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Durability and degradation of vapor-fed direct dimethyl ether high temperature polymer electrolyte membrane fuel cells

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Abstract

Dimethyl ether (DME) combines high energy density with easy handling and low toxicity and is therefore an attractive fuel. The absence of carbon-carbon bonds allows for electro-oxidation with good kinetics and it is therefore particularly interesting for use in fuel cells. This work presents the first durability studies of vapor-fed direct dimethyl ether fuel cells with phosphoric acid doped polybenzimidazole membranes as electrolytes. Fuel cells are operated in direct DME mode at 160 and 200 °C and the cell voltage at a constant current load of 100 mA cm⁻² is recorded over more than 200 h. Regular electrochemical impedance spectroscopy and polarization data are used as diagnostic measures to monitor the cell characteristics. It is shown that the cell performance deteriorates severely within 200 h of operation at 160 or 200 °C. The degradation is connected to different modes that ultimately result in both increasing polarization resistance and increasing area specific resistance, which may be connected to the chemical incompatibility between the fuel and the electrolyte.

1 Introduction

The high temperature polymer electrolyte membrane (HT-PEM) fuel cells constructed around phosphoric acid doped polybenzimidazole (PBI) membranes were originally developed as direct methanol fuel cells more than 20 years ago [1, 2]. The main advantages over the already established Nafion[®] based low temperature PEM systems were the reduced fuel crossover and the nearly zero electro-osmotic drag coefficient of water and methanol [3-6]. The higher operating temperature also promotes the electrode reactions [1, 7, 8] and enhances the impurity tolerance of the catalysts [1, 9, 10]. Furthermore, the one-phase gaseous system at temperatures well above 100 °C reduces the adverse effects of electrode flooding, which is a major shortcoming of liquid-fed direct methanol fuel cells [11]. These have been very convincing arguments for this technology and triggered substantial research in the field of direct methanol [12, 13] or reformat [14-22] fed HT-PEM fuel cells

While degradation rates as low as $0.5 \mu\text{V h}^{-1}$ have been achieved for PBI/phosphoric acid-based cells at 160 °C and 200 mA cm^2 with hydrogen and air over 9200 h [23], cells fed directly with methanol/water vapor mixtures [12, 13, 15] or reformates with high methanol residual contents [18] degrade at a much faster rate. This is, at least partly, due to the severe chemical incompatibility between the methanol fed to the anode and the phosphoric acid within the polymer membrane and electrode structures, resulting in formation of methyl phosphates with lower proton conductivity and higher volatility than phosphoric acid [24]. A similar mechanism may also be part of the explanation of the fast degradation observed for cells with phosphoric acid-based electrolytes fed with ethanol [25, 26]. The alkyl phosphate formation is suppressed by the presence of water, and increasing the water to methanol ratio and maintaining the methanol content in the anode feed reformat at <5% was recently demonstrated to effectively improve durability [21].

The methyl ether derivative of methanol, dimethyl ether (DME), combines high energy density, low toxicity, easy handling, and availability from renewable sources [27]. These assets make it a particularly interesting fuel, which has triggered substantial research in the field of direct DME fuel cells [28].

The electro-oxidation of DME to carbon dioxide is a complex process releasing 12 electrons [29, 30] and, like for the electro-oxidation of methanol to carbon dioxide, high catalyst loadings are generally used to compensate for the sluggish reaction kinetics. Therefore, research is currently directed towards reducing the large anode activation overpotential through the development of novel catalysts and electrode designs, for example by introducing heteropolyacids in the electrode structures [31] or by introducing new anode catalysts based on various Pt/Ru/Pd-based alloys [32-35] or Pt-Cu nanochains [36].

The first reports describing direct DME high temperature PEM fuel cells were recently published, and it was identified that the vapor feed presents a rational solution to the concentration polarization caused by the low solubility of DME in liquid water [37, 38]. This work presents the first durability studies of vapor-fed direct DME HT-PEM fuel cells based on phosphoric acid doped PBI membranes. The cells were operated at a constant current load at 160 or 200 °C and periodically characterized by polarization curves, electrochemical impedance spectroscopy and acid loss. The severe performance degradation observed during 200-300 h of operation was connected to increasing polarization resistance, likely due to catalyst poisoning or acid depletion, and conductivity decay of the membrane due to chemical incompatibility between the fuel and the electrolyte.

