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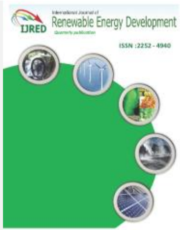

Evaluation of Cathode Gas Composition and Temperature Influences on Alkaline Anion Exchange Membrane Fuel Cell (AAEMFC) Performance

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ABSTRACT: The effects of different temperatures (55, 65, 75 and 85 °C) and cathode gas compositions (O_2, synthetic air, air and 90% synthetic air+10% CO_2) on alkaline anion exchange membrane fuel cell (AAEMFC) were evaluated. Membrane electrode assemblies (MEA) were fabricated using commercial anion exchange membrane (AEM) in OH^- form and Pt catalyst. Polarization curves and voltage responses during constant current were performed in order to describe the influences of temperature and gas composition on the AAEMFC performance. The experimental results showed that the fuel cell performance increases with elevating temperatures for all applied gas compositions. Highest power density of 34.7 mW cm^{-2} was achieved for pure O_2 as cathode feed. A decrease to 20.3 mW cm^{-2} was observed when cathode gas composition was changed to synthetic air due to reduction of the O_2 partial pressure. The presence of CO_2 in atmospheric air applied to the cathode stream caused a further drop of the maximum power density to 15.2 mW cm^{-2} driven by neutralization of OH^- ions with CO_2.

Keywords: alkaline membrane, CO_2, single cell, air, synthetic air

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1. Introduction

Global energy demand is increasing day by day because of growing population, expanding economies and technologies. Due to the rising energy demand much attention has been devoted to the renewable energy development. The replacement of conventional energy sources used nowadays with renewable energy sources will contribute with the reduction of CO_2 emission. The promising high efficiencies of fuel cells for usage from portables to power plants have attracted much attention from commercial and governmental entities.

Proton exchange membrane fuel cell (PEMFC) is the most investigated and well developed type. However, some hurdles such as dependency on precious metals like Pt and expensive electrolyte membrane material limit its commercialization. The promising advantages of the alkaline anion exchange membrane fuel cell (AAEMFC) have been recognized in the recent years (Arges *et al.* 2010; Merle, Wessling & Nijmeijer 2011; Zeng & Varcoe 2011). Alkaline environment facilitates the kinetics for oxygen reduction and fuel oxidation

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reaction and eliminates the need for precious metal electrocatalysts (Varcoe & Slade 2005; Lu *et al.* 2008; Arges *et al.* 2010). However, AAEMFCs have some drawbacks such as degradation of anion exchange functional groups (ammonium groups) in alkali media that leads to membrane degradation and low ion conductivity due to low electrochemical mobility of OH^- ions compared to proton mobility (Lee *et al.* 2011).

The use of pure hydrogen and highly purified oxygen has been employed to evaluate fuel cell performances. However, the costs of such pure gases increases the overall cost of the electricity produced in the fuel cell. For this reason, fuel cell researchers evaluate the use of reformed gases and atmospheric air to be used in the fuel cells. It is known that the CO_2 contained in the fuel and in the oxidant gases influence the fuel cell performance and is described to decrease the membrane conductivity by the equilibrium reaction of CO_2 with the hydroxide anions present in the membrane (Matsui *et al.* 2010). Nevertheless, there are contradictory studies that state that the CO_2 might have a negative influence on the fuel cell performance (Matsui *et al.* 2010), while other studies state that the introduction of high concentration of CO_2 might be beneficial to the fuel cell performance when the membrane is in carbonate form (Zhou *et al.* 2009; Unlu *et al.* 2009). In this approach, different concentrations of CO_2 were given to the cathode gas and the performance of an AAEMFC with the anion exchange membrane (AEM) in hydroxide-form was analyzed.

Further studies in AAEMFC field are being carried out in order to analyze the long-term effect of carbon dioxide on the membrane and thus on the fuel cell performance. Moreover, an understanding of the influence of each single parameter on AAEMFC performance are subject of next studies. In this work, the impact of cathode gas composition and temperature on performance of AAEMFC were investigated.

