent on the application. One interesting approach for passive operation is free-breathing fuel cells, i.e. cells in which the oxygen needed by the cell reaction is taken directly from the surrounding air by diffusion and natural convection. Studies on free-breathing fuel cells are presented, e.g. in [3–13].

In this contribution, the effect of the cathode structure on the performance of planar free-breathing polymer electrolyte membrane fuel cell (PEMFC) introduced in [13] is studied. Three different gas diffusion backings (GDBs) with three different current collector plate structures were used on the cathode. The difference in the current collector plates was the width of the opening between the current collecting ribs.

The structure of cathode current collector plate has an effect on losses occurring in an operating fuel cell. If there are large openings between current collecting ribs, the total resistance is increased as the current produced in the middle of the openings has a longer way to reach the current collector. However, simultaneously, the effective area for oxygen diffusion is increased and thus, mass diffusion overpotential is decreased. With rigid and thicker GDBs this effect should be smaller because the oxygen has a longer way to diffuse enabling a more homogeneous oxygen concentration profile on the electrode. Moreover, a thin and compressible GDB is more compressed under the ribs causing loss of porosity, which increases mass diffusion limitations. With fewer ribs supporting a compressible GDB, there may be poor contact

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between MEA and GDB in the middle of the openings increasing the contact resistance of those parts.

2. Experimental

The cell (active area approximately 6 cm^2) components used in the measurements were the same as in [13] except for the cathode GDBs and current collector plates. The used GDBs were ®SIGRACET PGP 30 AA #18802 carbon sheet made by SGL Technologies GmbH, platinum-coated (both sides) titanium sinter similar to that presented in [14], and a certain carbon paper. Ti sinter and #18802 are mechanically rigid GDB materials, whereas carbon paper is thin and more compressible GDB. The used cathode current collector plates were made of 2 mm thick gold-plated 316 stainless steel. The difference between the current collector plates was the size of the openings between current collecting ribs. The ribs were 1 mm wide and they were straight in contrast to one diagonal rib used in [13]. The widths of the openings were 2, 5, and 10 mm.

The measurements were conducted with the same measurement system as in [13]. In all of the measurements, dry hydrogen having purity of 99.999% was fed in atmospheric pressure to the anode from a pressure bottle. The minimum flow-rate of hydrogen was 7 $cm^3\,min^{-1}$ and for larger flows a current-based relation of 14 $cm^3\,min^{-1}\,A^{-1}$ (stoichiometry of 2) was used. Besides the hydrogen flow control, the cell used passive methods of operation, i.e. it had no external heating, it was fully free-breathing, and it did not have any active control on the water balance.

The performance of the cell was characterized with polarization measurements, and current interruption method was used for the estimation of the cell resistance. The polarization curves were measured by scanning the current with 50 mA steps (100 mA for carbon paper GDB because of the large current scale) and simultaneously measuring the voltage of the fuel cell. The voltage was allowed to stabilize for 60 s at each measurement point before the next current step. Before each polarization curve measurement, the fuel cell was let to stabilize at the current density of 100 mA cm^{-2} for 15 min. Most of the polarization measurements were conducted in horizontal (the cathode side upwards) orientation. One measurement with carbon paper GDB and the current collector plate with 2 mm openings was also conducted in vertical orientation in order to see the effect of orientation.

Long-term measurements were also performed with carbon paper GDB and the current collector plate with 2 mm openings because the polarization measurements implied that the cell is prone to flooding. Long-term measurements were performed approximately for 20 h with current densities of 200 and 400 mA cm^{-2} both in horizontal and vertical orientation.

Temperature of the cell from top of the cathode side GDB was measured with Microscanner™ D501 infrared thermometer made by Exergen Co. Vaisala HMI41 relative humidity and temperature indicator with HMP42 probe was used for measuring the temperature and relative humidity of ambient air.