2 Experimental

The membrane electrode assemblies (MEAs) were prepared by sandwiching a phosphoric acid doped poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole) (PBI) membrane from Danish Power Systems ApS (11 H₃PO₄ per polymer repeat unit; thickness approximately 80 μm after doping with phosphoric acid) between anodes with 4 mg cm⁻² total metal loading of a Pt-Ru/C catalyst (40 wt% Pt, 20 wt% Ru and 40 wt% C, Johnson Matthey) and cathodes with 1 mg cm⁻² Pt loading (Pt/C catalyst, 57 wt% Pt, 43 wt% C, Johnson Matthey). The anode and cathode catalyst inks were prepared based on ethanol (96 wt%) as dispersant, without any other additives [39]. The inks were sprayed onto non-woven carbon cloth (Freudenberg H2315C2) using a spray robot (Exacta-Coat, SONO-TEK). The MEAs (23 cm² active surface area) were mounted into the cell housings without prior hot pressing. A break-in procedure was carried out by heating the cells to 120 °C, then turning on the gas flows. The cells were fed with 45 mL min⁻¹ hydrogen and 189 mL min⁻¹ air on the anode and cathode side, respectively, corresponding to λ_{H₂} / λ_{air} of 1.5/2 at 200 mA cm⁻², assuming 25 cm² electrode area. The cells were heated further to 160 °C and left at 200 mA cm⁻² overnight for activation. Reference polarization curves were recorded with the indicated gas flows below 200 mA cm⁻² and λ_{H₂} / λ_{air} of 1.5 / 2 at current loads ≥200 mA cm⁻². Subsequently, the desired operation temperature was set and the fuel was changed to a mixture of 25 mol% DME (99.9%, Gerling Holz & Co.) and 75 mol% water, produced by converging DME from a pressurized bottle with steam generated by pumping water into an evaporator through a capillary, using a Shimadzu LC-20AD pump. The gas compositions were calculated based on the flow of liquid water fed to the evaporator and the DME flow controlled using a mass flow controller (Brooks). The anode feed rate corresponded to λ_{DME} = 1 at 1 A cm⁻². The cells were operated at 100 mA cm⁻² for several days until the cell voltage had decreased to 30 mV. All polarization curves were recorded from low to high current densities using an AMREL ZVL100-10-40L eLOAD current sink. The

measurements were done by increasing the reactant flows, where applicable, and stepping the current simultaneously. The resulting cell voltage was recorded after 90 s stabilization time. The electrochemical impedance spectra were recorded using a VersaStat 4 from Princeton Applied Research, in the 100 kHz to 0.1 Hz range with 10 points per decade, 5 mV amplitude. The measurements were done after overnight standing at set current, before recording of polarization curves, to ensure steady-state conditions.

The fuel cell exhausts were led through a water trap to collect escaping phosphorous-containing species for quantification. The water was analyzed for phosphate content by the phosphoantimonymolybdenum blue complex method and quantified using UV-VIS spectroscopy [40, 41]. The UV-VIS spectra were recorded using a SPECORD 210 PLUS in the wavelength range 750-950 nm. The color reagent solution was made by dissolving 0.60 g (0.49 mmol) ammonium molybdate tetrahydrate (Sigma-Aldrich) and 0.024 g (0.039 mmol) potassium antimony(III) tartrate hydrate (Sigma-Aldrich) in 30 mL Milli-Q water. Then, 10 mL of each 7.4 mol L⁻¹ (aq.) sulfuric acid (Sigma-Aldrich), 0.44 mol L⁻¹ (aq.) ammonium sulfamate (Sigma-Aldrich) and 0.40 mol L⁻¹ (aq.) ascorbic acid (Sigma-Aldrich) were added to the solution. For the analysis, 1.0 mL of the color reagent was added to 6.0 mL of the analyte solution. The solutions were kept for several days before analysis to hydrolyze phosphoric acid derivatives formed during cell operation. A phosphate standard (Sigma-Aldrich) was used for calibration.

Scanning electron microscopy (SEM) images of MEA cross-sections prepared by ion milling (Hitachi E-3500) were obtained using a Zeiss Evo SEM MA10 equipped with an INCA EDS system from Oxford Instruments. Images were formed using secondary or backscattered electrons.

The chemical compatibility between phosphoric acid and DME was evaluated by bubbling DME through 85 wt% phosphoric acid (Sigma-Aldrich) at 150 or 200 °C. Sampling was carried out on a daily basis and the nuclear magnetic resonance (NMR) spectra were recorded using a Bruker Ascend with an operating frequency of 400, 100 and 162 MHz for ^1H , ^{13}C and ^{31}P , respectively. Deuterated dimethylsulfoxide ($\text{DMSO-}d_6$, Sigma-Aldrich) was used as solvent and the solvent residual signals at 2.50 and 39.51 ppm were used as reference for ^1H and ^{13}C , respectively. The H_3PO_4 signal at 0.00 ppm was used as internal reference for the ^{31}P nucleus.

The conductivity of the phosphoric acid doped PBI membrane (11 H_3PO_4 per polymer repeat unit) was recorded by clamping the membrane between two pieces of porous carbon paper (Toray) in a cell with graphite flow fields on both sides. The cell was placed in an oven for temperature control and the atmosphere was controlled by feeding decompressed air, pure DME or a water/DME mixture on both sides. The water/DME mixture was produced by converging DME with steam produced by pumping liquid water through an evaporator, as described above for the fuel cell tests. The conductivity was calculated based on the resistance recorded by electrochemical impedance spectroscopy (VersaStat 3, Princeton Applied Research) at 10 mV amplitude in the frequency range 1 MHz to 10 Hz, taken as the impedance at the real axis intersection.

3 Results and discussion

Before operation in direct DME mode, the cells were preconditioned at 200 mA cm^{-2} for about 20 h at 160 °C with a feed of pure H_2 and air to the anode and cathode, respectively. During this period, the cell voltage at 200 mA cm^{-2} was stable at about 0.6 V for both cells, as shown in Figure

1 (red curves), which corresponds reasonable to the state-of-the-art performance under these conditions [23, 42, 43].

After the initial conditioning period, the anode compartment feed was changed to a mixture of DME (25 mol%) and water (75 mol%), representing the stoichiometric composition for complete oxidation of DME to carbon dioxide. The current load was decreased to 100 mA cm^{-2} and the cell voltage was recorded as a function of time at 160 and 200 °C as shown by the black lines in Figure 1.