2. Material and Methods

2.1. Preparation of membrane electrode assemblies

The catalyst ink was prepared by dispersing commercial carbon supported platinum catalyst (40% wt Pt/C) (Alfa Aesar, A. Johnson Matthey, Karlsruhe, Germany) in deionized water (1 Pt/C : 100 H_2O weight ratio) and ionomer (As4, quaternary ammonium type, Tokuyama Corp., Tsukuba, Japan) solution via sonication. Ionomer was used in order to ensure better mobility of OH^- and water in the membrane and to reduce the distance between catalyst particles (Mamlouk *et al*. 2011). The mass ratio between catalyst and ionomer was 7 to 3 (Pt/C: Ionomer=7:3). The ink was sprayed (Fig. 1(a)) on to the gas diffusion layers (GDL) (H2315I2 C6 from Freudenberg FCCT KG, Weinheim, Germany) with the Pt loading of 1 mg/cm^2. MEAs were fabricated by sandwiching hydroxide-form membrane (A201, Tokuyama Corp., Tsukuba, Japan) in two catalyst coated GDL (4.84 cm^2) and using hot press (Fig. 1(b)) with 0.5 kN pressure at 80 °C for 10 min.

2.2. Hardware and Operating Conditions

The fabricated MEAs were assembled in 5 cm^2 cell hardware (Fuel Cell Technologies, Inc., Albuquerque, USA). Gas sealing was supplied by using teflon material as gasket and with a uniform torque of 11.5 Nm. The hardware consists of a pair of graphite blocks (Poco Graphite, Inc., Decatur, US) with serpentine flow-pattern, gold plated current collectors and aluminum end plates. Single cell hardware was connected in a Fuel Cell System G100 (Greenlight Innovation, Burnaby, Canada) that was equipped with mass-flow controllers, temperature controllers, humidifier, gas composition and pressure regulators.


(a) Spraying of catalyst ink
(b) Hotpressing of MEA

Fig. 1 Fabrication of membrane electrode assembly (MEA) by spraying the catalyst ink with a spray gun onto the gas diffusion layer (GDL) (a) and by hotpressing two prepared GDLs onto an ion exchange membrane (b).

By preliminary gas chromatography analysis it was found that flow rates about 0.010 nlpm for 90% synthetic air + 10% CO_2 (10% CO_2) were in the low limit of the test stand's mass flow controller and therefore only flows starting from 0.166 nlpm were used for the cathode flow. Therefore, performance curves were run with 6:10 stoichiometry for H_2/O_2, synthetic air, air or 10% CO_2, respectively.

Initial conditioning was applied to the MEA in order to convert CO_3^{2-} ions to OH^- ions through hydroxide cycle in the cell and to humidify the membrane. During initial conditioning step, humidified H_2 and O_2 gases were fed into the fuel cell with constant flows 0.2 nlpm, 0.1 nlpm respectively and 95% relative humidity (RH). Gas inlet temperatures were 55 °C, absolute pressure was 2 bar for both sides and MEA was performed at constant current (resulting voltage between 0.6 and 0.7 V) for 2 h.

The influence of temperature on the AAEMFC performance was studied using two different test methods that are current-voltage (I/V) curves and recording of voltage under constant current during cycling of chosen temperatures (temperature cycling test).

The I/V curves for O_2 were taken after 2 h conditioning. Then the cathode gas was changed to synthetic air, air or 10% CO_2 respectively while anode gas (H_2) remained the same. After introducing the new cathode gas mixtures the cell was operated at constant current for 1 h to obtain steady voltage value because voltage change was observed when gas compositions were shifted from initial conditioning to the testing parameters.

First polarization curves were performed at 55 °C. Afterwards, temperature was increased to 65, 75 and 85 °C while 95% RH and 2 bar pressure were kept constant. Two polarization curves were carried out for each temperature step.