3. Results

3.1. Polarization measurements

The results from the polarization measurements and corresponding resistance curves with #18802 GDB are presented in Fig. 1. There is only little difference in cell performance between different current collector plates. With the narrowest openings the resistance was smallest as assumed, but the difference between 2 and 5 mm openings is almost negligible. More significant, but still rather small, increase in resistance can be seen with 10 mm openings. Even though there is very little difference in the polarization curves, the bending down of the curve starts at slightly smaller currents with the narrowest openings than with wider ones. It can be concluded that with the narrowest openings the mass diffusion overpotential is slightly increased, but this effect is smoothened because the GDB is rather thick and thus, there is a long way for oxygen to diffuse to the electrode enabling more homogeneous oxygen concentration throughout the active area.

The temperature and relative humidity of ambient air during the polarization measurements with #18802 were approximately 19 °C and 19–23%, respectively. The cell temperature at 200 mA cm^{-2} varied between 24.0 and 24.5 °C. The highest temperature was achieved at the middle, and lowest at the edges of active area. The cell voltage fluctuation was approximately 20 mV at 200 mA cm^{-2}.

Comparing the measured polarization curves to those reported in [13] it can be noticed that the performance of the cell is somewhat decreased. A polarization curve from [13]

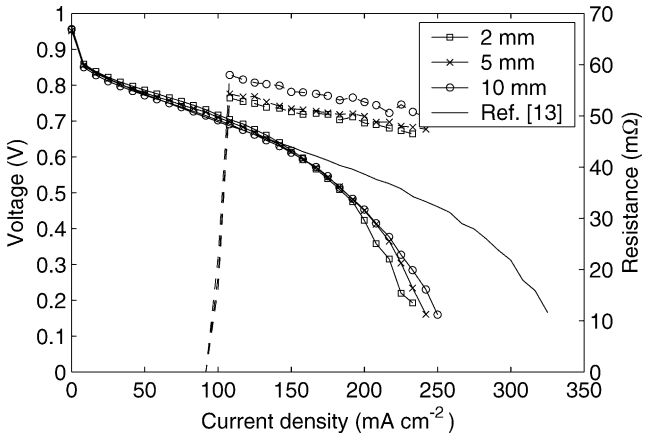

Fig. 1. Polarization (solid line) and resistance (dashed line) curves for #18802 GDB with different current collector plates. The notation in the legend tells the width of the opening in the cathode current collector plate. Curve Ref. [13] is a polarization curve redrawn from [13] in order to simplify the comparison.

is redrawn in Fig. 1 in order to simplify the comparison. The polarization curves coincide in the lower and middle parts of the current density range. At approximately 150 mA cm^{-2} the curves measured in this study start to bend down faster than the one redrawn from [13] implying increased mass diffusion overpotential. This cannot be explained only by the difference in the current collector plate structure as there is only very little difference between the curves measured in this study, even though the difference in free area for oxygen diffusion was significant.

The measurements presented in [13] were conducted in summer and temperature in laboratory was approximately 23 °C, and thus, also the cell temperature was higher than in the measurements presented here. The saturation pressure of water is an exponential function of temperature, and thus, air can take significantly more water vapor before liquid water saturation even with temperature difference of only few degrees. Moreover, diffusion is also slightly increased with increased temperature. Thus, it seems that ambient conditions may have notable effect on the cell performance, especially in terms of mass diffusion overpotential.

The polarization and resistance curves with Ti sinter GDB are presented in Fig. 2. Also with Ti sinter the effect of current collector plate is quite small. However, with 10 mm openings there is no apparent bending down of the polarization curve implying that with achieved current densities no significant mass transfer limitations was occurred. The ambient temperature and relative humidity during the measurements were approximately 17.5–18.5 °C and 12–19%, respectively. The cell temperature at 400 mA cm^{-2} varied between 27.0 and 28.5 °C with no apparent differences between different cell configurations. The cell voltage fluctuation was approximately 20–40 mV at 400 mA cm^{-2}.