For the cell operated at 160 °C, the initial cell voltage with DME fuel at 100 mA cm^{-2} was 330 mV. During the initial 200 h of operation, the cell voltage had decreased to 319 mV, with an average cell voltage decay rate of $63 \text{ } \mu\text{V h}^{-1}$. After about 230 h, the cell voltage started to decline at a faster rate ($5500 \text{ } \mu\text{V h}^{-1}$) and after 280 h, no current could be drawn from the cell with DME as fuel.

The cell operated at 200 °C showed a slightly higher initial cell voltage of 495 mV, as a result of faster catalyst kinetics and higher electrolyte conductivity at the higher temperatures. During the first 55 h, the cell voltage decreased to 437 mV, with an average cell voltage decay rate of $2100 \text{ } \mu\text{V h}^{-1}$. This was followed by a period of 30 h with an even higher decay rate of $7900 \text{ } \mu\text{V h}^{-1}$. After about 90 h of operation the cell voltage was 211 mV, and it thereafter decreased steadily by $1500 \text{ } \mu\text{V h}^{-1}$ until no current could be drawn after 212 h.

Figure 1 Cell voltage development during the initial pre-conditioning with H₂ anode feed at 200 mA cm⁻² (red curve) and with DME/water anode feed at a current load of 100 mA cm⁻² at 160 °C (top) and 200 °C (bottom). The vertical lines of points are polarization curves.

The periodically recorded polarization curves of the cell operated at 160 and 200 °C are shown in Figure 2. The polarization curves of the cells after the pre-conditioning period with hydrogen are shown for comparison. One apparent observation from the polarization curves of the cells after changing the anode feed to the DME/water mixture is the large activation over-potential for the DME oxidation reaction. The sluggish reaction kinetics manifests as a large voltage drop in the low current density region. The initial peak power densities for the cells at 160 and 200 °C were 42 and 98 mW cm⁻², respectively. The latter is 12% higher than previously reported data for non-pressurized systems [44]. After 116-119 hours of operation the peak power densities of the two cells had decreased to 41 and 22 mW cm⁻², respectively.

Figure 2 Polarization data for the cells operated at 160 °C (top) and 200 °C (bottom) for different durations with anode feeds of pure H₂ (red, 160 °C) or the DME/water mixture (gray scale).

The polarization data were fitted to the Tafel equation by non-linear regression assuming a constant ohmic resistive contribution in the fitted current density range, and the fitting parameters are graphically presented in Figure 3. For the cell operated at 160 °C, it is evident that the fitted value for the ohmic resistance decreased slightly during the first 200 h of operation. This performance improvement during the first few hundred hours of operation is commonly observed for HT-PEM fuel cells and referred to as the break-in period, and is assigned to activation connected to redistribution and hydration of the phosphoric acid within the electrode structures [23]. After 200 h at 160 °C, the fitted ohmic resistance value was increasing rapidly until a critical point where no current could be drawn from the cell. At 200 °C, no initial decline in area specific resistance was

observed and after about 170 h it reached $1.5 \Omega \text{ cm}^2$. This was followed by an apparent slight decrease in area specific resistance, which was an artifact from poor fitting quality.

The Tafel slope with pure hydrogen was 0.1 V dec.^{-1} , which increased to around 0.2 V dec.^{-1} when the anode feed was changed to DME due to the changed electro-oxidation mechanism. Towards the end of the test period, the Tafel slope had increased to 0.36 and 0.45 V dec.^{-1} at 160 and 200 °C, respectively, indicating a gradual change in the DME electro-oxidation mechanism. This can be connected acid loss in the catalyst layers or due to gradual poisoning of the catalyst by reaction intermediates or side-reaction products on both the anode [45] and cathode [46] sides.

Figure 3 Area specific resistance (top) and Tafel slopes (bottom) obtained by fitting the polarization data for the DME/water fed cells to the Tafel equation. The data points at 24 h (red) correspond to H_2 anode feed at 160 °C, while the following data correspond to direct DME mode.

The electrochemical impedance spectroscopy (EIS) measurements were performed just prior to recording of polarization curves. This ensured that the investigated system was in steady state, which is crucial to obtain reliable results from EIS. Selected spectra in Nyquist representation for the cells operated at 160 and 200 °C are shown in Figure 4. The EIS of the cells operating with hydrogen at 160 and 200 °C were in good agreement with data reported in literature for cells operating under similar conditions [21, 47]. When the anode feed was changed to the DME/steam mixture, the intermediate frequency resistance instantly increased. This is connected to increased polarization/charge transfer resistances due to the sluggish DME oxidation, as also supported by the Tafel analysis. The magnitude of the intermediate frequency resistance greatly increased during the experiment and seemed more severe at 200 °C than at 160 °C. Furthermore, the appearance of the spectra gradually changed during the stability test and new semi-circles seemed to evolve. This is a clear indication of a major degradation mode that is electrode-related, which may be due to gradual poisoning of the catalysts by DME or by species formed by side-reactions [45, 46] or by phosphoric acid depletion within the electrodes. The former would result in decreased catalyst activity while the latter would result in ionic conductivity decay within the electrodes and reduced number of active sites with ionic contact, which remains to be explored in more detail.

Figure 4 Periodically recorded electrochemical impedance spectra at 100 mA cm^{-2} for the cells operated at $160 \text{ }^{\circ}\text{C}$ (top) or $200 \text{ }^{\circ}\text{C}$ (bottom).