Temperature cycling tests were carried out at galvanostatic mode (at constant current) for all four cathode gases in order to be able to examine the effect of temperature on performance independently from influences such as changeable water content in the cell. Current was applied that led to a voltage response between 0.5 to 0.6 V at the start of the test and was kept constant until the test has been completed. Anode/cathode flows were 6:10 stoichiometry like in the case of I/V tests. Each temperature was hold for 1 h. Then the following temperature was set up. Voltage response was recorded during the test.

Additionally temperature impact on membrane conductivity was examined via linear sweep voltammetry (LSV). LSV data were obtained using a potentiostat (Solartron Modulab 2100A, Farnborough, Hampshire, UK). To understand the behavior of OH^- form membrane and to be able to compare with previous MEA tests, no pretreatment was applied to the membrane before assembling into the cell. Test was run under 1 nlpm O_2, RH (95%) and was kept constant during test when temperature was changing from 55 to 85 °C with holding times (1 h), scanned in the potential range between -0.3/+0.3 V with a scan rate 10 mV/s at ambient pressure. LSV was performed for all temperatures at the end of the holding time.

For the study of cathode gas composition impact on AAEMFC performance, voltage reply was saved during constant current operation at 0.06 A. In order to avoid the effects of applying different flow rates, constant current gas composition test was performed under constant flow rates (H_2: 0.042 nlpm; O_2, synthetic air, air and 90% synthetic air+10% CO_2: 0.166 nlpm)

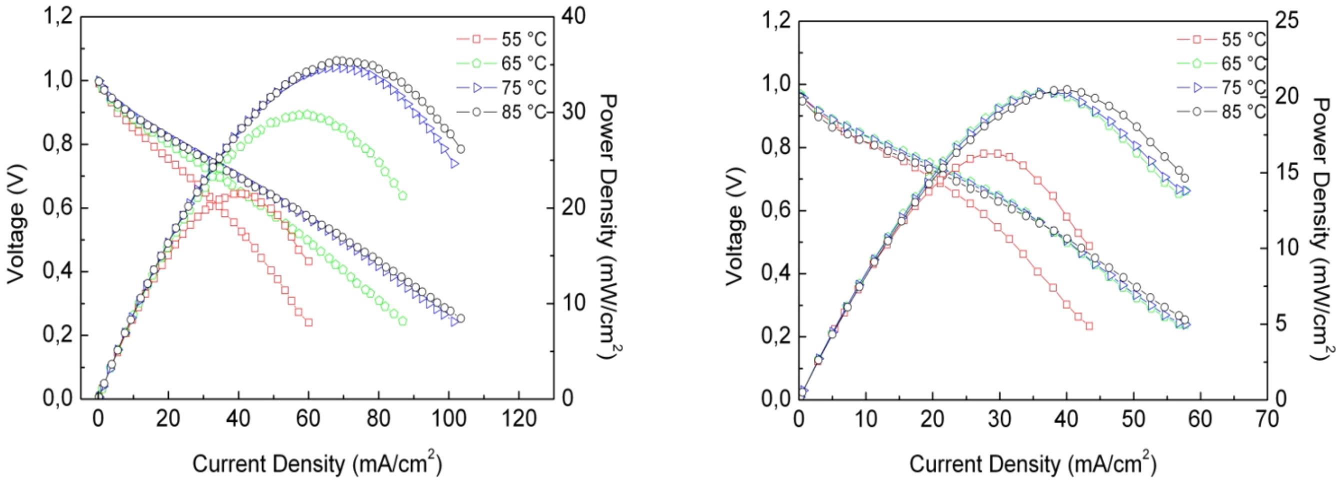
3. Results and Discussions

3.1 Effects of Temperature

The AAEMFC performance was first evaluated from the polarization curves at operation temperatures from 65 to 85°C with four different cathode gas compositions (Fig. 2). Different cathode flows have been supplied while the oxygen amount was kept constant by using same stoichiometry (10) for all cathode gases. The stoichiometric amounts of H_2 and O_2 were calculated using Faraday´s law.