The polarization and resistance curves with carbon paper GDB are presented in Fig. 3. With thin and compressible GDB the effect of openings is significant. With 2 mm openings the resistance is significantly smaller than with 5 mm openings, but the mass diffusion overpotential is higher

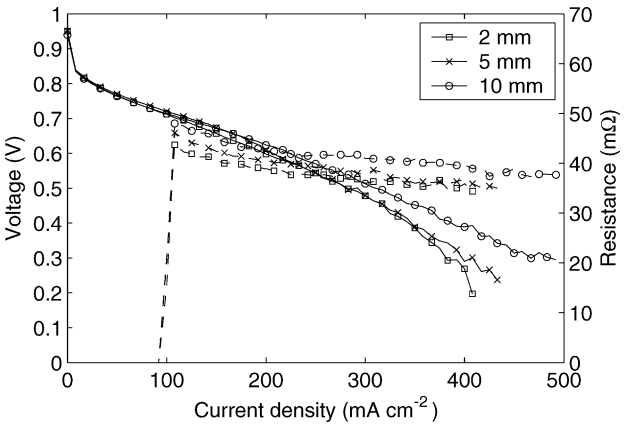

Fig. 2. Polarization (solid line) and resistance (dashed line) curves for Ti sinter GDB with different current collector plates. In order to make the figure clearer, every other measurement point marker is removed.

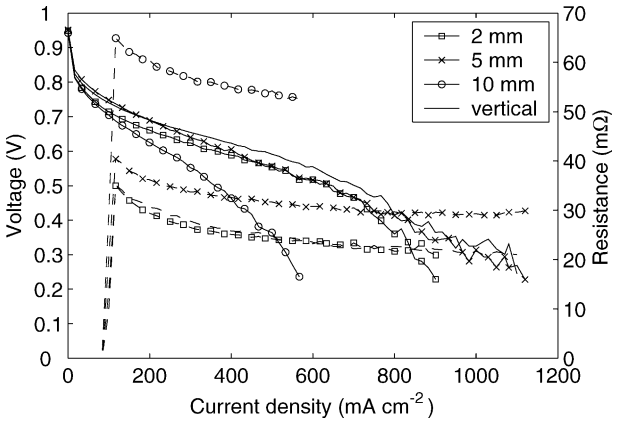

Fig. 3. Polarization (solid line) and resistance (dashed line) curves for carbon paper GDB with different current collector plates. Notation 'vertical' refers to the measurement in the cell for vertically oriented. In order to make the figure clearer, every other measurement point marker is removed.

inducing a slightly poorer performance. With 10 mm openings the resistance increased tremendously causing significantly poorer performance than with smaller openings. With large openings there is poor mechanical support on most parts of the GDB and thus, also the contact on those parts is poor causing high contact resistance.

Even though with 5 mm openings the performance of the cell was at its best, this cell configuration is not practical for real applications. Thin and soft GDB should be properly protected in order to avoid possible sharp objects penetrating the GBD and MEA. Even a small hole in the MEA can cause the cell to stop functioning as hydrogen can leak to the cathode and directly react with oxygen. Thus, the openings on the cathode side should be small, if thin and compressible GDB is used.

The ambient temperature and relative humidity during the polarization measurements with carbon paper GDB were approximately 17–18 °C and 10–19%, respectively. The cell temperature at 400 mA cm^{-2} was approximately 24–26 °C for 2 and 5 mm openings, and 26–30 °C for 10 mm openings. At 800 mA cm^{-2} the cell temperature was approximately 33–39 °C for 2 and 5 mm openings, and at 1100 mA cm^{-2} approximately 42–52 °C for 5 mm openings. The cell voltage fluctuation was 10 mV at 400 mA cm^{-2} and increased with higher current densities. At highest current densities the voltage fluctuation was almost 100 mV. Especially with 5 mm openings there can be seen quite radical fluctuation also in average voltage at high current densities.