A closer look at the high frequency intercept as shown in the insets in Figure 4 also indicate that the area specific resistance changed during the stability test. The high frequency resistance was initially lowered compared to the reference cell at both 160 and $200 \text{ }^{\circ}\text{C}$. This is due to the high partial pressure of water vapor in the anode feed, which initially enhances the proton conductivity [1]. This was followed by a gradual shift to higher values for both cells, indicating a continuous increase of the internal resistance in the cells. The evolution of the area specific resistance obtained from the EIS data by fitting to the (LR)R(CR)(CRLO) (see Figure S1) equivalent circuit is shown in Figure 5a. At both 160 and $200 \text{ }^{\circ}\text{C}$, the results support the direct observations from the polarization curves and the corresponding parameters obtained by fitting to the Tafel equation.

The area specific series resistance of both cells with dry hydrogen fuel was almost the same, 0.23 and 0.22 $\Omega \text{ cm}^2$. When the fuel was changed from dry hydrogen to the DME/steam mixture, series resistance decreased slightly to 0.20 and 0.18 $\Omega \text{ cm}^2$ at 160 and 200 $^{\circ}\text{C}$ due to the humidification. The series resistance of the cell operated at 160 $^{\circ}\text{C}$ remained stable at close to 0.2 $\Omega \text{ cm}^2$ during the initial 144 h. After 190 h, the series resistance started to increase at a high rate and passed 0.4 $\Omega \text{ cm}^2$ after 283 h. The series resistance development for the cell operated at 200 $^{\circ}\text{C}$ was different, and increased rapidly from about 0.18 $\Omega \text{ cm}^2$ after 44 h to 0.33 $\Omega \text{ cm}^2$ after 92 h. This was followed by a nearly linear increase after 100 h, reaching 0.44 $\Omega \text{ cm}^2$ after 215 h. The increase in series resistance can be attributed to different modes of electrolyte loss. The understanding is further complicated by the electrode related degradation revealed by EIS spectroscopy and Tafel analysis, which clearly shows that the performance degradation is not solely due to the increasing area specific resistance.

Figure 5 (a) Series resistance from the EIS data after fitting to a (LR)R(CR)(CRLO) equivalent circuit. The red points indicate resistance values for the cells operated with dry hydrogen at 160 °C; (b) Cumulative loss of H₃PO₄ from the electrodes determined colorimetrically from the collected condensate at the anode and cathode outlets for the cells operating at 100 mA cm⁻² at 160 or 200 °C.

It is clear that the analysis of the polarization behavior and EIS data indicate that the degradation modes are connected to different processes. It is also evident that catalyst degradation or deactivation is resulting in gradually increasing polarization losses, which seems more severe and faster at 200 °C than at 160 °C.

The increasing area specific resistance indicate that conductivity decay in the membrane, or within the electrode structures, represent another significant mode of degradation. The *post-mortem* cross-sectional SEM images of the MEAs, as shown in Figure S2, do not provide any solid evidence for a significant membrane thinning compared to a pristine MEA, which could be a

consequence of large acid losses from the membranes [23]. A cross-sectional SEM micrograph of a pristine MEA with a membrane from the same batch (but with electrodes from a different batch) is shown in Figure S3 for comparison. The membrane thickness before and after the test was around 45 μm . However, it does not necessarily provide a picture representative of the conditions in a running cell due to dimensional changes of the membrane that depend on the operating conditions [48]. The layered cake structures observed in the anodes, and as also seen from the EDS elemental mapping in Figure S4, originate from the electrode preparation and is due to small differences in the solid content of the ink batches. The catalyst layer thickness was 15-20 μm for the cathode and in the vicinity of 30-40 μm for the anode, but partial delamination and crumbling during sample preparation resulted in large uncertainty in the thickness determination.

The cumulative phosphoric acid loss, as determined colorimetrically [27] from the collected condensate at the anode and cathode outlets, for the cells operating at 160 and 200 $^{\circ}\text{C}$ are shown in Figure 5b. As previously reported [43] for HT-PEM fuel cells operating with a hydrogen feed to the anode, the acid loss was significantly increased when the temperature was increased from 160 to 200 $^{\circ}\text{C}$. The water supplied together with the DME in the anode feed is likely further promoting the acid loss, as water suppresses the phosphoric acid condensation into higher phosphorous oxoacid species with higher volatility. A steam distillation mechanism has been suggested as an acid loss mechanism at higher temperatures and water activities [49]. The amount of lost phosphoric acid was linearly proportional to the operation time, and as previously reported for hydrogen/air cells [49] the phosphoric acid loss on the cathode side was higher than at the anode side. Lower acid collection on the anode side is common, especially when pure hydrogen and small stoichiometries are used on the anode side, leading to a very low anodic exhaust flow as most hydrogen is consumed. Acid collection may be in the order of one percent

of the cathode collection in such cases [50]. However, in this case, the anodic exhaust flow is significantly larger with excess DME and water and produced CO₂ and higher acid collection rates are to be expected. During operation, and particularly at higher current loads, there is an accumulation of phosphoric acid at the anode side driven by electrochemical migration of phosphoric acid anions, which makes the acid more available to the transport out of the cell. This has been visualized using advanced imaging techniques [51, 52] and recently confirmed electrochemically [53-55]. It is worth noting that the total amounts of collected acid at the cell outlets are relatively small and correspond to less than one percent of the total acid inventory of the MEAs. The rate of acid loss is strongly depending on the electrodes and the quantification acid loss is further complicated by condensation e.g. flow fields and cell housing which will most likely lead to an underestimation of the severity of this degradation mode when only based on acid collection [43].