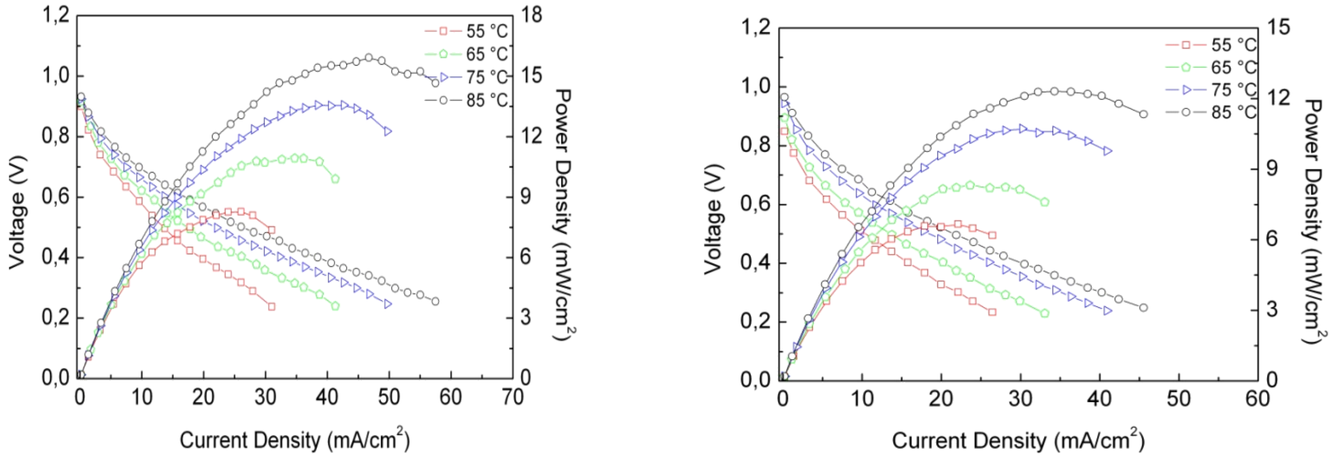
As expected, an increase of the power density with enhance in the temperature was observed for all four gas compositions as demonstrated in Fig. 2. By rising the temperature, available thermal energy in the system raises that leads sufficient energy for reactants to reach the activated state. Hereby, reaction rate and exchange current density increase with improved electrokinetics (O´Hayre *et al.* 2006). Second factor is the improvement of membrane conductivity and gas diffusivity at higher temperatures (Grew *et al.* 2011).

For pure O_2, a maximum peak power density of 34.7 mW cm^{-2} was produced by the MEA for 75 °C (Fig. 2(a)) and did not enhance further by rising the temperature to 85 °C. The catalytic activity has achieved its upper value already by 75 °C and could not provide higher electron transfer rates. Thus fuel cell performance attained its maximum value. Similar effect was observed in Fig. 2b in which synthetic air has been introduced as cathode gas. Here the maximum catalytic activity occurred already at 65 °C, yielding a maximum power density of 20.3 mW cm^{-2}. For CO_2 containing gases (Fig. 2(c) and (d)) also a significant performance increase was perceived when raising temperature from 55 to 85 °C. This effect can be explained by the CO_2 solubility in aqueous media. Carbon dioxide solubility in the electrolyte is strongly temperature dependent and decreases at higher temperatures. Therefore, the O_2 reduction with H_2O is the preferable reaction at higher temperatures instead of the O_2 reduction reaction with



(a) O_2

(b) Synthetic air (79% N_2 +21% O_2)



(c) Atm air

(d) 90% Synthetic air+10% CO_2

Fig. 2 Effect of temperature on performance at four different cathode gas compositions. Polarization and power density curves under operating conditions; Anode gas: H_2, catalyst: Pt/C with loading 1 mg/cm^2 absolute pressure: 2 bar, RH: 95% for both anode and cathode sides.