There was liquid water saturation observed on the top of the cathode surface with carbon paper GDB. Very small visible water pearls started to form onto top of the GDB approximately at 300 mA cm^{-2} with 2 and 5 mm openings. Larger water droplets started to form next to the ribs approximately at 500 mA cm^{-2}. At higher current densities with 5 mm openings (over 900 mA cm^{-2}) the amount of liquid water started to decrease as the cell heated up, and approximately at 1100 mA cm^{-2} practically all liquid water

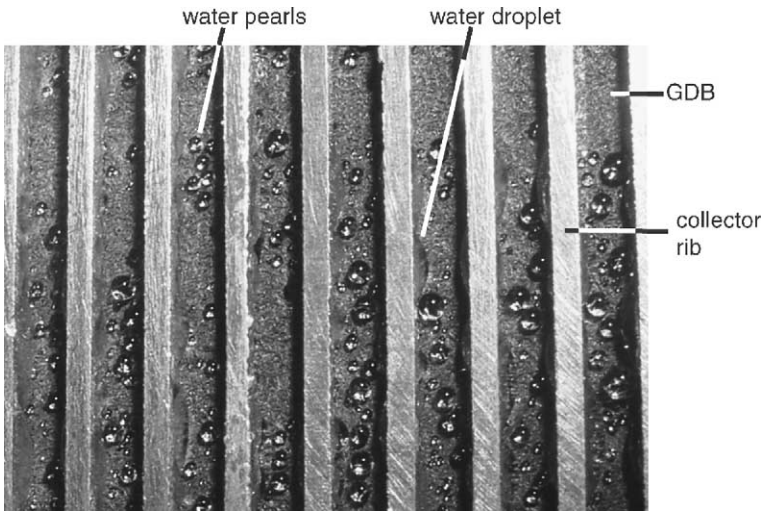

Fig. 4. Formation of liquid water pearls on the surface of the GDB and larger droplets next to the ribs. Photograph is from the measurement with 2 mm openings at 550 mA cm^{-2}.

was disappeared. With 10 mm openings there was water formation only next to the ribs, and the first water droplets started to form approximately at 200 mA cm^{-2}. Liquid water formation is illustrated in Fig. 4 which is a photograph from the measurement with 2 mm openings at 550 mA cm^{-2}.

The polarization and resistance curves with 2 mm openings and the cell in vertical direction are also presented in Fig. 3. The cell performance is slightly better than with 5 mm openings in horizontal direction with a maximum power density of approximately 360 mW cm^{-2}. The resistance of the cell is virtually the same as in horizontal direction, but the improved cell performance implies that the mass diffusion overpotential is decreased. The cell temperature was slightly lower at higher current densities in vertical direction, e.g. 32–37 °C at 800 mA cm^{-2}. The cell voltage fluctuation was almost half of that in horizontal direction except for the highest current densities, in which the fluctuation was similar.

The formation of liquid water on the surface of the GDB started later than in horizontal direction and also the amount of liquid water was smaller throughout the current density range. First very small water pearls were observed approximately at 400 mA cm^{-2}. Slightly larger water droplets started to form next to the ribs approximately at 600 mA cm^{-2}. The amount of water started to decrease approximately at 800 mA cm^{-2} and at 1000 mA cm^{-2} virtually all liquid water disappeared.

Improved cell performance, slightly lower cell temperature at high current densities, smaller cell voltage fluctuation, and less liquid water saturation imply that the convection on the surface of the cell is improved when the cell is vertically oriented. Enhanced convection removes heat and water more effectively from the cell and simultaneously brings more fresh oxygen to the cell. With thick GDB there was no apparent difference in the performance of the cell in different directions [13]. This implies that with thick GDB the mass transfer limitations are mainly due to the diffusion in GDB. With thin GDB the mass transfer limitations caused by convection on the surface of the cell also seems to be significant.

3.2. Long-term measurements

The results of long-term measurements are presented in Fig. 5. There is significant difference in the cell performance in different orientations. In vertical direction the cell performance was stable throughout the measurement. The slight changes may be due to possible changes in ambient conditions. In short time-scale there is a voltage fluctuation of 3–4 mV at 200 mA cm^{-2} and 5–7 mV at 400 mA cm^{-2}. In both directions the cell temperature stabilized to approximately 23–25 °C with lower and 28–32 °C with higher current density.