Formation of methyl phosphates as a result of a chemical reaction between methanol and phosphoric acid at high temperatures was recently described as a major degradation mode of HT-PEM fuel cells operated on methanol [24]. In order to investigate if a similar degradation mode could be involved with DME as a fuel as well, the MEAs were rapidly taken out after the durability tests and small pieces were cut off and placed in DMSO-*d*₆. The ¹H NMR spectra of the MEA extracts of the cells that had been operated at 160 and 200 °C, are shown in show in Figure 6a and 6b, respectively. In addition to signals corresponding to H₃PO₄, DME and methanol characteristic signals from methyl phosphates (methyl phosphoric acid esters) were observed in the spectra [24], although at relatively low contents (<1 mol% for at both 160 and 200 °C).

Figure 6 ^1H NMR spectra of the MEA extracts after fuel cells operation in direct DME mode at 160 °C (a) and 200 °C (b). The insets show the enlarged 3.0-3.7 ppm spectral regions.

Further steps towards assessing the chemical compatibility between phosphoric acid and DME were therefore taken. A model system was constructed where DME was bubbled through phosphoric acid at 150 or 200 °C for up to 5 days. The ^1H , ^{13}C and ^{31}P NMR spectra of the crude phosphoric acid solution after DME bubbling for 5 days at 200 °C are shown in Figure 8a, 8b and 8c, respectively. While the broad singlet centered at around 9 ppm in the ^1H NMR spectrum was assigned to phosphoric acid, the three doublets at 3.51, 3.56 and 3.62 ppm are characteristic signals [24] from monomethyl dihydrogen phosphate (MMP), dimethyl hydrogen phosphate (DMP) and trimethyl phosphate (TMP), respectively. The weak signal at 3.19 ppm was assigned to DME

dissolved in the phosphoric acid. The signal at 3.16 ppm was assigned to methanol, which is formed in equimolar amounts during the methyl phosphate formation as shown in the reaction scheme in Figure 7, also showing the chemical structures of the methyl phosphate species and the corresponding peak assignments. Despite the equimolar formation of methanol, the amount should be small since methanol is highly volatile and may also react with the phosphoric acid itself. The methyl phosphate formation was further supported by the ^{13}C NMR data, showing three characteristic signals [24] for MMP, DMP and TMP at 52.5, 53.2 and 53.6 ppm, respectively. In addition to the signals around -13 ppm in the ^{31}P NMR spectrum assigned to phosphoric acid condensation products [56], the spectrum showed signals originating from MMP, DMP and TMP at 0.49, 1.41 and 2.83 ppm, respectively. The ^1H , ^{13}C and ^{31}P NMR of the model system kept at 150 °C showed the same signals as observed at 200 °C, indicating substantial formation of methyl phosphates even lower temperatures.

Figure 7 Crude ^1H (a), ^{13}C (b) and ^{31}P (c) NMR spectra and peak assignments after bubbling DME through 85 wt.% H_3PO_4 at 200 °C (reflux) during vigorous stirring for five days. Chemical structure of the different phosphoric acid methyl esters obtained from H_3PO_4 and DME and the corresponding peak assignments (bottom).

The remarkably high conductivity of phosphoric acid is due to the high degree of hydrogen bond network frustration [57, 58], and the formation of organic phosphate derivatives likely disturbs this even at relatively low contents. It has recently been reported that the methyl phosphates formed in the phosphoric acid-methanol system tremendously reduces the proton conductivity in solution and on the PBI membrane level, where 3 mol% of MMP in phosphoric acid resulted in 7 times conductivity decay compared to the pure acid [24].

To monitor the impact of methyl phosphate formation on the membrane level in the presence of DME, the through plane proton conductivity of a phosphoric acid doped PBI membrane was recorded as a function of time under pure DME atmosphere or under a DME/water gas mixture with the same composition as used in the anode feed in the fuel cell tests. The conductivity data are summarized in Figure 8. As a reference point, the through-plane conductivity was initially recorded under air at 150 and 200 °C for 16-20 h and ranged from about 10 to 30 mS cm^{-1} , which is slightly lower than the typical in-plane conductivity reported for membranes based on PBI with comparable acid contents at 160-180 °C (30-40 mS cm^{-1}) [59, 60]. When the resistance is measured through the plane of the membrane, the total membrane resistance is small and as a four-point measurement is not practical, the contributions from contacts and leads become relatively more significant. This may lead to a slight underestimation of the membrane conductivity.

After the initial conditioning period, the atmosphere in the conductivity cell was changed to pure DME (at 150 and 200 °C) or a mixture of DME and water vapor (200 °C). At 150 °C, the conductivity decreased from about 22 mS cm⁻¹ to 10-15 mS cm⁻¹ after only a few hours under DME atmosphere. After the conductivity test, the membrane was placed in DMSO-*d*₆. The ¹H, ¹³C and ³¹P NMR spectra of the membrane extracts after the conductivity test showed intense characteristic signals corresponding to MMP, DMP and TMP (Figure S5). It was noticed that liquid droplets condensed near the cell outlet during the conductivity test (see Figure S6), and further NMR analysis of the condensed liquid showed that it contained phosphoric acid as well as the various methyl phosphates (Figure S7).

The conductivity of the membrane treated under pure DME at 200 °C decreased rapidly during the first hours, and after 20 h it had been lowered by an order of magnitude. The NMR spectra of the membrane extract after the conductivity test showed no or very weak signals corresponding to methyl phosphates. However, again liquid droplets were condensed close to the cell outlet and the ¹H, ¹³C and ³¹P NMR spectra of the condensed liquid revealed the characteristic signals from phosphoric acid as well as MMP, DMP and TMP (Figure S8).