CO_2. That leads the concentration of OH^- ions increase, CO_3^{2-} and HCO_3^- ions decrease in the membrane (Duan & Sun 2003; Grew *et al.* 2011). Also it can be observed that in the case of O_2 and synthetic air, activation region is very similar as it was demonstrated in the response curves Fig. 2(a) and (b). However, it showed an enhancing trend with temperature increase for the CO_2 contained gas compositions air and 10% CO_2 (Fig. 2(c) and (d)). Although, CO_2 amount in air is 392.41 ppm CO_2 (Pieter Tans 2012), activation region slightly increases with higher temperature in Fig. 2(c) while this difference is more obvious in the case of 10% CO_2 (Fig. 2(d)). This effect is driven by the neutralization of alkali by CO_2. The exposure of alkaline membrane to CO_2 containing gas causes the neutralization of the alkali due to the formation of HCO_3^- and CO_3^- ions. This neutralization will result in a decrease of catalytic activity (depending on the pH at triphasic interface) and ion conductivity (Yanagi & Fukuta 2008). Nevetheless, increasing temperature will cause more OH^- formation and higher catalytic activity.

Fig. 3(a) and (b) represent the results of temperature cycling tests in the case of O_2 and air feed to cathode, respectively. Only O_2 and air results were discussed in this paper. However, same behavior was observed for other gas compositions as well. Temperature increase (from 55 to 85 °C) results an enhancement of fuel cell performance for all four different cathode gases at temperature cycling tests.

As presented in Fig. 3(a), higher voltage change was gained once temperature increased from 55 to 65 °C in the case of O_2 feed at cathode side. Although, voltage still increases with rising temperature, increase rate slows down from 65 to 85 °C

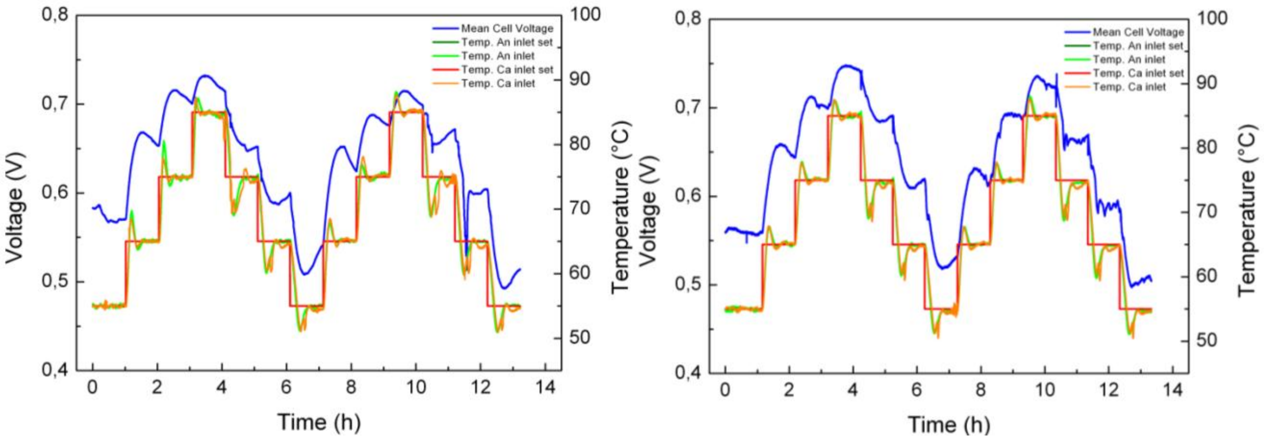


Fig. 3 Voltage response of fuel cell operating at 0.09A (a), 0.03 A (b), absolute pressure 2 bar at both side, with 95% RH and temperatures 55, 65, 75 and 85 °C. The anode and cathode feeds were humidified H_2/O_2 (a), H_2/Air (b) with stoichiometry 6:10, respectively. Holding time was 1 h for each temperature regime