After an hour of operation there was small water pearls on the surface of the GDB at 200 mA cm^{-2}, and also few

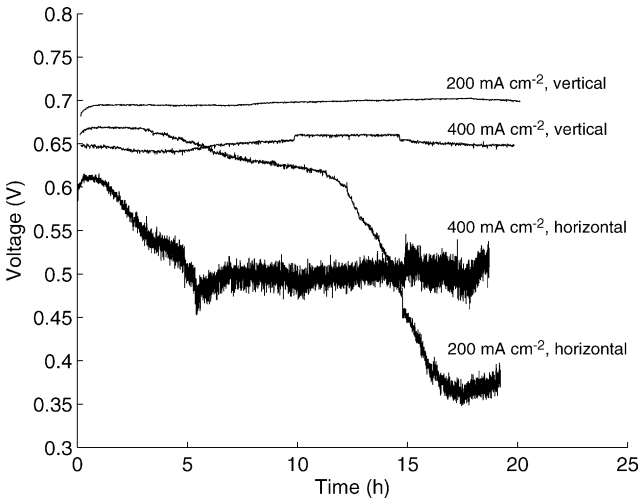

Fig. 5. Results from the long-term measurements. The current density and cell orientation are indicated next to the corresponding curve in the figure.

droplets next to the ribs at 400 mA cm^{-2}. After few hours the amount of liquid water seemed to remain constant and rather similar with both current densities. There were some water pearls and droplets present, and also a small blockage of water on the lower corner of the cell that was situated above the end of the hydrogen channel.

In horizontal direction there are significant changes in the cell performance as a function of time. After an hour of operation at 200 mA cm^{-2} there was small water pearls on the surface of the GDB and also very small droplets next to the ribs. Approximately after 3.5 h there were first small blockages of water. After approximately 15 h of operation the amount of water seemed to remain constant. Most of the GDB surface above the active area was blocked with liquid water. There was only some area above the hydrogen inlet that remained dry. Liquid water increased significantly the mass diffusion overpotential, as can be seen from Fig. 5. The cell voltage is decreased by approximately 0.3 V. Moreover, the cell became more unstable as there is a voltage fluctuation of approximately 20 mV.

The cell performance at 400 mA cm^{-2} is not as radically changed as at 200 mA cm^{-2}, most probably due to higher cell temperature which decreased the amount of liquid water saturation. The cell voltage fluctuation was approximately 10 mV in the beginning and increased up to 40 mV as more water was formed on the surface of the GDB. First blockage of water was formed approximately in 1.5 h, and the amount of water increased until approximately 5 h of operation. After that almost one third of the GDB surface above the active area was blocked by liquid water. Water was mainly formed above the parts where the end of the hydrogen flow channel was. A photograph of liquid water blockages after the amount of water visibly seemed to remain constant is illustrated in Fig. 6.

4. Summary and discussion

The effect of cathode structure on the performance of planar free-breathing fuel cell was studied. Three different kinds of GDBs and current collector plates on the cathode were used. The GDBs used were thick carbon sheet, Ti sinter, and carbon paper. Difference between current collector plates was the size of the openings between current collecting ribs.

The polarization measurements showed that with thicker and mechanically rigid GDBs the effect of current collector plate is not a critical factor. The best performance was achieved with largest openings, which offered more effective area for mass transfer through the GDB. With thinner and compressible carbon paper the effect of current collector plate was significant. With 2 mm openings the resistance was smallest but mass diffusion overpotential was higher than with 5 mm openings. With 10 mm openings the resistance of the cell increased significantly most probably due to poor contact in the middle of the openings, and thus, the cell performance was decreased. The best performance in horizontal cell direction was achieved with 5 mm openings. However, with compressible carbon paper GDB it is not practical to use wide openings because there is a risk of penetrating the MEA with a sharp object unless the cell is otherwise protected.