The conductivity of the membrane recorded under an atmosphere of a DME/steam mixture of the same composition as used during the direct DME fuel cell test slightly increased initially due to the hydration of the membrane and possibly hydrolysis of the phosphoric acid oligomers [61]. Although the conductivity remained stable during the 50 h test period, the NMR examination of the membrane extracts showed traces of MMP (Figure S9). It is moreover worth noting that the timescale of 50 h is very short from a fuel cell durability point of view.

Figure 8 Conductivity of H₃PO₄ doped *m*-PBI membranes at 150 and 200 °C under non-humidified air (solid markers), and under pure DME or under a mixture of DME (25 mol%) and steam (75 mol%) (open markers).

Besides lowering conductivity, organic phosphate formation will also likely lead to an increase of acid loss. The boiling points of the methyl phosphate derivatives are relatively low (174 and 197 °C for dimethyl hydrogen phosphate and trimethyl phosphate, respectively [62]), which is close to the working temperatures of the fuel cells and may also explain the relatively low content of methyl phosphates observed in the MEA extracts after operation. The vapor pressures of the pure esters are thus close to ambient pressure and although the activities, when diluted in phosphoric acid, are small, the vapor pressures of the esters must be orders of magnitude higher than that of ortho-phosphoric acid. The volatile esters will increase acid evaporation as efficient phosphoric acid carriers. If short term degradation mechanisms can be mitigated, the increased acid loss will have pronounced degrading effect on long term operation. The apparent short term effect on the electrode kinetics shown in this study is most likely caused by decreased protonic conductivity and increased acid loss in the catalyst layer, both of which will result in higher polarization.

This work on vapor fed direct DME high temperature PEM fuel cells based on phosphoric acid doped PBI reported herein clearly show severe degradation during 1-2 weeks of operation at 160-200 °C. The fast cell degradation is, at least partly, due to the chemical incompatibility between the fuel and the electrolyte. Methyl phosphates are formed within the MEA during operation from the chemical reaction between DME and phosphoric acid, which results in conductivity decay. The stoichiometric amount of steam supplied together with the DME suppresses the methyl phosphate formation but may accelerate the acid loss. Methyl phosphate formation may also be involved in the electrode performance deterioration [45, 46], but remains to be investigated in more detail. Based on the findings reported herein, the most apparent degradation mitigation strategy should focus on suppressing methyl phosphate formation, either through water management or by introducing a fuel processing step as typically used in methanol fueled systems [21].

4 Conclusions

High temperature polymer electrolyte membranes fuel cells based on phosphoric acid doped polybenzimidazole membranes with a direct dimethyl ether anode feed degrade severely during 1-2 weeks of operation at 160-200 °C. The increasing polarization resistance indicate a degradation mechanism that is connected to deterioration of the electrode performance, and is likely due to catalyst poisoning and/or acid depletion within the electrodes. Furthermore, phosphoric acid loss and formation of methyl phosphates as a result of a chemical reaction between the fuel and the electrolyte result in a detrimental conductivity decay of the membrane and/or within the electrode structures. It manifests as a steady increase of the area specific resistance. The degradation mitigation should be directed towards suppressing the methyl phosphate formation, either by

careful control of the cell humidification and water management or by integrating a pre-reforming step of the fuel.

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References

- [1] J.S. Wainright, J.T. Wang, D. Weng, R.F. Savinell, M. Litt, J. Electrochem. Soc. 142 (1995) L121-L123.
- [2] Q. Li, J.O. Jensen, R.F. Savinell, N.J. Bjerrum, Prog. Polym. Sci. 34 (2009) 449-477.
- [3] D. Weng, J.S. Wainright, U. Landau, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1260-1263.
- [4] J.T. Wang, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1233-1239.
- [5] B.S. Pivovar, Y.X. Wang, E.L. Cussler, J. Membr. Sci. 154 (1999) 155-162.
- [6] L. Gubler, D. Kramer, J. Belack, O. Ünsal, T.J. Schmidt, G.G. Scherer, J. Electrochem. Soc. 154 (2007) B981-B987.
- [7] J.T. Wang, J.S. Wainright, R.F. Savinell, M. Litt, J. Appl. Electrochem. 26 (1996) 751-756.
- [8] Q. Li, H.A. Hjuler, N.J. Bjerrum, Electrochim. Acta 45 (2000) 4219-4226.
- [9] Q. Li, R. He, J.-A. Gao, J.O. Jensen, N.J. Bjerrum, J. Electrochem. Soc. 150 (2003) A1599-A1605.
- [10] G. Qian, B.C. Benicewicz, ECS Trans. 41 (2011) 1441-1448.