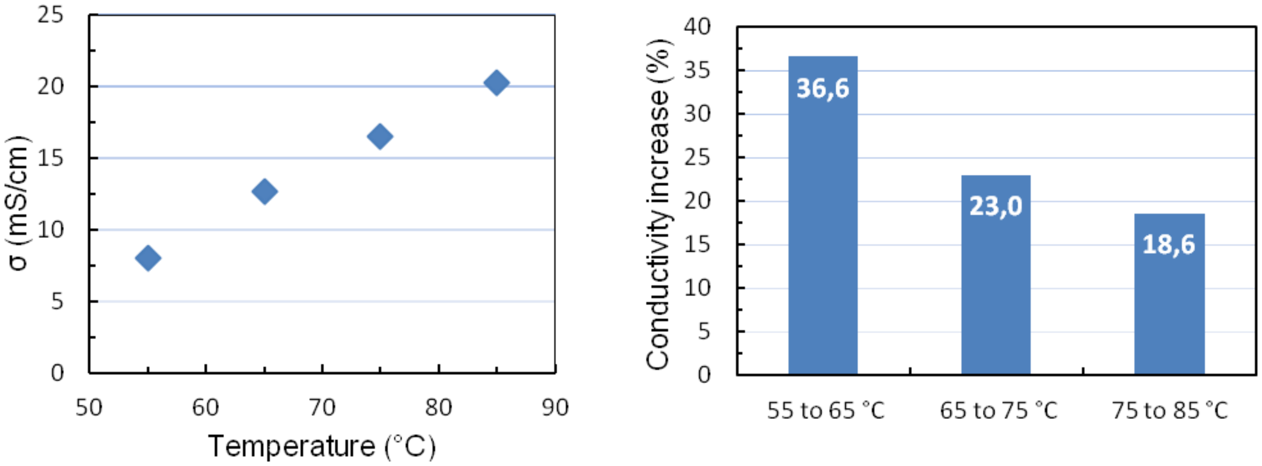


Fig. 4 Conductivity vs. temperature plot of commercial membrane. Scanned in the potential range between -0.3/+0.3 V with a scan rate 10 mV/s in the ambient pressure. Right hand side figure presents the conductivity increase in percentage for each temperature steps.

so voltage gain between 75 and 85 °C is less than between 65 and 75 °C.

Temperature cycling with air (Fig. 3(b)) showed a similar trend as O_2. Elevated temperatures gave higher voltage. Nevertheless, impact on voltage gain with temperature increasing 65 to 75 °C and 75 to 85 °C was more severe for air compared to O_2. The fluctuation of voltage at 10-13th hours (Fig. 3(b)) is due to the mass transportation problem in the presence of liquid water in the channels (Siefert & Litster 2011).

Linear Sweep voltammetry (LSV) test was carried out to investigate dependency of membrane conductivity on temperature. Results reported that membrane conductivity increases at higher temperatures. However, rate of rise was not linear and a decreasing trend was observed from low to higher temperatures (Fig. 4). The conductivity gains were 36.6, 23.0 and 18.6% once temperature was shifted from 55 to 65, 65 to 75 and 75 to 85 °C, respectively.

All these three separate tests (I/V curves, temperature cycling tests and LSV) point out that elevated temperatures enhance fuel cell performance and membrane conductivity. Nevertheless, temperature cycling test with O_2 (Fig. 3(a)) and air (Fig. 3(b)) exhibited that voltage increase lessens from 65 to 85 °C which correlates with the result of current-voltage curves (see Fig. 2(a)) and conductivity measurements of the membrane at these temperatures (see Fig. 4). That effect is more noticeable in the case of O_2 compared to air.