In [13] there was not seen any apparent difference in cell performance in different cell orientations with thick carbon sheet GDB. With thin carbon paper GDB the cell performed somewhat better in vertical than in horizontal direction. This seemed to be caused by more effective convection on the cell surface. There was also a significant difference in long-term operation between different cell orientations. In vertical direction the cell showed a stable performance. In horizontal direction the cell was prone to flooding, which caused a

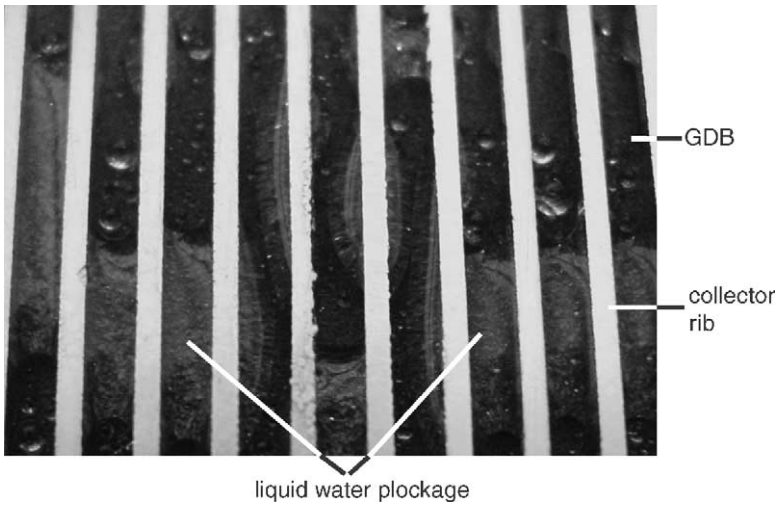

Fig. 6. Photograph from the long-term measurement at 400 mA cm^{-2} and the cell in horizontal orientation after the amount of water seemed to remain constant. Most of the water is formed above the end of the hydrogen channel. Channel is as in [13] with the inlet in upper right corner and outlet in lower left corner of the figure.

significant increase in mass diffusion overpotential and also increased the cell voltage fluctuation in short time-scale.

Despite the fact that the cell was prone to flooding, it seems that this kind of cell design is very potential power source for portable applications, e.g. to be integrated into the cover of a laptop computer. Very high power densities for free-breathing fuel cell were achieved, and the cell operated stably for several hours in vertical direction. The long-term operation was not stable in horizontal orientation. However, if the usage of an application is such that it is idle most of the time, the cell could be used also in horizontal direction.

It was observed in long-term measurements that most of the liquid water that was formed on the surface of the cathode GDB was on the parts above the end of the hydrogen channel. Dry hydrogen flow fed into the anode is able to transport some of the water that is diffused through the membrane. However, as the hydrogen gets humidified along the channel less water is transported with the flow, and the effect can be so significant that parts of the cathode side gets flooded by liquid water.

The results presented in this paper make the modeling of this kind of cell rather complex task. The mass transfer cannot be considered only in gas phase as there was liquid water observed on the surface of the cathode side gas diffusion backing. Moreover, there was measured a temperature difference of several degrees between different parts of the cell. Because the saturation pressure of water vapor is an exponential function of temperature, even a small temperature difference can cause significantly different water transfer properties. Thus, the cell cannot be considered isothermal, and the energy equations have to be taken into account. It was also noticed that most of the liquid water was formed above the end parts of the hydrogen channel. This implies that the assumption of constant water drag coefficient, as is made in most of the PEMFC modeling studies, may not be valid for this kind of a cell design.

The free-breathing cathode structure brings even more complexity for modeling of this kind of cell design. As there is no forced convection present, the cathode side mass transfer is taken place by diffusion and natural convection. The species concentrations on the surface of the GDB are dependent on the convection occurring on the surface, and thus, fixed boundary conditions for species concentrations cannot be used. Thus, also the convection occurring outside the cell should be taken into account. The modeling studies on natural convection are mainly semi-empirical and are based on averaged heat and mass transfer coefficients, and thus, the implementation of convection into the rest of the cell model can be an extremely difficult task.

Acknowledgements

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