- [11] D. Kramer, E. Lehmann, G. Frei, P. Vontobel, A. Wokaun, G.G. Scherer, Nucl. Instrum. Methods Phys. Res. A 542 (2005) 52-60.
- [12] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, R. Lopez-Vizcaíno, Energy Fuels 22 (2008) 3335-3345.
- [13] S.S. Araya, S.J. Andreasen, H.V. Nielsen, S.K. Kær, Int. J. Hydrogen Energy 37 (2012) 18231-18242.
- [14] C. Pan, R. He, Q. Li, J.O. Jensen, N.J. Bjerrum, H.A. Hjulmand, A.B. Jensen, J. Power Sources 145 (2005) 392-398.
- [15] S.S. Araya, S.J. Andreasen, S.K. Kær, Energies 5 (2012) 4251-4267.
- [16] T. Ossiander, C. Heinzl, S. Gleich, F. Schönberger, P. Völkl, M. Welsch, C. Scheu, J. Membr. Sci. 454 (2014) 12-19.
- [17] T. Ossiander, M. Perchthaler, C. Heinzl, C. Scheu, J. Power Sources 267 (2014) 323-328.
- [18] M. Boaventura, I. Alves, P. Ribeirinha, A. Mendes, Int. J. Hydrogen Energy 41 (2016) 19771-19780.
- [19] R. Kerr, H.R. García, M. Rastedt, P. Wagner, S.M. Alfaro, M.T. Romero, C. Terkelsen, T. Steenberg, H.A. Hjuler, Int. J. Hydrogen Energy 40 (2015) 16860-16866.
- [20] S.S. Araya, I.F. Grigoras, F. Zhou, S.J. Andreasen, S.K. Kær, Int. J. Hydrogen Energy 39 (2014) 18343-18350.
- [21] S. Thomas, J.R. Vang, S.S. Araya, S.K. Kær, Appl. Energy 192 (2017) 422-436.
- [22] J. Zhang, Y. Xiang, S.F. Lu, S.P. Jiang, Adv. Sustain. Syst. 2 (2018) 1700184.
- [23] T. Søndergaard, L.N. Cleemann, H. Becker, D. Aili, T. Steenberg, H.A. Hjuler, L. Seerup, Q. Li, J.O. Jensen, J. Power Sources 342 (2017) 570-578.
- [24] D. Aili, A. Vassiliev, J.O. Jensen, T.J. Schmidt, Q. Li, J. Power Sources 279 (2015) 517-521.

- [25] J. Lobato, P. Cañizares, M.A. Rodrigo, J.J. Linares, *Fuel Cells* 9 (2009) 597-604.
- [26] S. Fan, D.P. Wilkinson, H. Wang, *J. Electrochem. Soc.* 159 (2012) B570-B577.
- [27] T.A. Semelsberger, R.L. Borup, H.L. Greene, *J. Power Sources* 156 (2006) 497-511.
- [28] A. Serov, C. Kwak, *Appl. Catal. B* 91 (2009) 1-10.
- [29] J.T. Müller, P.M. Urban, W.F. Hölderich, K.M. Colbow, J. Zhang, D.P. Wilkinson, *J. Electrochem. Soc.* 147 (2000) 4058-4060.
- [30] Q. Li, G. Wu, C.M. Johnston, P. Zelenay, *Electrocatalysis* 5 (2014) 310-317.
- [31] J.R. Ferrell, M.C. Kuo, A.M. Herring, *J. Power Sources* 195 (2010) 39-45.
- [32] J.-H. Yu, H.-G. Choi, S.M. Cho, *Electrochem. Commun.* 7 (2005) 1385-1388.
- [33] G. Kerangueven, C. Coutanceau, E. Sibert, J.M. Léger, C. Lamy, *J. Power Sources* 157 (2006) 318-324.
- [34] Q. Li, X. Wen, G. Wu, H.T. Chung, R. Gao, P. Zelenay, *Angew. Chem. Int. Ed.* 54 (2015) 7524-7528.
- [35] D. Kashyap, H. Teller, A. Schechter, *J. Power Sources* 396 (2018) 335-344.
- [36] B. Gavriel, R. Sharabi, L. Elbaz, *ChemSusChem* 10 (2017) 3069-3074.
- [37] J.O. Jensen, A. Vassiliev, M.I. Olsen, Q. Li, C. Pan, L.N. Cleemann, T. Steenberg, H.A. Hjuler, N.J. Bjerrum, *J. Power Sources* 211 (2012) 173-176.
- [38] J. Neutzler, G. Qian, K. Huang, B. Benicewicz, *J. Power Sources* 216 (2012) 471-474.
- [39] S. Martin, Q. Li, T. Steenberg, J.O. Jensen, *J. Power Sources* 272 (2014) 559-566.
- [40] Y.H. Jeong, J.H. Jung, E. Choi, S. Han, A.I. Begley, S.J. Yoo, J.H. Jang, H.-J. Kim, S.W. Nam, K.-Y. Lee, J.Y. Kim, *J. Power Sources* 299 (2015) 480-484.
- [41] S. Han, Y.H. Jeong, J.H. Jung, A. Begley, E. Choi, S.J. Yoo, J.H. Jang, H.-J. Kim, S.W. Nam, J.Y. Kim, *J. Sens.* 2016 (2016) 8.