3.2 Effects of Gas Composition

Gas composition impact was studied by cycling the four selected cathode gases at constant current (0.06 A) and various time regimes. Cathode gas compositions and holding times of cycles were varied whereas other

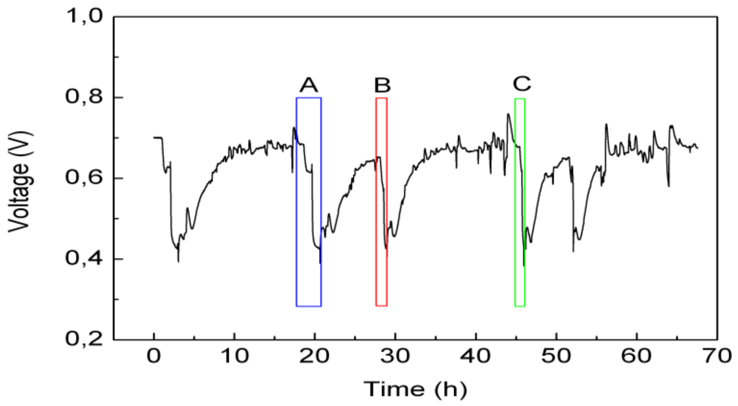
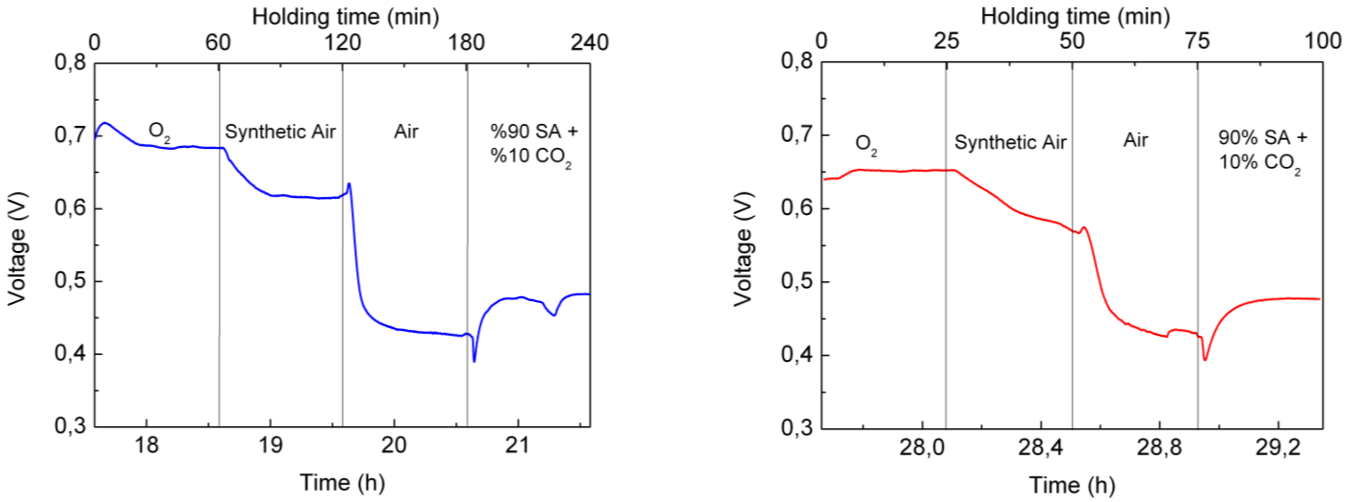
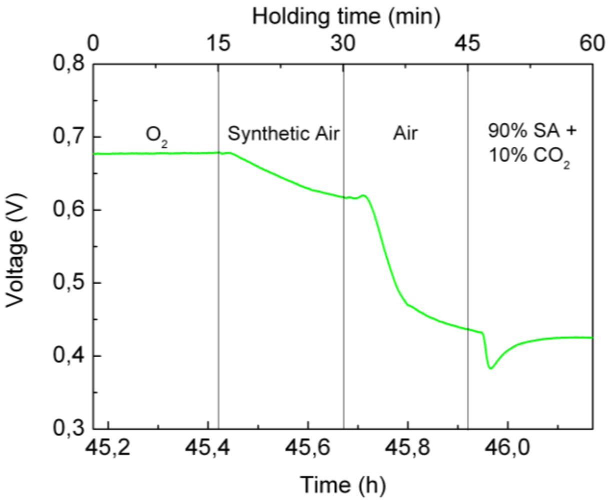