- [42] D. Aili, J. Zhang, M.T. Dalsgaard Jakobsen, H. Zhu, T. Yang, J. Liu, M. Forsyth, C. Pan, J.O. Jensen, L.N. Cleemann, S.P. Jiang, Q. Li, *J. Mater. Chem. A* 4 (2016) 4019-4024.
- [43] T. Søndergaard, L.N. Cleemann, H. Becker, T. Steenberg, H.A. Hjuler, L. Seerup, Q. Li, J.O. Jensen, *J. Electrochem. Soc.* 165 (2018) F3053-F3062.
- [44] A. Vassiliev, J.O. Jensen, Q. Li, C. Pan, L.N. Cleemann, T. Steenberg, H.A. Hjuler, N.J. Bjerrum, *ECS Trans.* 50 (2013) 869-876.
- [45] L.-H. Xing, G.-P. Yin, Z.-B. Wang, S. Zhang, Y.-Z. Gao, C.-Y. Du, *J. Power Sources* 198 (2012) 170-175.
- [46] L.-H. Xing, G.-P. Yin, C.-Y. Du, S.-X. Cui, M.-H. Zuo, H.-P. Wang, *Int. J. Hydrogen Energy* 42 (2017) 16695-16699.
- [47] J. Zhang, D. Aili, J. Bradley, H. Kuang, C. Pan, R. De Marco, Q. Li, S.P. Jiang, *J. Electrochem. Soc.* 164 (2017) F1615-F1625.
- [48] W. Maier, T. Arlt, C. Wannek, I. Manke, H. Riesemeier, P. Krüger, J. Scholta, W. Lehnert, J. Banhart, D. Stolten, *Electrochem. Commun.* 12 (2010) 1436-1438.
- [49] S. Yu, L. Xiao, B.C. Benicewicz, *Fuel Cells* 8 (2008) 165-174.
- [50] A. Kannan, Q. Li, L.N. Cleemann, J.O. Jensen, *Fuel Cells* 18 (2018) 103-112.
- [51] S.H. Eberhardt, M. Toulec, F. Marone, M. Stampanoni, F.N. Büchi, T.J. Schmidt, *J. Electrochem. Soc.* 162 (2015) F310-F316.
- [52] S.H. Eberhardt, F. Marone, M. Stampanoni, F.N. Büchi, T.J. Schmidt, *J. Electrochem. Soc.* 163 (2016) F842-F847.
- [53] H. Becker, L.N. Cleemann, D. Aili, J.O. Jensen, Q. Li, *Electrochem. Commun.* 82 (2017) 21-24.

- [54] H. Becker, U. Reimer, D. Aili, L.N. Cleemann, J.O. Jensen, W. Lehnert, Q. Li, J. Electrochem. Soc. 165 (2018) F863-F869.
- [55] J. Halter, S. Thomas, S.K. Kær, T.J. Schmidt, F.N. Büchi, J. Power Sources, 399 (2018) 151-156.
- [56] L.X. Xiao, H.F. Zhang, E. Scanlon, L.S. Ramanathan, E.W. Choe, D. Rogers, T. Apple, B.C. Benicewicz, Chem. Mater. 17 (2005) 5328-5333.
- [57] L. Vilčiauskas, M.E. Tuckerman, G. Bester, S.J. Paddison, K.D. Kreuer, Nat. Chem. 4 (2012) 461-466.
- [58] J.-P. Melchior, K.-D. Kreuer, J. Maier, Phys. Chem. Chem. Phys. 19 (2017) 587-600.
- [59] D. Aili, Q. Li, E. Christensen, J.O. Jensen, N.J. Bjerrum, Polym. Int. 60 (2011) 1201-1207.
- [60] D. Aili, L.N. Cleemann, Q. Li, J.O. Jensen, E. Christensen, N.J. Bjerrum, J. Mater. Chem. 22 (2012) 5444-5453.
- [61] Y.L. Ma, J.S. Wainright, M.H. Litt, R.F. Savinell, J. Electrochem. Soc. 151 (2004) A8-A16.
- [62] Physical Constants of Organic Compounds, in: J.R. Rumble (Ed.), CRC Handbook of Chemistry and Physics, CRC Press/Taylor & Francis, Boca Raton, FL, 99th edition (Internet Version 2018).

Figure captions

Figure 1 Cell voltage development during the initial pre-conditioning with H₂ anode feed at 200 mA cm⁻² (red curve) and with DME/water anode feed at a current load of 100 mA cm⁻² at 160 °C (top) and 200 °C (bottom). The vertical lines of points are polarization curves.

Figure 2 Polarization data for the cells operated at 160 °C (top) and 200 °C (bottom) for different durations with anode feeds of pure H₂ (red, 160 °C) or the DME/water mixture (gray scale).

Figure 3 Area specific resistance (top) and Tafel slopes (bottom) obtained by fitting the polarization data for the DME/water fed cells to the Tafel equation. The data points at 24 h (red) correspond to H₂ anode feed at 160 °C, while the following data correspond to direct DME mode.

Figure 4 Periodically recorded electrochemical impedance spectra at 100 mA cm⁻² for the cells operated at 160 °C (top) or 200 °C (bottom).

Figure 5 (a) Series resistance from the EIS data after fitting to a (LR)R(CR)(CRLO) equivalent circuit. The red points indicate resistance values for the cells operated with dry hydrogen at 160 °C; (b) Cumulative loss of H₃PO₄ from the electrodes determined colorimetrically from the collected condensate at the anode and cathode outlets for the cells operating at 100 mA cm⁻² at 160 or 200 °C.

Figure 6 ¹H NMR spectra of the MEA extracts after fuel cells operation in direct DME mode at 160 °C (a) and 200 °C (b). The insets show the enlarged 3.0-3.7 ppm spectral regions.

Figure 7 Crude ^1H (a), ^{13}C (b) and ^{31}P (c) NMR spectra and peak assignments after bubbling DME through 85 wt.% H_3PO_4 at 200 °C (reflux) during vigorous stirring for five days. Chemical structure of the different phosphoric acid methyl esters obtained from H_3PO_4 and DME and the corresponding peak assignments (bottom).

Figure 8 Conductivity of H_3PO_4 doped *m*-PBI membranes at 150 and 200 °C under non-humidified air (solid markers), and under pure DME or under a mixture of DME (25 mol%) and steam (75 mol%) (open markers).