Fig. 5. Gas composition cycling at constant current (0.06 A). Four different gas compositions (O_2, synthetic air, air and 10% CO_2) were fed as cathode stream with a constant flow rate 0.166 nlpm. H_2 flow was 0.042 nlpm to anode. Three various holding times for each gas composition were carried out at these three separated cycle (A, B and C; 60, 25 and 15 min, respectively)



(a) 60 min holding time regarding section A in Fig. 5

(b) 25 min holding time regarding section B in Fig. 5



(c) 15 min holding time regarding section C in Fig. 5

Fig. 6. The enlarged view of four different holding time (60, 25 and 15 min) cycles from Fig 5 (Gas composition cycling at constant current (0.06 A))

test parameters were kept constant. Fig. 5 presents the 60, 25 and 15 min holding times marked as A, B and C, respectively. As is shown in Fig. 5 no irreversible effect on the performance of AAEMFC caused by gas composition change was observed during the experiment time as cell voltage reached approximately initial voltage value after exposing MEA with pure O_2 at the end of each gas cycle. This behavior is driven by the self-purging mechanism of the membrane in which HCO_3^- ions are converted to CO_3^{2-} and OH^- ions under power generation (Varcoe *et al.* 2008; Yanagi & Fukuta 2008). Hereby, voltage output increases and reaches the range of the initial voltage again.

All cycles demonstrated the similar behavior for O_2, synthetic air and air utilization at cathode stream (see Fig. 6). Highest voltage responses were gained in the case of pure O_2 flow. It is know that reduction of oxygen partial pressure on catalyst layer and GDL causes voltage decrease (Weydahl *et al.* 2008). Therefore, voltage drop was reported at synthetic air (21% O_2) flow. Decrease was fast at the beginning of the synthetic air application then equilibrium was reached and voltage stayed constant. The most severe voltage drop was recorded when cathode gas was changed to air due to neutralization of alkali by CO_2. $CO_3^{2-}$and $HCO_3^-$are larger and less conductive in comparison to OH^- ions causing performance decrease. As gas composition is changed from synthetic air to air, CO_2 absorbed to the AEM so fast and all OH^- ions converted to CO_3^{2-} and HCO_3^- ions. Therefore, just CO_3^{2-} and HCO_3^- ions were present in the membrane after a certain holding time under air exposure (Yanagi & Fukuta 2008).

When gas composition was shifted from air to 10% CO_2, voltage response increased after an initial voltage drop as demonstrated in Fig. 6(a) for the 60 min holding cycle. That effect could also be observed for 25 min at Fig. 6(b) though it did not arise for 15 min (see Fig. 6(c)). However, achieved voltage values are still significantly lower than for O_2 and synthetic air.

4. Conclusion

The performance of AAEMFC has been investigated as a function of temperature and gas composition. Results show that the performance is increasing with rising of the temperature due to better exchange current density, enhanced electrokinetics and improvement of the membrane conductivity at higher temperatures. Temperature cycling at constant current presented that voltage rises with temperature elevation from 55 to 85 °C for all cathode gas mixtures. However, rising rate lessens from 65 to 85 °C which means voltage gain between 55 to 65 °C is more than the voltage gains at further temperature steps (65-75 °C and 75-85 °C). Moreover, linear sweep voltammetry test showed that membrane conductivity enhance with higher temperatures, as well.

Cathode gas composition influence was explored by varying the cathode gas compositions under constant current and recording voltage responses. It was found that pure O_2 gives the highest voltage values. Voltage decrease was reported for synthetic air due to the reduction of oxygen partial pressure on catalyst layer and GDL. Additional, voltage drop was recorded when cathode gas was changed to air because of the neutralization of alkali by CO_2 which causes lower conductivity and catalytic activity of Pt. A slightly recovery of voltage was observed for 10% CO_2 at 60 and 25 min cycles but it was still lower than the voltage value with O_2 and synthetic air. Gas cycling and neutralization of the alkali by CO_2 did not cause any irreversible effect on AAEMFC. Approximately, initial voltage value was reached after purging pure O_2 after each cycle.

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